Dry reforming of methane over the cobalt catalyst: Theoretical insights into the reaction kinetics and mechanism for catalyst deactivation

Shuyue Chen, Jeremie Zaffran, Bo Yang

Abstract

Cobalt shows high catalytic activity for the important dry reforming of methane (DRM) reaction. However, it is prone to deactivation and the corresponding mechanism remains controversial. In this work, we combined density functional theory calculations and microkinetic modeling to study the active site and reaction mechanism of Co catalyzed DRM reaction, employing face centered cubic Co(111) and Co(211) as models. It was found that the step site over Co(211) is the active site for the reaction, and on Co(111), the C + O and CH + O paths are the preferred reaction pathways, while the C + O path is dominant on Co(211). The dissociation of CH4 is the rate-controlling step of DRM over both Co(111) and Co(211). We found that Co(111) is mainly deactivated due to carbon deposition whilst Co(211) undergoes surface oxidization. In addition, Co(111) tends to follow the surface carbon coupling mechanism, and surface carbon clusters formed will lead to catalyst deactivation.

1. Introduction

According to the global greenhouse gas emissions data released by Intergovernmental Panel on Climate Change (IPCC) in 2014, carbon dioxide accounts for 65% of total greenhouse gas emissions, followed by methane. The greenhouse effect caused by greenhouse gas emissions can have a great impact on the ecological environment. In addition to emissions reduction, developing a process to utilize greenhouse gases provides a new direction for solving this problem. Methane reforming with carbon dioxide, i.e. dry reforming of methane (DRM), converts these two greenhouse gases into two clean fuel gases, carbon monoxide and hydrogen, i.e. synthetic gas (syngas) [1,2], which can be further used in the Fischer-Tropsch process to synthesize desired hydrocarbons [3,4]. However, due to the lack of highly active and stable catalysts, the attractive DRM reaction is still not maturely industrialized.

It was found that highly active and deactivation-resistant precious metal catalysts, such as Rh and Ru, can be used for DRM [5–7], but the high price and low reserves limit their further development. In addition to the noble metals, cheap and earth-abundant transition metals are considered as alternatives [8]. Ni has attracted considerable attentions due to its high activity and large reserves, but the disadvantage of the Ni catalyst is also obvious that it is easily deactivated through carbon deposition [9–15]. Another widely used inexpensive transition metal catalyst is cobalt [16,17]. Previous studies indicated that Co could show a nickel-like activity for the DRM reaction, but the stability problems still exist, and the deactivation mechanism of Co is still under debate [18–22].

In comparison to the detailed analysis on the deactivation mechanism of Co catalysts in Fischer-Tropsch synthesis studies reported in the literature [23–25], similar discussions from a computational perspective under DRM reaction conditions is missing. Experimental evidence showed that, in the DRM process, the Co catalyst can be deactivated mainly through two mechanisms, namely oxidation and carbon deposition [21,26–29]. It was demonstrated experimentally that the deactivation mechanism is strongly dependent on the loading of Co [21,26–29]. While highly metal-loaded catalysts are mainly deactivated via coke formation, low metal loading mainly leads to Co oxidation [26–28]. Jose-Alonso et al. found that the 1 wt % Co catalyst was abruptly deactivated by oxidation, while the catalyst with a Co content of 9 wt % showed high carbon deposition due to the large size of Co particles present on the support [21]. Therefore, the deactivation might be related to the size of metallic nanoparticles. It could be further inferred that differences in size may result in different ratios of surface active sites, resulting in different deactivation mechanisms.

In general, the support can affect the size and structure of the metal particle [30,31], form interfacial active sites with the metal [32], and...
even directly participate in the catalytic reaction, thereby affecting the activity and stability [33]. However, it was found that the presence of support influences the activity and stability mainly by varying the adsorption of intermediate and the energy barriers of key elementary steps in the reaction. Here, we focus on how the activity and stability of Co in DRM reactions are affected by species adsorption and activation barriers [34]. These insights should also be applicable to the discussion of the activity and stability of supported Co catalysts.

