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1 Introduction

The methanation of syngas has recently received considerable attention as a promising way that enables the utilization of syngas and the production of synthetic natural gas. Ni-based catalysts are known to be active for the reactions related to CO. Commonly, supported nickel is the preferred catalyst in methane synthesis from syngas due to raw material sources, cost, and better activity.¹⁻⁴ For example, Ma *et al.*¹ have concluded that the coral reef-like Ni/Al₂O₃ catalysts exhibited better activity and selectivity than the conventional Ni/Al₂O₃– H₂O catalysts for methanation of syngas, and the CO conversion and CH₄ selectivity could remain above 98% and 85%, respectively. In the similar procedure described above, the studies by Gao *et al.*² have shown that nearly 100% CO conversion and 90% CH₄ yield can been achieved over Ni nanoparticles supported on

Insight into the mechanism of methane synthesis from syngas on a Ni(111) surface: a theoretical study⁺

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The mechanism of methane synthesis from syngas on a Ni(111) surface has been systematically investigated using the density functional theory method together with the periodic slab model, which covers the main existence form of CH_x (x = 1-3) species and all possible formation pathways. Our results show that CO hydrogenation to a HCO intermediate is more favorable than CO desorption and CO direct dissociation on Ni(111); starting from HCO, six possible formation pathways of CH_x (x = 1-3) species are considered: (i) HCO \rightarrow CH, (ii) HCO \rightarrow HCOH \rightarrow CH, (iii) HCO \rightarrow HCOH \rightarrow CH₂ (iv) HCO \rightarrow CH₂O \rightarrow CH₂O \rightarrow CH₂O (iv) HCO \rightarrow CH₂O \rightarrow CH₂O \rightarrow CH₂O \rightarrow CH₂O (iv) HCO \rightarrow CH₂O \rightarrow CH₂O \rightarrow CH₂O (iv) HCO \rightarrow CH₂O (iv) HCO (HCOH) \rightarrow CH (iv) two parallel reaction pathways (i) and (iv), followed by the sequential hydrogenation of CH species to CH₄. Meanwhile, surface C is mainly formed by the pathway of CO \rightarrow HCO (HCOH) \rightarrow CH \rightarrow C. Furthermore, beginning with the key CH intermediate, CH preferred to be hydrogenated to CH₂ rather than being dissociated into C.

the barium hexaaluminate (BHA) as CO methanation catalyst. Moreover, Liu et al.5 have verified that Ni catalyst embedded in a micro-channel reactor can present the high activity and stability, which exhibits the excellent catalytic performance for methanation reaction and the reliability in the long-term use. However, carbon deposition and coke are the serious challenges for nickel catalysts resulting in deactivation when the catalyst is applied in the production of synthetic natural gas. As reported, carbon deposition is supposed to be derived from thermal decomposition of hydrocarbons. Besides, it has been recognized that the inactive carbon may occur either via CO direct dissociation or CO disproportionation during methanation.6-8 Many experimental studies have shown that the accumulation of much reactive carbonaceous deposits is related to carbon formation at the temperatures above 350 °C.1-4,6-9 One effective way to prevent carbon deposition is to carry out the reaction at the low temperatures and at the high H₂/CO ratios.⁹ Above results show that carbon deposition is closely related to the actual reaction conditions, CO methanation on Ni catalyst is always related to carbon formation due to strongly exothermic and thermodynamically feasible.2,4,5 The existence of carbon slows down the heat transfer to the catalyst, which causes the deactivation and even destroy the catalyst mechanically. A H₂/ CO ratio about 3 is applicable in industrial operation.¹⁰ The resulting risk of carbon formation has to be offset by improved operation achieved by optimization at different scales, including the reaction on the catalyst surface and at the catalyst pellet, actual reactor, and process levels. Such an approach should rely as much as possible on a fundamental and detailed



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understanding about the reaction system. However, the detailed reaction information has not been mentioned. Therefore, the fundamental understanding about the detailed processes of syngas to methane and the form of surface active species at the atomic level is necessary for a rational design of better Ni-based catalysts.

Extensive theoretical studies have focused on the formation pathway of surface hydrocarbon (CH_r) species involving in the reactions related to CO, one is produced by the direct C-O bond breaking, followed by hydrogenation (carbide mechanism), or vice versa (hydrogen-assisted CO dissociation mechanism); then, CH_r undergoes the hydrogenation to produce CH₄.¹¹⁻²⁰ Gupta et al.21 have reported that over metal Ru, CO firstly dissociates into the active carbon species, which are successively hydrogenated to CH, CH₂, CH₃, and finally CH₄. However, the adverse viewpoint is presented, Vannice et al.22 have shown that CH₄ formation is also detected over surfaces that do not readily dissociate CO such as Pd, Pt and Ir. Kaichev et al.23 have also found that CO dissociation as the source of surface carbon is unlikely even on defect-rich Ni surface. Therefore, the mechanism must include other routes apart from CO direct dissociation. Rupprechtera et al.24 have studied CO hydrogenation to CH_xO on the ion-bombarded Pd (111), followed by the C-O bond scission of CH_xO to CH_x , and further hydrogenation to CH₄. Fuente et al.²⁵ proposed that the carbonaceous species CH_r are formed by the C-O bond cleavage of the hydrogenated intermediates CH_xO. Choi and Liu²⁶ investigated CO hydrogenation on Rh(111), suggesting that CO hydrogenation to HCO is more favorable than CO direct dissociation, CH₃ species is formed by CH₃O dissociation, finally, CH₄ is formed by CH₃ hydrogenation. Qi et al.27 have found that CO successive hydrogenation on both fcc-Mo₂C(100) and hcp-Mo₂C(101) surfaces firstly produce CH2OH, followed by its C-O bond breaking to CH₂ species, finally, CH₄ is formed by CH₂ hydrogenation. Andersson et al.28 have indicated that HCO species plays an important role in CO methanation on Ni surfaces, followed by the C-O bond breaking of HCO to CH species, and further hydrogenation to CH₄. Inderwildi et al.²⁹⁻³¹ suggested that HCO is identified as the intermediate in the dominant reaction pathway. Unfortunately, to the best of our knowledge, the studies about the formation mechanisms of carbonaceous species CH_r on Ni catalyst, as well as the main existence form of CH_x species is still very limited. Moreover, few detailed mechanism of Ni-catalyzed syngas to CH₄ and coke formation have been reported.

