Structure sensitivity of CO methanation on Co (0 0 0 1), (1 0 ·1 2) and (1 1 ·2 0) surfaces: Density functional theory calculations

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Density functional theory (DFT) calculations have been carried out to investigate the structural sensitivity of the elementary processes in CO methanation at low coverage of 0.25 ML, including CO dissociation via either direct or H-assisted path and CHx (x = 0–3) hydrogenation, on Co (0 0 0 1), (1 0 ·1 2) and (1 1 ·2 0) surfaces. CO direct dissociation was found to be structurally most sensitive, whereas CHx hydrogenation is structurally least sensitive. Specifically, the barrier of CO direct dissociation, H-assisted dissociation and CHx hydrogenation on different surfaces varies in range of 1.12, 0.54 and 0.34 eV, respectively. Regardless of Co surfaces considered, the CO activation is the rate-limiting step of methanation reactions, which would proceed through the H-assisted pathway on Co (0 0 0 1), whereas through both direct and H-assisted pathways on more active Co (1 0 ·1 2) and (1 1 ·2 0) surfaces. The structure sensitivity of CO activation leads to methanation reaction structural sensitive.

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1. Introduction

The nature of the active sites and structure sensitivity of heterogeneous catalysis has been a longstanding subject of catalysis. The understanding of the structure sensitivity of reactions has progressed enormously with the development of theoretical calculations and ultra-high vacuum technology. For instance, using scan tunneling microscope (STM) and density functional theory (DFT) calculations, Dahl et al. [1] found that the N2 dissociation on Ru (0 0 0 1) is at least nine orders of magnitude slower than that on steps. The reaction barrier on steps was calculated to be 1.5 eV lower than that on flat surfaces. DFT calculation and experimental studies showed CO dissociation is extremely structure sensitive and flat Rh surface cannot dissociate CO under most conditions [2]. The same was also found for NO dissociation on flat and stepped Ru (0 0 0 1) [3,4]. DFT calculations showed that the transition state (TS) of various diatomic molecules on monatomic steps involving for instance so-called B5 sites is kinetically more favorable than the TS on close packed surfaces. It was only after the origin of the structure sensitivity of reaction is well understood that the catalysts can be discovered based on rational design.

The methanation reaction has attracted much interest as an alternative to the preferential oxidation of CO (PROX) [5] for removing similar remote amount of CO from the hydrogen feed to proton exchange membrane fuel cells. Industrially, it is a technologically important reaction to remove CO and CO2 from the hydrogen supply for ammonia production [6,7]. Methanation is also used in connection with gasification of coal and Fischer–Tropsch synthesis [8,9]. In addition, methanation is one of the simplest catalytic reactions and can serve as a test bed for the fundamental understanding of heterogeneous catalysis.

A number of experimental [10–25] and theoretical studies [26–30] have been conducted to elucidate the reaction mechanism and to investigate the structure dependence of the methanation reaction. Two possible mechanisms for CO methanation have been proposed, i.e., CO dissociation followed by hydrogenation (direct CO dissociation mechanism), or vice versa (hydrogen-assisted CO dissociation mechanism) to produce CHx (x = 0–3) species, which then undergo sequential hydrogenation, leading to the formation of methane eventually. By the kinetics analysis and H2/D2 isotope experiment, Bell et al. [16,17] suggest that the CO activation is fast through direct dissociation route over Ru catalysts, and that CH3 hydrogenation is rate determining for the synthesis of methane. Ho and Harriott [18] proposed that hydrogen-assisted CO dissociation is the rate limiting step in methanation reaction on nickel catalysts, and this assumption was confirmed by Coenen et al. [21] using isotope labeling method. The H-assisted CO dissociation on Ni is also supported by the DFT calculations that proceed via COH intermediate [22]. Surface science experiments on Co single crystals showed that direct CO dissociation on Co (1 1 ·2 0) and Co (1 0 ·1 2) are much faster compared to the close packed Co (0 0 0 1), and that the apparent activation energy for methane formation on Co (1 1 ·2 0) is equal to the value observed on Co (0 0 0 1) surface.