We noticed that there are two crystallographic structures of Co, i.e. face centered cubic (FCC) and hexagon close-packed (HCP), and transition between these two structures can happen under different conditions [35-38]. Typically, at low temperatures, Co prefers the form of HCP phase, and when the temperature rises to 700 K and above, HCP Co will be transformed to FCC Co [35]. Kitakami and co-workers also studied the effect of Co particle size on the crystalline phase below 673 K. It was found that when the metal particle diameter is smaller than 200 Å, cobalt is in the form of FCC phase, and when the particle diameter is larger than 400 Å, cobalt would prefer the HCP crystal structure [37]. Considering that the typical operating temperature of the DRM reaction is around 873 – 1123 K and the diameter of Co particles are usually less than 400 Å [39]. It was also found experimentally that under the conditions of DRM reaction, Co exists as FCC structure on different oxide supports [40,41]. Therefore, we adopt the FCC Co in the current study. Since the deactivation process may be structure sensitive, we also investigate the reactions on different facets of FCC Co. It was widely reported in the literature that smaller particles would possess more low-coordination step sites such as fcc-(211), whilst larger particles show a higher ratio of fcc-(111) terrace sites [42,43]. It was also found experimentally and theoretically that Co(111) is the dominant surface of large FCC Co nanoparticles [41], and on small-sized particles stepped surfaces are abundant which may give rise to a different deactivation mechanism.

To the best of our knowledge, there is no thorough computational study in the literature reporting the reaction kinetics of DRM at different sites over Co and a detailed analysis on the catalyst deactivation process. In this work, we used the (111) and (211) surfaces of FCC Co as models to represent different surface sites on the catalyst. Using DFT calculations combined with microkinetic simulations, reaction rates of possible reaction pathways of DRM on different Co surfaces were calculated, and the corresponding surface dominant species and rate controlling species were analyzed. Finally, insights into the mechanism of deactivation of Co catalysts during the DRM reactions on different surfaces were provided, and possible strategies for future design of active and stable Co catalysts were suggested.

2. Computational methods

2.1. DFT calculations

All the DFT calculations were performed with the VASP software [44–46]. The projector-augmented wave (PAW) method was used to describe the ion core and its interaction with valence electrons [47]. Electron exchange and correlation was treated with the BEEF-vdW functional, which is widely used in surface properties calculations [48–55]. The energy cutoff was set to 500 eV. The energy convergence criterion was set to 10⁻⁴ eV, and the force convergence was set to 0.05 eV/Å. We also included the spin polarization in all the calculations, and transition states were searched using the constrained minimization method [56–58].

We first optimized the lattice of FCC Co. The optimized lattice parameter was 3.536 Å, which was found close to the experimental value of 3.550 Å. And the magnetic moment of Co calculated in this work is 1.72 μB/atom, which is very close to the experimental value (1.71 μB/atom) and previous theoretical results (1.63 μB/atom) [59,60]. Then we built four-layer p(3 × 3) Co(111) and twelve-layer p (1 × 3) Co(211) slabs for the calculations related with the adsorption and transition states, and the k-point was set to 3 × 3 × 1 and 4 × 3 × 1, respectively [61]. The bottom two and six layers in the slabs of Co(111) and Co(211), respectively, were fixed at the bulk structure and the rest of the atoms in the slabs were allowed to relax during the structural optimizations. The vacuum space introduced for each slab was with a height of 15 Å to avoid the periodic interactions. The adsorption energy of surface species was calculated using the following equation.

\[ E_{\text{ad}} = E_{\text{slab/ads}} - E_{\text{ads}} - E_{\text{slab}} \]  

Where, \( E_{\text{ad}} \) is the adsorption energy, \( E_{\text{slab/ads}} \), \( E_{\text{ads}} \) and \( E_{\text{slab}} \) is the energy of slab with adsorbates, the energy of adsorbate in gas phase and the energy of slab, respectively.