In this study, the mechanism of methane formation from syngas on Ni(111) surface has been systematically investigated by density functional theory method. Firstly, the stable adsorption configurations of all possible species are obtained; then, both reaction energy and activation barrier of all possible elementary reactions involved in CH_4 formation and carbon deposition from syngas have been discussed; further, the favorable formation pathway of CH_4 and carbon deposition from syngas are identified; in addition, the fundamental mechanism understanding is expected to contribute to the design of the improved Ni-based catalyst for CH_4 formation from syngas.

2 Computational details

This work was conducted by the Vienna Ab Initio Simulation Package (VASP) with the frozen-core projector-augmented wave (PAW) method. The spin-polarized Perdew–Wang (PW91) generalized gradient approximation (GGA) functional was employed for the exchange–correlation energy.^{32–34} A cutoff energy of 340 eV was employed for the plane-wave expansion. Methfessel–Paxton smearing was employed with $\sigma = 0.1$ eV.²⁰ A $p(3 \times 3)$ lateral super cell was used with a 5 × 5 × 1 Monkhorst– Pack *k*-point mesh throughout the study.^{18,35} Activation barriers and minimum energy paths (MEPs) of elementary steps have been computed using the climbing image nudged elastic band (CI-NEB). After the standard transition state (TS) searching, the TS is further optimized by the dimer method until the residual forces are less than 0.05 eV Å⁻¹.

Ni(111) surfaces are modeled using a three-layer $p(3 \times 3)$ slab with a 15 Å vacuum thickness, which have been widely employed in the previous studies.^{18–20} According to the surface morphology of Ni(111), as shown in Fig. 1, four adsorption sites exist: top, bridge, hexagonal-close-packed (hcp) and face-centered-cubic (fcc) sites. The bottom layer is fixed in their bulk positions, while the upper two layers together with the adsorbed species are fully relaxed until the residual forces of each relaxed ion are less than 0.03 eV Å⁻¹. The lattice constants of Ni bulk are fully optimized to 3.54 Å with the *k*-points of $6 \times 6 \times 6$, which is in good agreement with the experimental values of 3.52 Å.^{34,36-39}

For a reaction such as AB \rightarrow A + B on Ni(111) surface, the reaction energy (ΔH) and activation barrier (E_a) are calculated on the basis of the following formulas:

$$\Delta H = E_{(A+B)/Ni(111)} - E_{AB/Ni(111)}$$
$$E_{a} = E_{TS/Ni(111)} - E_{AB/Ni(111)}$$

where $E_{(A+B)/Ni(111)}$ is the total energy for the co-adsorbed A and B on Ni(111) surface, and $E_{TS/Ni(111)}$ is the total energy of transition state on Ni surface. $E_{AB/Ni(111)}$ is the total energy of adsorbate AB–Ni(111) system in the equilibrium state. The negative value of ΔH denotes that the reaction is exothermic, *vice versa*, the positive value denotes endothermic.

3 Results and discussion

3.1 Adsorptions of all possible species

The adsorption energy, E_{ads} , is always regarded as a measure of strength of adsorbate–substrate adsorption. E_{ads} is defined as follows:



Fig. 1 The structure and adsorption sites of Ni(111) surface (a) side view; (b) top view.

where $E_{\text{mol/Ni(111)}}$ is the total energy of adsorbate-Ni(111) substrate system in the equilibrium state, $E_{\text{Ni(111)}}$ and E_{mol} are the total energies of Ni(111) substrate and free adsorbate alone, respectively. With this definition, the more negative values reflect the strong interaction of adsorbed species with Ni(111) surface.

Adsorptions of all possible species involved in methane synthesis from syngas have been considered. Fig. 2 presents the most stable adsorption configurations; Table 1 lists the key geometric parameters and the corresponding adsorption energies.

3.1.1 C, H and O. C atom prefers to adsorb at the hcp and fcc sites; O atom prefers to adsorb at the fcc site. H atom prefers to adsorb at the fcc and hcp sites due to the nearly close adsorption energy, as shown in Fig. 2(a)-(c). The adsorption energy of C in this study is -6.82 eV with PW91 functional, which agrees with others calculated results using PBE functional (-6.78 eV,17 -6.61 eV (ref. 37) and -6.67 eV (ref. 40)), PW91 functional (-6.86 eV (ref. 32)) and RPBE functional (-6.00 eV (ref. 35) and -6.22 eV (ref. 39)). The adsorption energies of H atom at the fcc and hcp sites are -2.78 and -2.77 eV with PW91 functional, respectively, which is close to the previously reported results (-2.81 eV,¹⁷ -2.86 eV (ref. 40) and -2.95 (ref. 41) with PBE, -2.83 eV (ref. 32) with PW91, and -2.8 eV (ref. 35) and -2.65 eV (ref. 39) with RPBE), suggesting that the result of H adsorption energy is less sensitive to DFT functional. The adsorption energy of O with PW91 functional in this study is -5.76 eV, which is in accordance with the previous values using PBE functional (-5.67 eV (ref. 17) and -5.74 eV (ref. 32)).