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which reflects the nature of the similar rate limiting step on the surfaces. These authors proposed that α-hydrogenation of a C\textsubscript{6}H\textsubscript{2n+1} surface species is the rate limiting in FT reactions [23,24]. Iglesia et al. [26] proposed a Fischer–Tropsch synthesis pathway limited by H-assisted CO dissociation on both Fe and Co by combining experiment and theoretical calculation. Jiao et al. [27] observed that step surface has higher activity than flat surface for CO activation and CH\textsubscript{3} are formed mainly via the HCO intermediate dissociation on double stepped Co (0001) surface. Recently, Shetty and van Santen [28] reported that Co direct dissociation is easier than H-assisted pathway on open Co (1 0 1)B and Ru (1 0 1)B surfaces. The hydrogenation of CH\textsubscript{3} (x = 0–3) on flat and stepped Co (0 0 0 1) is studied by Hu and co-workers [29] using DFT calculations. They found that CH\textsubscript{3} hydrogenation (CH\textsubscript{3} + H \rightarrow CH\textsubscript{4}) is the most difficult among all the hydrogenation steps and CH\textsubscript{3} hydrogenation process is not structure sensitive.

Nickel is the commonly used catalyst for methanation [30] due to its high selectivity towards methane and lower price. However, cobalt has attracted much attention due to higher reactivity [31] and resistance towards carbon deposition [32]. To shed light on the structure sensitivity of CO methanation on Co in particular surface orientations, we systematically investigated two possible pathways proceeding via either direct or H-assisted CO dissociation using DFT, on the close packed Co (0 0 0 1), and more open Co (1 0 1 2) and (1 1 2 0) surfaces. The results are compared with previous UHV and real catalytic experiments, and the dependence of the structure sensitivity on reaction conditions is discussed.

2. Calculation methods

All the spin-polarized DFT calculations were carried out using the Vienna ab initio simulation package (VASP) [33,34]. Projector augmented wave (PAW) [35,36] potentials and the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional were used [37]. The kinetic energy cutoff for the plane wave basis set was specified by 400 eV. During the electronic optimization, the change of the total energy and the band structure energy are converged to 10\textsuperscript{-4} eV/atom. When the forces on the ions are below 10\textsuperscript{-2} eV/Å, the optimizations have been considered to be converged.

Calculated lattice constant of hcp Co are a = 2.49 Å and c = 4.03 Å, which agrees well with previous calculation (a = 2.56 Å and c = 4.14 Å) [38] and experimental measurement (a = 2.51 Å and c = 4.06 Å) [39]. Co (0 0 0 1), (1 0 1 2) and (1 1 2 0) surfaces are represented as four closed packed layers, twelve layers and seven layers with p(2 × 2) periodicity consisting of 16, 48 and 56 cobalt atoms, respectively. In order to avoiding the periodic interactions, the two neighboring slabs are separated by a vacuum of 15 Å. Monkhorst–Pack mesh k-points sampling of (7 × 7 × 1), (3 × 7 × 1) and (4 × 4 × 1) was separately used for (0 0 0 1), (1 0 1 2) and (1 1 2 0) surface calculations. The bottom two, six and three layers were kept fixed for (0 0 0 1), (1 0 1 2) and (1 1 2 0) surfaces, while the other cobalt layers and the adsorbates were relaxed completely, respectively.

An efficient force reversed method [40] was used to determine the transition states and a force tolerance of 0.03 eV/Å was used. A couple of the transition states identified were selected and calculated again using the climbing-image nudged elastic band (CI-NEB) method [41] implemented in VASP to guarantee the same transition states found.