It was found by several studies that the calculations of gaseous CO₂ and CO may be inaccurate using DFT [62,63]. One possible approach to solve this problem is to correct gaseous energies of CO₂ or CO to make sure that the calculated reaction Gibbs free energies with DFT data are identical to the experimental values. In this work, the standard reaction Gibbs free energy calculated for the DRM reaction at 298 K is 1.90 eV, which is very close to the experimental value of 1.77 eV, suggesting that no correction should be made for the energies of CO₂ and CO here.

2.2. Microkinetic modeling

Steady state approximation and transition state theory were used for microkinetic simulation. The CatMAP software package developed by Nørskov’s group was used [64], which has been proved to be a powerful tool for obtaining kinetic insights into surface catalytic reactions by applying the mean-field assumption [49–54,65,66]. The simulation temperature was set to 873 – 1073 K and the total pressure was 1 bar. Methane conversion considered was 5% and the ratio between CH₄ and CO₂ in the gaseous reactant was 1:1. Further details of the thermodynamic corrections for gaseous species and surface intermediates were given in the Supporting Information (S1).

We also resorted to the degree of rate control (DRC) analysis method developed by the Campbell group [67,68], which has been proved as a useful tool to probe the surface key intermediates and transition states in the catalytic process [49–54,65,69,70]. The values of DRC can be determined by calculating the response of reaction rate to changes in the free energy of the intermediate and transition states using the following equation:

\[ X_i = \left(-\frac{3N_r}{\delta G/k_B T}E_i \right)_{pp} \]  

Where, \( r \) is the overall reaction rate and \( G \) is the free energy of each intermediate or transition state, \( k_B \) is the Boltzmann constant and \( T \) is the temperature. For a transition state, the value of DRC should be between 0 and 1. The higher the DRC value, the greater the effect of the transition state on the rate. The value of intermediates should be 0 or negative and related to the coverage of the intermediate and the number of site required by the rate controlling transition state (RCTS) [67,68].

3. Results and discussion

3.1. Reaction network of the DRM reaction on Co surfaces

Scheme 1 shows the possible DRM reaction network, including three CO₂ activation steps and different pathways from methane to the product CO, which are similar to those reported in the literature on Ni, Pt and Pd catalysts [71–73]. We divide the elementary steps into the following types: (1) Direct and H-assisted dissociation of CO₂; (2) Hydrogenation of O* to OH*; (3) Dehydrogenation of CH₄ to CH₂; (x = 0–3); (4) CH₃* coupling with O*/OH* to form CH₂O*/CH₂OH*; (5) Dehydrogenation of CH₂O*/CH₂OH* and (6) The coupling of
surface $H^*$ to form gaseous $H_2$. The configurations of adsorption and transition states are shown in Figs. S1–S3 of the SI.

### 3.1.2. Reaction mechanism and active sites

Scheme 1(a) shows different CO$_2$ activation pathways for CO production. One can see that CO$_2$ can be directly decomposed into CO$^*$ and O$^*$, or combined with the H$^*$ produced from methane dehydrogenation, to give COOH$^*$ or HCOO$^*$. COOH$^*$ is then decomposed into either CO$^*$ or O$^*$, or combined with the H$^*$ produced from methane dehydrogenation, to give COOH$^*$ or HCOO$^*$. COOH$^*$ is then decomposed into either CO$^*$ or OH$^*$, or CO$^*$ + O$^*$ followed by CO$^*$ dehydrogenation to generate CO$_2$. Dissociation of HCOO$^*$ would produce O$^*$ and CHO$^*$ followed by CHO$^*$ dehydrogenation to generate CO. The reaction barriers of different elementary steps in the pathways of CO$_2$ activation are listed in Table 1. One can see from Table 1 that the barrier of CO$_2$ direct dissociation (R1) is much lower than that of H-assisted dissociation on both Co(111) and Co(211), indicating that the direct dissociation of CO$_2$ might be favored in comparison with the H-assisted activation pathways.