3.1.2 CO. CO prefers to adsorb at the fcc and hcp sites, as shown in Fig. 2(d), the corresponding adsorption energies with PW91 functional in this study are -1.90 and -1.91 eV, respectively, which agrees with the previously reported results using PBE (-1.92 eV (ref. 17) and -2.09 eV (ref. 37)) and using PW91



Fig. 2 The most stable configurations of adsorbed species involved in CO hydrogenation on Ni(111) surface. The blue, gray, red and white balls represent Ni, C, O and H atoms, respectively.

functional (-1.91 eV (ref. 32) and -2.01 eV (ref. 34)), whereas the value (-0.39 eV (ref. 42)) reported by Remediakis *et al.* using RPBE is lower than our result. The C–O bond length is elongated from 1.143 Å in gas phase CO (the experimental value is 1.130 Å (ref. 43)) to 1.194 Å, the C–O bond is perpendicular to the surface.

3.1.3 OH and H₂O. OH species is adsorbed perpendicularly to the surface at the fcc site with its oxygen binding to three Ni atoms, as shown in Fig. 2(e); the average values of the O–Ni distance is 1.970 Å, the O–H distance is 0.973 Å, and the adsorption energy (-3.54 eV) is identical to others values by PBE functional $(-3.42 \text{ eV},^{17} - 3.34 \text{ eV} (\text{ref. 37}) \text{ and } -3.19 \text{ eV} (\text{ref. 41})) and PW91 functional <math>(-3.42 \text{ eV} (\text{ref. 32})).$

 H_2O adsorbs at the top site with the O–Ni distance of 2.177 Å by donating the lone pair of oxygen, as shown in Fig. 2(f), the O–H bond length is 0.980 Å, and the adsorption energy (-0.33 eV) is in agreement with the results obtained by PBE functional (-0.29 eV (ref. 17) and -0.47 eV (ref. 37)) and PW91 functional (-0.31 eV (ref. 32)).

3.1.4 CH_x (x = 1-4) species. CH is likely to adsorb at the hcp and fcc sites through C atoms, as shown in Fig. 2(g). Adsorbed CH has C_{3v} symmetry, CH is perpendicular to the surface with the C-Ni and C-H bond lengths of 1.844 and 1.103 Å, respectively; the adsorption energies at the fcc and hcp sites are -6.47 and -6.45 eV, respectively, which are in good agreement with those reported using PBE functional (-6.43 eV,¹⁷ -6.84 eV (ref. 37) and -6.48 eV (ref. 40)), and that reported in the literatures (-5.9 eV (ref. 35) and -5.70 eV (ref. 39)) using RPBE functional.

CH₂ is adsorbed asymmetrically at the fcc site, as shown in Fig. 2(h). One C–H bond is elongated to 1.167 Å with its H atom close to a Ni atom, the distance of C–Ni and H–Ni are 1.975 and 1.746 Å, respectively; whereas the other C–H bond points away from the surface, and has a length of 1.103 Å, two C–Ni distances are 1.910 and 1.906 Å, respectively; the adsorption energy of CH₂ is -4.07 eV, which agrees with the results using PBE functional (-4.01 eV (ref. 17) and -3.89 eV (ref. 40)), and that obtained in the literature (-3.3 eV (ref. 35) and -3.21 eV (ref. 39)) using RPBE functional.

CH₃ preferentially adsorbs at the fcc site through C atom with C_{3v} symmetry, as shown in Fig. 2(i). The adsorption energy of the most stable structures is -1.94 eV, which agree with the reported results with PBE functional (-1.91 eV,¹⁷ -1.86 eV (ref. 40) and -2.04 eV (ref. 41)), and that published in the literature (-1.3 eV (ref. 35) and -1.33 eV (ref. 39)) using RPBE functional. The average C–Ni distance is 2.108 Å, the C–H bond length is 1.122 Å.

CH₄ prefers to adsorb at the top site with only an adsorption energy of -0.02 eV, which agrees with the results obtained by Zhu *et al.* with PBE functional (-0.02 eV (ref. 17)), as shown in Fig. 2(j). The Ni–H distance is 2.515 Å with one H atom pointing down to the surface. One C–H bond is elongated to 1.105 Å with its H atom close to a Ni atom, other C–H bonds have the same length of 1.098 Å, which are close to the values of CH₄ in the gas phase (1.096 Å). Namely, CH₄ molecule is almost not distorted.

3.1.5 HCO and COH. HCO prefers to adsorb at the fcc and hcp sites, as shown in Fig. 2(k), C is adsorbed at the Ni–Ni

Table 1 Adsorption energies (E_{ads} , eV) of adsorption species involved in CO methanation on Ni(111)^{*a*}