The chemisorption energy \(E_{\text{ads}}\) of the intermediate A involved in CO methanation process can be expressed as \(E_{\text{ads}} = E_{\text{A/Slab}} - E_{\text{Slab}} - E_{\text{A}}\), where \(E_{\text{A/Slab}}\) and \(E_{\text{Slab}}\) are the total energies for the slab with chemisorbed species A and the clean surface, respectively, and \(E_{\text{A}}\) is the radical or molecule A in the gas phase. The reaction energies can be calculated as the difference between the total energies of the products and the reactants.

3. Results and discussions

3.1. Intermediates adsorption

The geometric structures of Co (0001), (1 0 1 2) and (1 1 2 0) surfaces are shown in Fig. 1. It can be seen that flat (0001) surface is hexagonal close packed and consists of hcp and fcc hollow adsorption sites. The (1 0 1 2) surface is a stepped surface with unique 4-fold hollow sites and bridge site at the step edge. The (1 1 2 0) surface is characterized by zigzag grooves, and has long and short ridge sites and hollow sites, respectively. The coordination number is nine on Co (0001) surface, higher than that of seven for Co atom at the step of (1 0 1 2) surface and the ridge of (1 1 2 0) surface.

We first calculated the adsorption of the intermediates (CO, HCO, CH\textsubscript{x} (x = 0–4), C, H, O) involved in CO methanation reactions on Co (0 0 0 1), (1 0 1 2) and (1 1 2 0) surfaces. The energetic and geometric information of the most stable state of various intermediates on all the three surfaces is listed in Table 1, and the selected corresponding structures are given in Fig. 2. Atomic adsorbates, carbon, oxygen and hydrogen, and CH\textsubscript{x} species (x = 1, 2) prefer hcp/fcc, 4-fold hollow and hollow sites on Co (0 0 0 1), (1 0 1 2) and (1 1 2 0) surfaces, respectively. Except that atomic H binds at the short bridge site on Co (1 1 2 0). Compared to CH and CH\textsubscript{2}, CH\textsubscript{3} and CH\textsubscript{4} tend to bind with less surface Co atoms as shown in Fig. 2(c and d) and (e and f). CH\textsubscript{2} binds in hcp, short bridge and bridge sites on Co (0 0 0 1), (1 0 1 2) and (1 1 2 0) surfaces respectively, and CH\textsubscript{4}
Table 1

Adsortion energy ($E_{ads}$, in eV) and favorable adsorption sites of the various adsorbates on Co $\{000\}$, $\{10^{-1} 2\}$ and $\{11 ^{-2} 0\}$ surfaces. All the adsorption energies are calculated with respect to the corresponding free radical or molecule in the gas phase.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$E_{ads}$</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>$-6.83$ eV</td>
<td>hcp</td>
</tr>
<tr>
<td>O</td>
<td>$-5.65$ eV</td>
<td>hcp</td>
</tr>
<tr>
<td>H</td>
<td>$-2.78$ eV</td>
<td>fcc</td>
</tr>
<tr>
<td>CO</td>
<td>$-1.64$ eV</td>
<td>Top</td>
</tr>
<tr>
<td>CH</td>
<td>$-6.30$ eV</td>
<td>hcp</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>$-3.95$ eV</td>
<td>hcp</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>$-1.89$ eV</td>
<td>hcp</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>$-0.02$ eV</td>
<td>Top</td>
</tr>
<tr>
<td>HCO</td>
<td>$-2.14$ eV</td>
<td>C-bridge–O-bridge</td>
</tr>
</tbody>
</table>

Fig. 2. Top view and side view (insets) of the selected key intermediates involved in CO methanation adsorbed on Co $\{000\}$ (up panel), $\{10^{-1} 2\}$ (middle panel) and $\{11 ^{-2} 0\}$ (bottom panel) surfaces: (a) CO, (b) HCO, (c) CH, (d) CH$_2$, (e) CH$_3$, and (f) CH$_4$ (grey: C atom; red: O atom). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.2. CO activation

As mentioned in the Introduction, CO activation can proceed by either direct or H assisted route. In the present work, we investigate both routes. Elementary reaction energies and activation energies are calculated with respect to the adsorbed reactants with infinite distance.