#### 3.1.2.1. From CH$_4$ to CO

Scheme 1(b) shows the different reaction pathways from CH$_4$ to H$_2$ and CO. Methane can be dehydrogenated to produce CH$_x$ ($x = 0$–3) species. Then the CH$_x$ species can couple with O$^*$ or OH$^*$ to form CH$_x$O or CH$_x$OH. These surface intermediates will undergo further dehydrogenation until the final product CO is formed. The energetics listed in Table 1 for the two Co surfaces reflect the following trends: (1) For CH$_x$*, the dehydrogenation barrier is lower than the corresponding coupling barrier of with O$^*$ or OH$^*$; (2) Compared with CH$_x$* coupling with OH$,^*$ the association with O$^*$ is kinetically favored; (3) For CH$_x$OH$^*$ species, the barrier for the O–H bond breaking is higher than to break the C–H bond; (4) The barrier of CH$_x$* coupling with O$^*$ or OH$^*$ on Co(211) is usually higher than on Co(111). However, it is impractical to determine the reactivity and main reaction pathways only from the barriers and reaction energies listed in Table 1. Therefore, we further carried out microkinetic simulations over Co(111) and Co(211).

#### 3.2. Microkinetic analysis of the DRM reaction on Co surfaces

##### 3.2.1. Reaction mechanism and active sites

In the microkinetic simulations, all the elementary steps presented in Table 1 are taken into consideration, and the reaction rates of the elementary steps at 973 K are listed in Table 2. After analyzing the reaction rates, the reactivity of the two Co surfaces and the main DRM reaction pathway can be determined. The reaction rate of the dominant reaction pathways of DRM are plotted in Fig. 1 as a function of temperature. It can be found from this figure that the reaction rate on Co(111) is lower than that on Co(211) at high reaction temperatures, but the reactivity of the terrace and step sites becomes identical at high reaction temperatures.

Regarding the mechanism of CO$_2$ activation, one can see from Table 2 that the rate of CO$_2$ direct dissociation is at least five orders of magnitude higher than that of H-assisted dissociation on both Co(111) and Co(211), indicating that the direct dissociation of CO$_2$ is favored. This is the same with the way of carbon dioxide activation on Ni, whereas Pd and Pt favor the hydrogen-assisted carbon dioxide dissociation [71,73,74]. The dominant reaction path on Co(111) is also the same as that on Ni(111) [71]. On Co(111), there are two dominant reaction pathways for CO formation, namely the C + O path and


Table 2
The net reaction rate of each elementary step calculated at the steady state and 973 K on Co(111) and Co(211).

<table>
<thead>
<tr>
<th>No.</th>
<th>elementary steps</th>
<th>reaction rate/site $s^{-1}$ Co(111)</th>
<th>reaction rate/site $s^{-1}$ Co(211)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$CO_2 + 2* \rightarrow CO* + O*$</td>
<td>$9.58 \times 10^{-6}$</td>
<td>$4.16 \times 10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>$CO* + H* \rightarrow COOH*$</td>
<td>$3.09 \times 10^{-5}$</td>
<td>$5.02 \times 10^{-5}$</td>
</tr>
<tr>
<td>3</td>
<td>$COOH* + * \rightarrow CO* + OH*$</td>
<td>$3.09 \times 10^{-5}$</td>
<td>$5.02 \times 10^{-5}$</td>
</tr>
<tr>
<td>4</td>
<td>$CO_2 + H* \rightarrow HCOO*$</td>
<td>$6.27 \times 10^{-5}$</td>
<td>$7.48 \times 10^{-5}$</td>
</tr>
<tr>
<td>5</td>
<td>$HCOO* + * \rightarrow CHO* + O*$</td>
<td>$6.27 \times 10^{-5}$</td>
<td>$7.48 \times 10^{-5}$</td>
</tr>
<tr>
<td>6</td>
<td>$CH_4 + 2* \rightarrow CH_2* + H*$</td>
<td>$9.58 \times 10^{-6}$</td>
<td>$4.16 \times 10^{-6}$</td>
</tr>
<tr>
<td>7</td>
<td>$CH_3* + H* \rightarrow CH* + H*$</td>
<td>$9.58 \times 10^{-6}$</td>
<td>$4.16 \times 10^{-6}$</td>
</tr>
<tr>
<td>8</td>
<td>$CH_2* + H* \rightarrow CH* + H*$</td>
<td>$9.58 \times 10^{-6}$</td>
<td>$4.16 \times 10^{-6}$</td>
</tr>
<tr>
<td>9</td>
<td>$CH* + O* \rightarrow CHO*$</td>
<td>$1.05 \times 10^{-5}$</td>
<td>$1.41 \times 10^{-5}$</td>
</tr>
<tr>
<td>10</td>
<td>$CH_3* + O* \rightarrow CH_2O*$</td>
<td>$4.92 \times 10^{-6}$</td>
<td>$3.03 \times 10^{-6}$</td>
</tr>
<tr>
<td>11</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>12</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>13</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>14</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>15</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>16</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>17</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>18</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>19</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>20</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>21</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>22</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>23</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>24</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>25</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>26</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>27</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>28</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>29</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>30</td>
<td>$CH_3O* + * \rightarrow CO* + O*$</td>
<td>$4.91 \times 10^{-6}$</td>
<td>$3.04 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