Species	$E_{\rm ads} ({\rm eV})$								
	Our results		Previous results						
	PW91		PBE	RPBE	PW91				
С	-6.82 (fcc)	-6.82 (hcp)	-6.78 (ref. 17), -6.61 (ref. 37), -6.67 (ref. 40)	-6.00 (ref. 35), -6.22 (ref. 39)	-6.86 (ref. 32)				
Н	-2.78 (fcc)	-2.77 (hcp)	-2.81 (ref. 17), -2.86 (ref. 40), -2.95 (ref. 41)	-2.8 (ref. 35), -2.65 (ref. 39)	-2.83 (ref. 32)				
0	-5.76 (fcc)		-5.67 (ref. 17)	-4.5 (ref. 35)	-5.74 (ref. 32)				
CO	-1.90 (fcc)	-1.91 (hcp)	-1.92 (ref. 17), -2.09 (ref. 37)	-1.5 (ref. 35), -0.39 (ref. 42)	-1.91 (ref. 32) -2.01 (ref. 34)				
ОН	-3.54 (fcc)		-3.42 (ref. 17), -3.34 (ref. 37), -3.19 (ref. 41)	-2.5 (ref. 35)	-3.42 (ref. 32)				
H_2O	-0.33 (top)		-0.29 (ref. 17), -0.47 (ref. 37)	-0.02 (ref. 35)	-0.31 (ref. 32)				
СН	-6.47 (fcc)	-6.45 (hcp)	-6.43 (ref. 17), -6.84 (ref. 37), -6.48 (ref. 40)	-5.9 (ref. 35), -5.70 (ref. 39)					
CH_2	-4.07 (fcc)		-4.01 (ref. 17), -3.89 (ref. 40)	-3.3 (ref. 35), -3.21 (ref. 39)					
CH ₃	-1.94 (fcc)		-1.91 (ref. 17), -1.86 (ref. 40), -2.04 (ref. 41)	-1.3 (ref. 35), -1.33 (ref. 39)					
CH_4	-0.02 (top)		-0.02 (ref. 17)						
HCO	-2.35 (fcc)	-2.36 (hcp)	-2.26 (ref. 17), -2.49 (ref. 37), -2.41 (ref. 41)	-1.8 (ref. 35)					
COH	-4.45 (fcc)	-4.45 (hcp)	-4.39 (ref. 17), -4.42 (ref. 37)	-2.1 (ref. 35)					
CH_2O	-0.84 (fcc)	-0.83 (hcp)	-0.75 (ref. 17), -1.03 (ref. 41)	-0.2 (ref. 35)					
CH_3O	-2.75 (fcc)		-2.63 (ref. 17), -2.59 (ref. 41)	-1.9 (ref. 35)					
HCOH	-3.91 (bridge)		-3.88 (ref. 17)	-2.4 (ref. 35)					
CH_2OH	-1.68 (bridge)		-1.54 (ref. 17), -1.68 (ref. 41)	-1.0 (ref. 35)					
CH_3OH	-0.37 (top)		-0.30 (ref. 17)	-0.03 (ref. 35), -0.02 (ref. 42)					

^{*a*} DFT methods: GGA-PBE: ref. 17 VASP code, GGA-PBE, 3×3 four-layer slab, $3 \times 3 \times 1$ *k*-points, energy cutoff of 400 eV. Ref. 37 SIESTA code, GGA-PBE, 2×2 four-layer slab, $5 \times 5 \times 1$ *k*-points, energy cutoff of 200 Ry. Ref. 40 DFT code, GGA-PBE, $4 (2 \times 2)$ unit cells, 5×5 *k*-points. Ref. 41 STATE code, GGA-PBE, 3×2 three-layer slab, $4 \times 6 \times 1$ *k*-points, energy cutoff of 25 Ry. GGA-RPBE: ref. 35 DACAPO code, GGA-RPBE, 2×2 three-layer slab, $5 \times 5 \times 1$ *k*-points, energy cutoff of 25 Ry. GGA-RPBE; 2×2 three-layer slab, 15 *k*-points. Ref. 42 DACAPO code, GGA-RPBE, 2×2 three-layer slab, $5 \times 5 \times 1$ *k*-points, energy cutoff of 25 Ry. GGA-RPBE; 2×2 three-layer slab, 15 *k*-points. Ref. 42 DACAPO code, GGA-RPBE, 2×2 three-layer slab, $5 \times 5 \times 1$ *k*-points, energy cutoff of 25 Ry. GGA-PW91: ref. 32 VASP code, GGA-PW91, 3×3 three-layer slab, $5 \times 5 \times 1$ *k*-points, energy cutoff of 500 eV. Ref. 34 VASP code, GGA-PW91, 3×3 four-layer slab, $3 \times 3 \times 1$ *k*-points, energy cutoff of 400 eV.

bridge site, and O binds with the top Ni atom, the corresponding adsorption energies of HCO at the fcc and hcp sites are -2.35 and -2.36 eV, respectively, which are consistent with the reported results with PBE functional (-2.26 eV,¹⁷ -2.49 eV (ref. 37) and -2.41 eV (ref. 41)). Whereas, the isomer, COH, has the same adsorption energy of -4.45 eV at the fcc and hcp sites, respectively, which are close to the previous DFT results with PBE functional (-4.39 eV (ref. 17) and -4.42 eV (ref. 37)). As seen in Fig. 2(l), the average C–Ni bond is 1.861 Å, the C–O and O–H distances are 1.338 and 0.981 Å, respectively, the C–O–H angle is 110.6°.

3.1.6 CH₂O and CH₃O. CH₂O binds on Ni(111) surface at the fcc and hcp sites with an adsorption energy of -0.84 and -0.83 eV, respectively; which agree with the previous results (-0.75 eV (ref. 17) and -1.03 eV (ref. 41) with PBE functional). CH₂O is adsorbed at the fcc site, in which atomic O is coordinated with two surface Ni atoms, atomic C binds with one Ni atom, as shown in Fig. 2(m), the C–Ni distance is 1.956 Å, the average O–Ni distance is 1.987 Å; the lengths of C–H and C–O bond are 1.103 and 1.385 Å, respectively.