3.2.1. Direct dissociation of CO

In this section, we studied the direct CO dissociation on flat Co $\{000\}$, open Co $\{10^{-1} 2\}$ and $\{11 ^{-2} 0\}$ surfaces. The calculated CO dissociation barriers ($E_a$) and reaction energies ($\Delta H$) on the surfaces are listed in Table 2, together with the important structural parameters at the transition states (TSSs). The structures for all the TSSs optimized are shown in Fig. 3.

As shown in Section 3.1, CO prefers the top, 4-fold hollow and short bridge site on Co $\{000\}$, $\{10^{-1} 2\}$ and $\{11 ^{-2} 0\}$ surfaces, which are taken as the initial states for CO direct dissociation. At the TSSs, C is near the hcp hollow, 4-fold hollow and long bridge site on Co $\{000\}$, $\{10^{-1} 2\}$ and $\{11 ^{-2} 0\}$ surfaces respectively, and O is

Table 2

Calculated elemental reaction barrier ($E_a$, in eV), reaction energy ($\Delta E$, in eV) and the distance ($d^{15}$, in Å) between the two reacting fragments at the transition state for CO dissociation (direct and H-assisted pathways) on Co $\{000\}$, $\{10^{-1} 2\}$ and $\{11 ^{-2} 0\}$ surfaces.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$E_a$</th>
<th>$\Delta E$</th>
<th>$d^{15}$</th>
<th>$E_a$</th>
<th>$\Delta E$</th>
<th>$d^{15}$</th>
<th>$E_a$</th>
<th>$\Delta E$</th>
<th>$d^{15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO $\rightarrow$ C + O</td>
<td>2.46 eV</td>
<td>0.69 eV</td>
<td>1.80 Å</td>
<td>1.34 eV</td>
<td>-0.58 eV</td>
<td>1.89 Å</td>
<td>1.39 eV</td>
<td>0.32 eV</td>
<td>1.94 Å</td>
</tr>
<tr>
<td>CO + H $\rightarrow$ HCO</td>
<td>1.18 eV</td>
<td>1.10 eV</td>
<td>1.12 Å</td>
<td>1.13 eV</td>
<td>0.36 eV</td>
<td>1.36 Å</td>
<td>0.95 eV</td>
<td>0.57 eV</td>
<td>1.64 Å</td>
</tr>
<tr>
<td>HCO $\rightarrow$ CH + O</td>
<td>0.73 eV</td>
<td>-0.80 eV</td>
<td>1.76 Å</td>
<td>1.04 eV</td>
<td>-0.91 eV</td>
<td>2.14 Å</td>
<td>0.72 eV</td>
<td>-0.54 eV</td>
<td>1.90 Å</td>
</tr>
</tbody>
</table>
near the bridge site. No surface Co atoms are shared by C and O (less site competition) on Co(11120), whereas one and two Co atoms are shared on Co(0001) and Co(1012) (stronger site competition) as shown in Fig. 3(a). CO dissociation TSs belong to late TSs, and corresponding C–O bond length are 1.80, 1.89 and 1.94 Å on Co(0001), (1012) and (1120) surfaces, respectively. The TS geometry on Co(1120) is different from previous finding [42] that C atom sits at the hollow site and O atom sits at the long bridge site, and the present TS is energetically more favorable (Fig. 4).