CH + O path, as shown in Fig. 1. In the C + O Path, CH4 is dehydrogenated to C* sequentially, and then C* couples with O*, formed from CO2 dissociation, to produce CO*. In the CH + O path, CH* couples with O* to form CHO* and finally CO* is obtained through dehydrogenation. As one can see from Fig. 1(a), on Co(111), the rate of CH + O path is around 1.5 orders of magnitude higher than that of the C + O path at 873 K, and the difference is narrowed down at 1073 K.

The rates of other reaction paths are all at least 3 orders of magnitude lower than the rate of the C + O path. In contrast, as shown in Fig. 1(b), the C + O path can be considered as the dominant reaction path on Co(211). The rates of other paths are at least 1.5 orders of magnitude lower than those of the C + O path. Based on our previous work, we found that the main reaction paths on Co are the same as on the Ni surfaces. [75] However, the reaction rate of Ni catalyst is higher, which is consistent with the experimental observation [76,77]. Meanwhile, as we mentioned in the introduction, the deactivation performance of Ni and Co is different, which will be discussed in the following sections.

3.2.2. Coverage of surface species and DRC analysis
We plotted in Fig. 2 the steady state coverage of dominant surface intermediates, including CO*, C* and O* on two Co surfaces. The coverage of other surface intermediates is close to 0 and thus omitted from Fig. 2. On Co(111), the coverage of CO* is around 0.2 monolayer (ML) at 873 K, and decreases to 0 when the temperature is higher than 973 K. The coverage of C* on the surface stays at 0 ML at different temperatures, whilst the coverage of O* slightly increases from 0 to 0.1 ML when the temperature rises from 873 to 1073 K. On Co(211), the coverage of O* increases from 0.6 ML (873 K) to about 0.8 ML (1073 K) with temperature. Therefore, one can find that the high coverage of oxygen on Co(211) may facilitate the oxidation of Co. The coverage of both CO* and C* on Co(211) is low at 873 K (about 0.1 ML) and drops to about 0 ML when the temperature rises.

Since the reverse water gas shift (RWGS) reaction, i.e. CO2 + H2 → CO + H2O, was reported as a major side reaction in the DRM reaction [78,79], we investigated the effect of this reaction on the coverage of O* over Co(111) and Co(211). We added the elementary step of H2O formation to the kinetic model, with other simulation conditions unchanged. The obtained coverage of O* at steady state are shown in Fig. S6. One can find from the figure that, upon considering the RWGS reaction, the coverage of O* is almost unchanged on Co(111), while on Co(211), the coverage is reduced by around 0.1 ML. However, the coverage of O* on Co(211) is still much higher than that on Co(111), even with the RWGS reaction included in the modeling.