 CH_3O prefers to adsorb at the fcc site through its O atom, as shown in Fig. 2(n). The average O–Ni bond length is 1.973 Å,

and the C–O bond is perpendicular to the surface with the length of 1.439 Å. Three C–H bond lengths are all 1.102 Å, the adsorption energy is -2.75 eV, which is close to the results obtained by Zhu *et al.* and Zhou *et al.* with PBE functional (-2.63 eV (ref. 17) and -2.59 eV (ref. 41)).

3.1.7 HCOH, CH₂OH and CH₃OH. For HCOH, the *trans*-HCOH structure is more stable than *cis*-HCOH structure; *trans*-HCOH prefers to adsorb at the bridge site *via* C atoms with the average C–Ni distance of 1.935 Å, and the C–H, C–O and O–H bond lengths are 1.111, 1.366 and 0.990 Å, respectively, as shown in Fig. 2(o), the adsorption energy is -3.91 eV, which is close to the previous result with PBE functional (-3.88 eV (ref. 17)).

CH₂OH preferentially adsorbs at the bridge site through its C and O atom with an adsorption energy of -1.68 eV, as shown in Fig. 2(p), which agrees with the values obtained using PBE functional (-1.54 eV (ref. 17) and -1.68 eV (ref. 41)). One C-Ni and one O-Ni bond are formed with the lengths of 1.939 and 2.126 Å, respectively; the average C-H bond length is 1.100 Å, and the O-H bond length is 0.982 Å, the C-O axis is almost parallel to Ni(111) surface with the C-O bond length of 1.460 Å.

 CH_3OH bonds weakly to the top site through its oxygen atom with the O–Ni distance of 2.179 Å, and the O–H bond is nearly

parallel to the surface with the length of 0.977 Å, as shown in Fig. 2(q), the C–O bond length is 1.454 Å, the average C–H bond length is 1.106 Å. Wang *et al.*⁴¹ have performed the similar calculations on Ni(111) surface, and found the same geometry as our work. The adsorption energy of CH₃OH is -0.37 eV, which is close to the result using PBE functional (-0.30 eV (ref. 17)).

3.2 Reaction paths of CO hydrogenation

For CO hydrogenation in syngas conversion, we firstly need to consider the dissociation of H₂ into H atoms, our results show that the adsorption of H_2 with the parallel model at the top and bridge sites is the most stable configurations, as shown in Fig. 3. Then, the dissociations of H_2 with the parallel model at the top and bridge sites have been considered, for the dissociation of H₂ at the top site, one H atom falls into hcp site and the other is adsorbed at the fcc site, this elementary reaction has a very small activation barrier of 0.13 eV, which is strongly exothermic by 1.05 eV. for the dissociation of H₂ at the bridge site, two dissociated H atoms are adsorbed at two adjacent fcc and hcp sites, this elementary reaction has only an activation barrier of 0.33 eV, and it is highly exothermic by 0.77 eV. Moreover, previous studies^{34,44,45} about H₂ dissociation on Ni(111) surface have also shown that H₂ dissociation can readily occur due to the extremely low activation barrier. Therefore, H₂ dissociation into H atom on Ni(111) can easily occur, as a result, for the hydrogenation reaction, we mainly consider the interaction of H atoms rather than H₂ molecule in this study.

In this section, CO hydrogenation to methane has been systematically investigated on Ni(111), the activation barriers (E_a) and the reaction energies (ΔH) of all possible elementary reactions involving in the process of CO methanation are listed in Table 2 (R1–R19). The structures of initial states (IS), transition states (TS), and final state (FS) for every elementary reaction are shown in Fig. 4–7, respectively.

3.2.1 Initial step of CO hydrogenation

R1. $CO^* + H^* \rightarrow COH^* + *$. Starting from the co-adsorption structure of CO and H at two adjacent fcc sites, COH is



Fig. 3 The potential energy diagram of $\rm H_2$ dissociation into H atoms together with the corresponding structures. Bond lengths are in Å. See Fig. 2 for color coding.

formed *via* the transition state TS1, as shown in Fig. 4(R1). In TS1, H is almost sitting at top of a Ni atom, the C–O bond is tilted with respect to the surface normal in order to coordinate H atom with the Ni surface, the O–H distance is shortened to 1.337 Å from 3.160 Å; this elementary step has an activation barrier of 1.94 eV with reaction energy of 0.92 eV. In addition, the previous barriers are 1.97 eV (ref. 17) and 1.81 eV (ref. 37) using PBE functional, 1.45 eV (ref. 42) using RPBE functional, and 2.04 eV (ref. 34) using PW91 functional.

R2. CO^{*} + *H*^{*} → *HCO*^{*} + *. Beginning with the co-adsorption structure of CO/H, CO interacts with H to produce HCO *via* the transition state TS2, as shown in Fig. 4(R2). In TS2, the activated complex is adsorbed at the fcc site, and the C-H distance is remarkably shortened compared to that in the co-adsorption state (1.165 vs. 2.696 Å), which is close to the C-H bond length of 1.112 Å in HCO configuration. The step has an activation barrier of 1.38 eV with reaction energy of 1.17 eV. In addition, the DFT-predicted barriers are 1.48 eV (ref. 17) and 1.35 eV (ref. 37) using PBE functional, 1.49 eV using RPBE functional, ⁴² and 1.55 eV using PW91 functional.³⁴

R3. $CO^* + * \rightarrow C^* + O^*$. CO is dissociated into the coadsorbed C and O fragment *via* the transition states TS3, as shown in Fig. 4(R3). In the co-adsorption C and O, C adsorbs at the hcp site, and O locates at the fcc site; the C–O bond length is greatly elongated from 1.194 Å in CO to 1.875 Å in TS3. The elementary step has an significantly high activation barrier of 3.74 eV with reaction energy of 1.42 eV, previously reported barriers for R3 vary considerably using PBE functional (2.94 eV (ref. 17) and 3.01 eV (ref. 37)), using RPBE (2.85 eV (ref. 28)) and using PW91 functional (2.92 eV (ref. 32) and 3.76 eV (ref. 34)), the differences may occur due to the use of different GGA functional.