Generally, the site competition of the dissociated fragments on the surface would raise the overall energetics and destabilize the corresponding TSs. This is indeed the case found on Co(0001) with the highest barrier of 2.46 eV and endothermic reaction energy ∆E of 0.69 eV. On Co(1120) where there is no site competition between C and O at the TS due to the ensemble effect at the step edge [43], the calculated barrier decreases dramatically to 1.39 eV, and the reaction energy remains endothermic with value of 0.32 eV. For Co(1012), though there might be significant site competition between C and O at the TS, the calculated barrier is however the lowest one with value of 1.34 eV, and corresponding reaction energy becomes even exothermic of −0.58 eV. The high activity of Co(1012) in term of the lowest barrier and exothermic reaction energy comes from the favorable 4-fold C adsorption involved at both the TS and the final state. As listed in Table 1, C binding at optimized 4-fold site of Co(1012) is much stronger than that at hollow site of Co(0001) and (1120) by 1.02 and 0.63 eV. Namely, it is the favorable 4-fold C adsorption overcompensating the site competition on Co(1012) which has the highest activity. The significant change of the barriers and reaction energies on the different surfaces considered in magnitude of 1.12 eV and 1.27 eV shows clearly that the direct CO dissociation is structurally very sensitive.

Note that the barrier for CO desorption on Co(0001), measured by corresponding binding energy of −1.64 eV, is less than that for forward C–O bond scission (2.46 eV), implying that CO desorption favors over its decomposition at elevated temperature on this surface. For the remaining two open surfaces, the C≡O bond scission barriers are less than those of the binding energies of adsorbed CO, and hence the CO decomposition is preferential.

3.2.2 H-assisted CO dissociation

Besides the direct CO dissociation, we also studied the hydrogen-assisted CO dissociation pathway. As seen from Fig. 3(b and c) and Table 2, atomic H addition to CO leads to a formyl intermediate (HCO) formation, with barriers of 1.18 eV, 1.13 eV and 0.95 eV on Co(0001), (1012) and (1120), respectively. The difference of the barriers is less than 0.23 eV, in contrast to that of CO direct dissociation. By careful examination of the TSs, we found that HCO formation on the three surfaces mainly involves CO bending and H displacement, which are less structure sensitive. The distance between C and H atoms is 1.12, 1.36 and 1.64 Å at the TSs. The elementary step is endothermic by 1.10, 0.36 and 0.57 eV on the three surfaces. The pronounced difference of the reaction energies comes from the different binding strength of HCO, as seen from Table 1.

Then, the adsorbed formyl intermediate HCO decomposes into O and CH, with the barriers of 0.73, 1.04 and 0.72 eV on Co(0001), (1012) and (1120) surfaces, respectively. As shown in Fig. 3, O
binds at the bridge site, and CH binds at the hollow (Co 000 1) or bridge (Co (1 0 1 2) and (1 1 2 0)) sites at the TSs. The step is exothermic by −0.80, −0.91 and −0.54 eV on the corresponding surfaces. Clearly, HCO decomposition is also less structure sensitive compared to CO direct dissociation. The higher barrier on Co (1 0 1 2) is larger stretching of C–O bond at the TS of 2.14 Å, compared to the corresponding values of 1.76 and 1.90 Å on Co (0 0 0 1) and Co (1 1 2 0).

From Fig. 5, we can see that the overall barriers for H-assisted CO dissociation with respect to separately adsorbed CO and H is 1.83, 1.40 and 1.29 eV on Co (0 0 0 1), (1 0 1 2) and (1 1 2 0), respectively. Corresponding reaction energies are 0.30, −0.55 and 0.04 eV. The change of the barriers and reaction energies on the different surfaces considered falls in magnitude of 0.54 eV and 0.85 eV. Compared to those of 1.12 eV and 1.27 eV for direct CO dissociation pathway, it is clear that the H-assisted pathway is relatively less structural sensitive.