The DRC analysis results are also shown in Fig. 2. One can find from the figure that, on both Co(111) and Co(211), transition state of CH4 dissociation is the RCTS at all the temperatures considered. On Co(111), the DRC value of CO* is around -0.5 at 873 K, and gets close to zero.

![Fig. 1](image_url)

Fig. 1. Reaction rates of the dominant reaction pathways (highlighted in the above panel) and the total rates of the DRM reaction on Co(111) and Co(211) as a function of temperature.
when temperature rises due to the decrease of CO coverage on the surface. In contrast, the DRC value of O* is close to 0 at 873 K, and becomes more negative to -0.25 at 1073 K. On Co(211) surface, O* is shown as the only rate controlling intermediates and becomes more rate-controlling with the increase of temperature. Although oxygen is not directly participating in the dissociation of CH₄, the presence of oxygen on the surface will influence the surface free sites that can be used for the dissociation reaction where one more free site is needed.

3.3. Deactivation mechanism of Co

3.3.1. Stability of C* and O* on two Co surfaces

In order to understand the behavior of C* and O* during the deactivation of Co catalysts, we hereby calculate the adsorption of C* and O* at different coverages on Co(111) and Co(211). For the extra calculations, we constructed four-layer (1 × 4) Co(211) slabs and placed different numbers of adsorbates at these sites. The k-points used for the above two slabs were (3 × 3 × 1) and (4 × 2 × 1) for Co(111) and Co(211), respectively. Other parameters and convergence criteria are the same with all the previous calculations.

Typically, carbon deposition can follow the dissolving mechanism or the surface coupling mechanism. In the dissolving mechanism, the surface C* species will dissolve into the bulk of metals to form carbide, and then precipitates at the rear side of the nanoparticles to form a carbon nanofilament [80]. In the surface coupling mechanism, the surface carbon species will couple with each other and form stable surface clustered structures [80]. In this section we will consider both mechanisms at different Co sites by determining the behavior of carbon at the surface and subsurface sites with different coverages. Regarding the oxidation process, as mentioned above, the coverage of O* at the step sites over Co(211) are much higher than that on Co(111), we therefore further verify the coverage dependent adsorption of O* at the surface sites of both surfaces.

The average adsorption Gibbs free energy of C* or O* adsorbed at the surface or subsurface site at different coverage can be calculated using the following equation:

\[
\Delta G(T, p, N_{ads}) = \frac{E_{Nads/slab} - E_{ads} - N\mu_{ads}}{N}
\]

Where, \(\Delta G(T, p, N_{ads})\), hereinafter referred to as \(\Delta G_{C}\) or \(\Delta G_{O}\), is the adsorption free energy of C* or O*, \(N\) is the number of adsorbates, \(E_{Nads/slab}\) and \(E_{ads}\) is the energy of slab with N number of adsorbates and the energy of clean surface, respectively. \(\mu_{ads}\) is the chemical potential of referenced C or O, which can be calculated from \(\mu_{C} = \mu_{CH4} - 2\mu_{H2}\) and \(\mu_{O} = \mu_{CO2(gas)} - \mu_{CO(gas)}\), respectively. The chemical potential can be calculated from the DFT energy with thermodynamic corrections at 973 K, and the pressures of gaseous species is the same with those used in the microkinetic simulations.

We summarize in Fig. 3 the average adsorption free energy of C* and O* on Co(111) and Co(211) as a function of coverage. The surface/subsurface \(\Delta G_{C}\) will determine whether the adsorbed carbon can diffuse from the surface sites to subsurface and which carbon deposition mechanism to follow on different Co surfaces [81]. We find that on Co(111), the surface/subsurface \(\Delta G_{C}\) at 0.25 ML are almost identical, indicating that the diffusion of C* between the surface and subsurface sites is thermodynamically neutral. As the coverage increases, the difference between \(\Delta G_{C}\) at the subsurface and surface becomes larger, and the surface carbon becomes more stable, indicating that the diffusion of C* from surface to subsurface becomes thermodynamically prohibited. In addition, we find that when the coverage is higher than 0.25 ML, surface carbon atoms tend to form clusters on Co(111) (see Fig. 3a), and are therefore stabilized. However, such cluster structures are not observed on Co(211), where C* adsorption is destabilized with coverages increased. More importantly, surface C* is more stable than subsurface C* at any coverage on Co(211), indicating that the diffusion of C* to subsurface is also thermodynamically prohibited.