Above results show that when CO and H is co-adsorbed on Ni(111) surface, Ni(111) exhibits rather low catalytic activity for CO direct dissociation, CO dominantly hydrogenate to form HCO, namely, HCO is the dominant product for CO initial step on Ni(111) surface. Therefore, CH_x (x = 1-3) formation from syngas is started with HCO species.

3.2.2 HCO and HCOH species reactions

R4. HCO^{*} → CH^{*} + O^{*}. HCO adsorbed at the hcp site is selected as the initial state for HCO dissociation into CH and O *via* the transition state TS4, as shown in Fig. 5(R4); in the final state, CH fragment is located at the hcp site, and O atom is adsorbed at the fcc site. In TS4, CH is adsorbed at the threefold hollow, O sits at the adjacent top site, and the cleaving C–O bond is stretched from 1.294 Å in HCO to 1.841 Å. This elementary reaction has an activation barrier of 1.16 eV with the reaction energy of -0.28 eV. The reported barrier with PBE functional (1.08 eV (ref. 17) and 1.28 eV (ref. 37)) on Ni(111) spans a small range.

R5. $HCO^* + H^* \rightarrow HCOH^* + ^*$. HCO can be hydrogenated to HCOH *via* the transition state TS5, as shown in Fig. 5(R5), both HCO and H are positioned at the fcc and hcp sites, respectively; in TS5, the O–H distance is contracted to 1.407 Å from 2.353 Å. This elementary step has the reaction energy of 0.34 eV with an activation barrier of 0.92 eV, which is close to the previously

Table 2	Activation barriers (E_a), reaction energies (ΔH) of all possible elementary reaction and the key geometrical parameters (d , Å) of transition
states in	volved in CO methanation on Ni(111) a

		Our results PW91				Previous results			
						PBE	RPBE	PW91	
	Reactions	$E_{\rm a}$ (eV)	$\Delta H (eV)$	$d_{\mathrm{x-y}}\left(\mathrm{\AA}\right)$		$E_{\rm a}$ (eV)			
R1	$CO + H \rightarrow COH$	1.94	0.92	О-Н	1.337	1.97 (ref. 17), 1.81 (ref. 37)	1.45 (ref. 42)	2.04 (ref. 34)	
R2	$CO + H \rightarrow HCO$	1.38	1.17	C-H	1.165	1.48 (ref. 17), 1.35 (ref. 37)	1.49 (ref. 42)	1.55 (ref. 34)	
R3	$CO \rightarrow C + O$	3.74	1.42	C-O	1.875	2.94 (ref. 17), 3.01 (ref. 37)	2.85 (ref. 28)	2.92 (ref. 32),	
							()	3.76 (ref. 34)	
R4	$HCO \rightarrow CH + O$	1.16	-0.28	C-O	1.841	1.08 (ref. 17), 1.28 (ref. 37)		()	
R5	$HCO + H \rightarrow HCOH$	0.92	0.34	O-H	1.407	1.14 (ref. 17)		1.06 (ref. 34)	
R6	$HCO + H \rightarrow CH_2O$	0.53	0.24	C-H	1.111	0.74 (ref. 17)	0.81 (ref. 42)	0.67 (ref. 34)	
R7	$HCOH \rightarrow CH + OH$	0.79	-0.47	C-O	1.919	0.80 (ref. 17)			
R8	$HCOH + H \rightarrow CH_2OH$	0.87	0.25	C-H	1.509	0.90 (ref. 17)			
R9	$CH_2O \rightarrow CH_2 + O$	1.41	-0.16	C-O	2.086	0.95 (ref. 17), 1.18 (ref. 20)			
R10	$CH_2O + H \rightarrow CH_2OH$	1.06	0.30	O-H	1.415	1.04 (ref. 17)			
R11	$CH_2OH \rightarrow CH_2 + OH$	0.85	-0.38	C-O	1.869	0.60 (ref. 17)			
R12	$CH_2O + H \rightarrow CH_3O$	0.65	-0.36	C-H	1.542	0.64 (ref. 17)	0.42 (ref. 42)		
R13	$CH_3O \rightarrow CH_3 + O$	1.53	-0.04	C-O	2.028	1.31 (ref. 17), 1.39 (ref. 20)	. ,		
R14	$CH_3O + H \rightarrow CH_3OH$	1.31	0.46	O-H	1.524	1.38 (ref. 17)	0.61 (ref. 42)		
R15	$CH + H \rightarrow CH_2$	0.74	0.34	C-H	1.674	0.69 (ref. 17)			
R16	$CH_2 + H \rightarrow CH_3$	0.77	-0.08	C-H	1.806	0.63 (ref. 17)			
R17	$CH_3 + H \rightarrow CH_4$	0.96	-0.17	C-H	1.619	0.90 (ref. 17)			
R18	$O + H \rightarrow OH$	1.21	0.06	O-H	1.343	1.35 (ref. 17), 1.34 (ref. 20),			
						1.16 (ref. 37)			
R19	$OH + H \rightarrow H_2O$	1.32	0.30	O-H	1.539	1.33 (ref. 17), 1.43 (ref. 20),			
						1.15 (ref. 37)			
R20	$\rm CO + \rm CO \rightarrow \rm C + \rm CO_2$	3.48	2.06	C-O	2.016	3.52 (ref. 37)	3.38 (ref. 35)		
R21	$COH \rightarrow C + OH$	2.01	0.66	C-H	2.161	2.01 (ref. 17), 2.07 (ref. 37)	. ,		
R22	$CH \rightarrow C + H$	1.38	0.46	C-O	1.745	1.33 (ref. 17), 1.32 (ref. 37)	1.40 (ref. 35),		
							1.38 (ret. 39)		