### 3.3. CH₅ Hydrogenation

Having studied CO activation, we then turn our attention to CH₅ (x=0–3) hydrogenation, and the results are given in Table 3 and plotted in Fig. 5. Regardless the three surfaces considered, the highest barrier occurs at CH₅ + H → CH₄ with value varying from 0.76 to 0.99 eV, followed by C + H → CH, CH + H → CH₂ and CH₂ + H → CH₃ with smaller barriers. It can be found that the maximum difference of the elementary reaction barrier between the three surfaces considered is 0.34 eV occurring for CH₅ + H → CH₃, compared to 0.10 eV for C + H → CH and CH + H → CH₂, and 0.23 eV for CH₂ + H → CH₄, respectively. Whereas the maximum difference of the reaction energies between the three surfaces is 0.42 eV for C + H → CH, compared to 0.19 eV for CH + H → CH₂, 0.25 eV for CH₂ + H → CH₃, and 0.17 eV for CH₃ + H → CH₄. Compared to the difference of the H-assisted CO dissociation barrier and reaction energy on the three surfaces (0.54 eV and 0.85 eV), the structural sensitivity of the CH₅ hydrogenation with the variation of the elementary reaction barriers and reaction energies in magnitude of 0.34 eV and 0.42 eV decreases further. The overall barriers and reaction energies variation of CH hydrogenation to CH₄ is 0.49 and 0.58 eV. Interestingly, the overall reaction is endothermic by 0.52 eV on (1 0 1 2) surface, whereas it becomes endothermic by between −0.06 eV on (1 1 2 0) as shown in Fig. 5. The reason is that as the valency increase, CH₅ adsorption is more and more structure sensitive as seen from Table 1. Actually, the small structural sensitivity of the CH₅ hydrogenation was also found on other metal surfaces by previous DFT studies [44]. With the methanation endothermic on (1 1 2 0), C–C coupling might become preferential and this would lead to a higher selectivity of the chain growth.

The least structure sensitivity of the CH₅ hydrogenation could be well rationalized by the geometric structure variation from the initial states to transition states. For CH₅ (x=0–2) hydrogenation, corresponding structure variation show a common feature, namely there is a little displacement of CH₅ species, and main change comes from the displacement of hydrogen atom from its initial position hollow site to an top site and bridge on Co (0 0 0 1) and (1 0 1 2) surfaces. The activation from the latter one therefore contributes mainly the activation energy. Generally, atomic hydrogen shows a nearly flat potential energy surface on many transition metal surfaces, and hydrogen diffusion barrier does not exhibit a strong dependence on surface structure. These lead to

### Table 3

#### Calculated elementary reaction barrier (Eₐ in eV), reaction energy (∆E, in eV) and the distance (d, in Å) between the two reacting fragments at the transition state for CH₅ (x=0–3) hydrogenation on Co (0 0 0 1), (1 0 1 2) and (1 1 2 0) surfaces.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>(0 0 0 1)</th>
<th>(1 0 1 2)</th>
<th>(1 1 2 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eₐ</td>
<td>∆E</td>
<td>d</td>
<td>Eₐ</td>
</tr>
<tr>
<td>C + H → CH</td>
<td>0.73</td>
<td>−0.39</td>
<td>1.69</td>
</tr>
<tr>
<td>CH + H → CH₂</td>
<td>0.55</td>
<td>0.33</td>
<td>1.60</td>
</tr>
<tr>
<td>CH₂ + H → CH₃</td>
<td>0.55</td>
<td>−0.13</td>
<td>1.75</td>
</tr>
<tr>
<td>CH₃ + H → CH₄</td>
<td>0.99</td>
<td>−0.07</td>
<td>1.59</td>
</tr>
</tbody>
</table>