For surface O*, it is also shown in Fig. 3 that higher coverage will result in weaker adsorption on the two cobalt surfaces studied. More importantly, the adsorption of O* on Co(211) is always more stable than that on Co(111) at all the coverages considered here. Combining with the microkinetic simulation results obtained from low coverage DFT energies shown in Fig. 2, these results suggest that O* deposition will preferentially take place on Co(211). Furthermore, the dissociation barrier of CO₂ on Co(211) is lower than on Co(111), indicating that the produce of O* on Co(211) surface is also kinetically favored. The
of the surface oxidation process of a catalyst is rather complex and may include several steps, such as deposition of oxygen, oxygen permeation into the bulk and surface reconstruction induced by oxygen. Among all these steps, deposition of surface oxygen should be the first, and higher coverage of oxygen deposition would indicate that the surface might be easier to be oxidized.

### 3.3.2. Kinetics of carbon deposition

After discussing the thermodynamic properties of C* at the surface or subsurface sites on two Co facets, the kinetics of carbon deposition on the surface of p(3 × 3) Co(111) and p(1 × 4) Co(211) are further studied. We calculated the barriers of the first step of surface coupling mechanism (C–C coupling), the first step of carbon dissolve mechanism (C* diffusion to subsurface) and CO* formation on two cobalt surfaces, and the results are summarized in Fig. 4.

On Co(111), the barrier of C–C coupling (1.07 eV) is lower than that of the diffusion of C* from surface to subsurface (1.23 eV) and CO* formation (1.59 eV), indicating the surface coupling mechanism on this surface is kinetically favored. On Co(211), the barrier of C* and O* association (1.74 eV) is the lowest among all three elementary steps considered, indicating that CO formation might be kinetically favored on this surface. The above results suggest that carbon deposition is preferred on Co(111), which is consistent with the experimental results that catalyst with large Co particles is readily deactivated due to carbon deposition [26,82,83]. Furthermore, we find that the carbon deposition over cobalt in DRM reaction follows the surface coupling mechanism rather than the dissolving mechanism.

### 3.3.3. Competition between the deposition and removal of surface carbon

According to the results presented above, the surface coupling mechanism is kinetically favored but thermodynamically unfavored in comparison with CO formation on Co(111) (Fig. 4a). To further understand the competition between the deposition and removal of surface carbon on Co(111), we calculated and compared the corresponding reaction rates at different temperatures. The relevant elementary steps considered are C* + C* → C2* + * and C* + O* → CO* + *.

It should be noted that the single direction arrow indicates an irreversible reaction while the double direction arrow for a reversible reaction.

We here consider the C–C bonding reaction as an irreversible reaction for the following reasons. Firstly, under the temperature conditions we considered in this work, the formation of C2* is always an exergonic process with the reaction Gibbs free energy closed to −0.64 eV (see Fig. S7). Secondly, C2* is not the end point of surface C* coupling due to the thermodynamically favored carbon cluster formation. Finally, the coverage of surface C2* at the beginning of the surface carbon deposition process is negligible, meaning that the reverse rate of the C–C bonding reaction should be low enough to be ignored. Regarding CO* formation, the reverse reaction could not be ignored since CO* is the main product and the concentration of CO* is much higher than that of C2*. Therefore, the ratio between the reaction rates can be calculated from the following equation

\[
\frac{k_C}{k_O} = \frac{k_C C_2^*}{k_C C O + \theta C O} = \frac{k_C C_2^*}{k_C C O + k_C C O (1 - \theta C O)}
\]

Where, \(k_C C\) represents the forward rate constant of C2* formation reaction, \(k_C O\) and \(k_C O\) are the forward and reverse rate constant of C* and O* association reaction, respectively. \(\theta C O\) is the coverage of C*, O*, CO* and free site from the above microkinetic simulations, respectively, implying that we are taking the steady state of DRM over the clean Co surface as the starting point of deactivation. We plot the calculation results of Eq. (4) against the reaction temperature in Fig. 5.