^{*a*} Ref. 20 CASTEP code, GGA-PBE, 3×3 three-layer slab, $3 \times 3 \times 1$ *k*-points, cutoff energy of 340 eV. Ref. 28 GGA-RPBE. Ref. 17, 32, 34, 35, 37 and 39–42, please see Table 1 for DFT methods.

reported barriers using PBE (1.14 eV (ref. 17)) and PW91 functional (1.06 eV (ref. 34)).

R6. $HCO^* + H^* \rightarrow CH_2O^* + ^*$. HCO can also be hydrogenated to CH₂O *via* the transition state TS6, as shown in Fig. 5(R6), both HCO and H are adsorbed at two adjacent fcc sites, this step has an activation barrier of 0.53 eV with reaction energy of 0.24 eV, the previous barriers are 0.74 eV using PBE functional,¹⁷ 0.81 eV using RPBE functional,⁴² and 0.67 eV using PW91 functional.³⁴ The transition state TS6 sits at the bridge site through C and O binding at two neighboring Ni atoms, and the C–H distance is contracted to 1.111 Å from 2.508 Å.

R7. HCOH^{*} + ^{*} → CH^{*} + OH^{*}. HCOH adsorbed at the bridge site is selected as the initial state, the C–O bond cleavage of HCOH can produce CH and OH fragments *via* the transition state TS7, as shown in Fig. 5(R7), both CH and OH fragments are adsorbed at two adjacent fcc sites. This step has the reaction energy of -0.47 eV with an activation barrier of 0.79 eV, which is close to the barrier using PBE functional (0.80 eV (ref. 17)). In TS7, the dissociated OH moves toward the top site, CH sits at the near hollow site, and the cleaving C–O bond is stretched to 1.919 Å from 1.366 Å in HCOH.

R8. $HCOH^* + H^* \rightarrow CH_2OH^* + *$. CH₂OH prefers to adsorb at the bridge site, HCOH also prefers at the bridge site, thus, the

configuration of HCOH located at the bridge site and H adsorbed at the adjacent fcc site is mainly considered, as shown in Fig. 5(R8). HCOH interaction with H to form CH_2OH *via* the transition state TS8 needs to overcome an activation barrier of 0.87 eV, which is identical to the previous DFT result with PBE functional (0.90 eV (ref. 17)), and this step has the reaction energy of 0.25 eV. In TS8, H moves toward the top site, HCOH sits at the near hollow site, and the C–H distance is shortened to 1.509 Å from 2.821 Å.

3.2.3 CH₂O and CH₃O species reactions

R9. $CH_2O^* \rightarrow CH_2^* + O^*$. The C–O bond scission of CH₂O can take place *via* the transition state TS9 to form CH₂ and O species, CH₂ and O fragment are adsorbed at two adjacent fcc sites, as shown in Fig. 6(R9). This reaction has an activation barrier of 1.41 eV with reaction energy of −0.16 eV; in TS9, the cleaving C–O bond is stretched from 1.385 Å to 2.086 Å, the detached O and the remaining CH₂ fragment are absorbed at two bridge sites, respectively.

R10. $CH_2O^* + H^* \rightarrow CH_2OH^* + *$. CH_2O can hydrogenate to CH_2OH via the transition state TS10, as shown in Fig. 6(R10), CH_2OH prefers to adsorb at the bridge site through C and O atom, the co-adsorption structure of CH_2O and H is adsorbed at two adjacent hcp sites. This step has the reaction energy of 0.30





Fig. 4 The potential energy diagram of CO hydrogenation and dissociation together with the corresponding structures. Bond lengths are in Å. See Fig. 2 for color coding.

Fig. 5 The possible reactions relevant to the dissociation and hydrogenation of HCO and HCOH intermediate on Ni(111) together with the corresponding structures. Bond lengths are in Å. See Fig. 2 for color coding.

eV, and the activation barrier of 1.06 eV is consistent with the previous DFT result with PBE functional (1.04 eV (ref. 17)). In TS10, CH_2O binds along a bridge site through C and O atom, H sits at the adjacent top site, the O–H distance is shortened to 1.415 Å from 2.818 Å.

R11. $CH_2OH^* + * \rightarrow CH_2^* + OH^*$. The C–O bond scission of CH₂OH can yield the co-adsorbed CH₂ and OH *via* the transition state TS11, as shown in Fig. 6(R11). In TS11, the dissociated OH moves toward the top site through O, CH₂ sits at the near hollow site, and the cleaving C–O bond is stretched to 1.869 Å from 1.460 Å in CH₂OH. This step has an activation barrier of 0.85 eV with reaction energy of -0.38 eV. In addition, the previous barrier is 0.60 eV (ref. 17) using PBE functional.

R12. $CH_2O^* + H^* \rightarrow CH_3O^* + *$. CH₂O can also hydrogenate to CH₃O *via* the transition state TS12, as shown in Fig. 6(R12), this step has the reaction energy of −0.36 eV with an activation barrier of 0.65 eV, which is close to the value using PBE functional (0.64 eV (ref. 17)). In TS12, CH₂O is adsorbed at the fcc site, H is located at the top site, and the C–H distance is contracted from 2.448 Å to 1.542 Å.