Fig. 5. Potential energy surface diagram for CO methanation on Co (0 0 0 1) (black line), (1 0 1 2) (red line) and (1 1 2 0) (blue line) surfaces. The dashed lines are assigned to direct CO dissociation and the solid lines represent H-assisted CO dissociation process. CO and CH₄ in the gas phase is used as the reference. The selected forward elementary reaction barriers are labeled in eV. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
CH$_x$ (x = 0–2) hydrogenation the least structural sensitive. For CH$_3$ hydrogenation, we note that in addition to the displacement of H as found in CH$_x$ (x = 0–2) hydrogenation, CH$_3$ moves from favorable hcp or bridge site to less favorable top site on Co (0 0 0 1), (1 0 1 2) and (1 1 2 0). This will cost an extra energy, which is actually the reason why the barrier of CH$_3$ hydrogenation is higher than those of CH$_x$ (x = 0–2) hydrogenation. On the other hand, as shown in Section 3.1, CH$_3$ adsorption is least structure sensitive among all the CH$_x$ (x = 0–3) species, with the adsorption energies variation of 0.19 eV at most between the three surfaces. This makes eventually CH$_3$ hydrogenation structural rather insensitive too.

4. Discussion

As seen from Table 2 and Fig. 5, CO direct dissociation on Co (1 0 1 2) and Co (1 1 2 0) is more exothermic than on Co (0 0 0 1) by 1.27 and 0.37 eV. Furthermore, compared to Co (0 0 0 1), the dissociation barriers on the two surfaces are substantially lowered (by 1.12 and 1.07 eV, respectively). Therefore, CO direct dissociation on Co (1 0 1 2) and Co (1 1 2 0) is more favorable than on Co (0 0 0 1) thermodynamically and kinetically. These results agree well with UHV studies [45] that under low pressure conditions CO is molecularly adsorbed on Co (0 0 0 1) between 100 and 450 K, and dissociative adsorption is preferred on Co (1 0 1 2) and Co (1 1 2 0) above room temperature [46].

However, in the presence of H$_2$, we found that the H-assisted CO dissociation is less endothermic by 0.39 eV compared to direct C–O bond scission on Co (0 0 0 1). The barrier for H-assisted CO dissociation with the overall barrier of 1.84 eV is also significantly lower than the barrier for CO direct dissociation (by 0.63 eV). In turn, the H-assisted CO dissociation mechanism is primarily responsible for CO methanation at low temperatures. On Co (1 0 1 2) and Co (1 1 2 0), H-assisted dissociation of CO has the similar overall barriers (1.40 eV and 1.29 eV) as those of direct CO dissociation (1.34 eV and 1.39 eV), offering another alternative route to CO activation.

Once CO is activated through either direct or H-assisted route, the resulting CH$_x$ (x = 1–3) intermediates can hydrogenate sequentially, with the formation of CH$_4$ eventually. Our calculations show that all the CH$_x$ hydrogenation steps are structural least sensitive, and CH$_3$ hydrogenation is the most difficult among the CH$_x$ (x = 0–3) hydrogenation steps. Compared to CH$_3$ hydrogenation, CO activation, proceeding through H-assisted or direct route, has a higher barrier by 0.84, 0.48 and 0.53 eV on Co (0 0 0 1), (1 0 1 2) and (1 1 2 0) surfaces, respectively (see Fig. 5). Therefore, CO activation is the most difficult at low coverage of 1/4 ML regardless of the surfaces considered. Specifically, HCO decomposition is the rate-limiting step (RLS) on Co (0 0 0 1), with a barrier of 1.83 eV, and CO/HCO decomposition is the RLS on Co (1 0 1 2) (1.34/1.40) and (1 1 2 0) (1.39/1.29) surfaces.

Geerlings’ experimental studies [23] (p = 1 bar; H$_2$:CO = 2:1; T = 220–300°C) show that methane and ethane formation have an equal activation energy of 70 kJ/mol on Co (0 0 0 1) and on Co (1 1 2 0). They propose that the reactions have similar rate determining steps of α-hydrogenation of CH$_2$H$_{2n+1}$ surface species. We have shown that direct CO activation is very structure sensitive: the open Co (1 0 1 2) and (1 1 2 0) surfaces have significantly lower barriers than that of Co (0 0 0 1) surface. However, in the presence of hydrogen, CO dissociation activity is greatly enhanced on the Co (0 0 0 1) surface. The difference of the barrier for CO activation between Co (0 0 0 1) and the open surface decreases to 0.54 eV. Our calculations correspond to low reactant coverage (1/4 ML) conditions. It could be expected that the activity difference between the two surfaces could be reduced at high pressure. The reason is that the more reactive Co (1 1 2 0) surface would have higher adsorbates coverage, thereby providing less adsorbate free active sites where reactants can be activated. At the same time, the higher adsorbates coverage on Co (1 1 2 0) decreases the CO activation more than Co (0 0 0 1) through a substantial destabilization of the adsorbed CO. Therefore, it seems that our calculations provide an alternative insight into Geerlings’ experimental results that if methane and ethane formation have the same rate limiting step of CO activation, the apparent activation energies could also be similar.