From Fig. 5, one can see that at 873 K, the rate of C2* formation is five times faster than that of CO formation. With the increase of temperature, the ratio decreases gradually, and is equal to 1 at the temperature around 973 K. This indicates that below 973 K, the rate of C–C...
coupling is higher than that of CO formation on Co(111). However, at high temperatures, i.e. above 973 K, C–C coupling rate tends to decrease in comparison with CO formation rate. Hence, our results suggest that carbon deposition is the main mechanism of deactivation on Co (111) surface at low temperatures, and that high temperatures prevent catalyst deactivation. Such observations agree well with experiments. Indeed, the coke formation on 10 wt% Co/Al2O3 catalyst is 0.25 g (carbon)/g catalyst$^{-1}$ h$^{-1}$ at 973 K [84], or 35% of reacted methane turns into carbon deposition on 7.6 wt% Co catalyst [85]. At high temperatures, e.g. 1023 K, no carbon deposition and deactivation during DRM reaction at 1073 K with 10 wt% Co/Al2O3 catalyst [86].

3.4. Insights into future cobalt-based catalyst design

Now we have clarified the reactivity and deactivation mechanism of the Co catalyst towards the DRM reaction. In general, the trend of both activity and stability of catalysts with different sizes can be derived from the ratios of the (211) and (111) surfaces. Smaller Co particles showing more low coordination sites would give higher DRM activity at lower reaction temperature condition but also higher deactivation possibility through oxidation. The possibility of carbon deposition over larger particles of Co, which are dominated by terrace sites, is strongly dependent on the reaction temperature, and higher temperatures will inhibit the coke formation. Based on these understandings, we further propose below some suggestions for the modification of Co-based catalysts.

In order to obtain balanced activity and stability of the DRM catalysts, we recently found that a good dopant should give rise to a proper adsorption energy of carbon to ensure that the C* formation process, e.g. CH$_4$ dissociation, is rate controlling to improve the carbon resistance, and relatively low dissociation barriers of CH$_4$ and CO$_2$ can be achieved to maintain a good activity [75]. By doping or forming an alloy, the adsorption of O* at the Co step is regulated and the oxidation of the Co catalyst can be inhibited. For Co with large particles and more (111) facets, our simulation suggests that high reaction temperature should be achieved to reduce carbon deposition.

4. Conclusions

In this work, the reactivity and reaction pathway of DRM on Co (111) and Co(211) were studied with a combined DFT calculation and microkinetic modeling approach. We found that the step site over Co (211) is the active site for the DRM reaction. On Co(111), the C + O and CH + O paths are the preferred reaction paths, while the C + O path is the only dominant path on Co(211). It was also found that the rate-controlling step of the DRM reaction is the same over Co(111) and Co(211), i.e. the dissociation of CH$_4$. We further studied the deactivation of two Co surfaces and showed the deactivation mechanism is facet dependent. Compared with Co(111), the stronger O* adsorption and lower CO$_2$ dissociation barrier on Co(211) leads to much higher O* coverage on the surface, indicating that O* deposition will preferentially take place on Co(211). In contrast, coupling of surface carbon atoms to carbon clusters is thermodynamically and kinetically favorable on Co(111). We also highlighted that Co deactivation through carbon deposition is temperature dependent, and the resistance to carbon deposition would be improved at high temperatures. Our results provide insights into understanding experimental observations of the different deactivation behavior of catalysts with different Co particle size and at different temperatures, based on which strategies for the design of Co-based catalysts were proposed.

CRediT authorship contribution statement

Shuyue Chen: Investigation, Data curation, Formal analysis, Writing - original draft. Jeremie Zafran: Writing - review & editing. Bo Yang: Conceptualization, Supervision, Funding acquisition, Project administration, Resources, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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