The RLS of CO activation is also found on Ni (2 1 1) surface by Norskov et al. [22]. They show that direct CO dissociation is the RLS up to temperatures of at least 850 K in the low CO coverage regime, whereas at the high coverage regime, CO dissociation via COH is RLS up until temperatures just below 850 K. In addition, they found that CO dissociation is highly structure sensitive and also is sensitive to the presence of hydrogen: Under ultra-high vacuum, with no hydrogen present, the dissociation proceeds through a direct route in which only undercoordinated sites (e.g., steps) are active. Under methanation conditions, the dissociation also proceeds most favorably over undercoordinated sites, but through a COH species.

By comparison of our results and those on Ni catalysts at low CO coverages, we found that Co surfaces have higher activity for CO activation, and hence higher activity for methanation than the corresponding Ni surfaces. However, nickel catalysts finally stand out as the preferred catalyst for methanation due to its superior selectivity towards methane. By a kinetics simulation, Van Santen et al. [47] implies that the methane selectivity can be improved by decreasing CH$_x$ species concentration (or increasing H concentration), since high concentrated CH$_x$ species will favor chain growth, and that the concentration of CH$_x$ species is controlled by CO activation activity. The kinetics analysis can well explain Geerlings’ [24] experimental studies, which show that the chain growth probability on the close packed Co (0 0 0 1) surface (α = 0.2) is lower than Co (1 0 1 2) and (1 1 2 0) (α = 0.3, 0.36). This is possibly because that the lower initial CO activation activity on Co (0 0 0 1) leads to lower CH$_x$ concentration, and more available free sites for H$_2$ dissociation (higher H concentration). Therefore, the possibilities for CH$_4$ formation are larger on Co (0 0 0 1). Likewise, the Ni catalysts having the low activities of CO activation, as confirmed by Norskov’s calculations, can also result in the high selectivity towards CH$_4$. To optimize the methanation catalysts, it is promising to slightly increase/decrease the CO activation activity on Ni/Co catalysts, respectively. The inert Co surfaces with large CO activation barrier and/or high hydrogen pressure should be desirable for methanation reactions.

5. Conclusions

A density functional theory study of structure sensitivity of the elementary processes (CO activation and CH$_3$ hydrogenation at low coverage) in CO methanation on Co (0 0 0 1), (1 0 1 2) and (1 1 2 0) surfaces is presented. We found that direct CO dissociation is structural most sensitive, and the higher activity on the open Co (1 0 1 2) and (1 1 2 0) surface comes from the favorable 4-fold binding site for carbon and the less site competition between dissociated carbon and oxygen at the transition states, respectively. While H-assisted CO dissociation is also structure sensitive and CH$_3$ hydrogenation is structure least sensitive, because the contribution of less structure sensitive adsorbed atomic hydrogen to the overall activation increases. The present calculations show that the H assisted CO activation pathway is favored over direct CO activation pathway on Co (0 0 0 1), whereas both pathways can proceed on Co (1 0 1 2) and (1 1 2 0) surfaces. It was found that CO activation is the rate-limiting step of methanation reactions regardless of the Co surfaces considered. The structure sensitivity of CO activation preferably
occurred on the open surfaces leads to CO methanation on Co surfaces also structure sensitive.

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References