R13. $CH_3O^* + * \rightarrow CH_3^* + O^*$. CH_3O dissociation to yield CH_3 and O via the transition state TS13 is shown in Fig. 6(R13). CH_3O prefers to adsorb at the fcc site, CH_3 fragment is located at the hcp site, the dissociating O atom is adsorbed at the fcc site. In TS13, the cleaving C–O bond is stretched from 1.439 Å to 2.028 Å, the remaining O and the detached CH_3 fragment are absorbed at the fcc and top sites, respectively. The activation barrier (1.53 eV) is close to those values with PBE functional (1.31 eV (ref. 17) and 1.39 eV (ref. 20)), and this reaction has only the reaction energy of -0.04 eV.

R14. $CH_3O^* + H^* \rightarrow CH_3OH^* + *$. CH₃OH can be formed by hydrogen addition to the O atom of CH₃O *via* the transition state TS14, as shown in Fig. 6(R14). In TS14, the atom H tends to leave the surface, and move to CH₃O, and the forming O–H bond is shorten to 1.524 Å from 3.013 Å. This step has the reaction energy of 0.46 eV with an activation barrier of 1.31 eV, which is close to the previous DFT result using PBE functional (1.38 eV (ref. 17)).

3.2.4 CH_x (x = 1-3) hydrogenation to CH_4

R15. CH^{*} + *H*^{*} → *CH*^{*}₂ + *. As for CH hydrogenation, in the initial state, CH species and H atom are co-adsorbed at the fcc and hcp sites, respectively. This step has the reaction energy of 0.34 eV with an activation barrier of 0.74 eV, which agrees with the reported barrier with PBE functional (0.69 eV (ref. 17)). In TS15, the C–H distance is shortened to 1.674 Å from 2.968 Å, H atom shift continues over the bridge site until CH₂ is formed at the neighboring hollow site, as shown in Fig. 7(R15).

R16. $CH_2^* + H^* \rightarrow CH_3^* + {}^*$. CH₂ hydrogenation is very similar to CH hydrogenation, this step possesses an activation barrier of 0.77 eV, which is close to the previous DFT result with PBE functional (0.63 eV (ref. 17)). In TS16, H atom moves to the top of a surface Ni atom, meanwhile, CH₂ is adsorbed at the fcc site, and the forming C–H bond is shorten to 1.806 Å from 2.977 Å, as



Fig. 6 The possible reactions relevant to the dissociation and hydrogenation of CH_2O and CH_3O on Ni(111) together with the corresponding structures. Bond lengths are in Å. See Fig. 2 for color coding.

shown in Fig. 7(R16). Further, CH_2 hydrogenation has the reaction energy of -0.08 eV.

R17. $CH_3^* + H^* \rightarrow CH_4 + 2^*$. The activation barrier of CH₃ hydrogenation to CH₄ (0.96 eV) is in agreement with the reported result with PBE functional (0.90 eV (ref. 17)), and this step has the reaction energy of −0.17 eV, as shown in Fig. 7(R17). In TS17, the C-H distance is shortened to 1.619 Å from 2.972 Å in the initial state, H and CH₃ sit at the top of the same surface Ni to achieve the C-Ni-H angle of 51.3°; in the final state, CH₄ is far away from the surface. CH₄ is the hydrocarbon with the lowest molecular weight, which has no unsaturated bonds, so it is not expected to bind strongly to a metal surface. Indeed, the strongest binding energy obtained in this study for CH₄ on Ni(111) is only −0.02 eV, this relative weak adsorption energy indicates that CH₄ would easily desorbs from the surface once it is formed.

R18. $O^* + H^* \rightarrow OH^* + {}^*$. After the generation of CH₄, O and H remain adsorbing on Ni(111) surface, the combination of these two species produces OH radical. In TS18, the O–H distance is shortened to 1.343 Å from 2.708 Å, as shown in Fig. 7(R18). This step has the reaction energy of 0.06 eV with an activation barrier of 1.21 eV, which is close to the reported barriers using PBE functional (1.35 eV,¹⁷ 1.34 eV (ref. 20) and 1.16 eV (ref. 37)).



Fig. 7 The possible reactions relevant to CH_x hydrogenation to CH_4 and H_2O formation on Ni(111) together with the corresponding structures. Bond lengths are in Å. See Fig. 2 for color coding.

R19. $OH^* + H^* \rightarrow H_2O^* + *$. As shown in Fig. 7(R19), in the initial state, OH and H are located at two adjacent fcc sites with the O–H distance of 2.726 Å. In TS19, OH has to leave the fcc site, and moves to the top Ni to attack H atom, the O–H distance is shortened to 1.539 Å. This step has the reaction energy of 0.30 eV, and the activation barrier (1.32 eV) is in good agreement with the previous results using PBE functional (1.33 eV,¹⁷ 1.43 eV (ref. 20) and 1.15 eV (ref. 37)).

3.2.5 Dominant pathway of CH₄ **formation.** Above results show that CO dissociation has a significantly high activation barrier of 3.74 eV due to a notable π -contribution,^{17,28,32,34,37,41} and the C–O bond breaking of CO is strongly endothermic. Because the C–O bond breaking of CO is so expensive, we will not consider this possibility. Alternatively, one can start the stepwise hydrogenation at either the O or C atom of CO to form COH or HCO species, respectively, in which CO hydrogenation to HCO is more favorable; thus, HCO species is the key intermediate for methane synthesis from syngas.

Once HCO intermediate is formed on Ni(111), it can either hydrogenate to HCOH *via* the O–H bond formation or CH₂O *via* the C–H bond formation, which need to overcome the barriers of 0.92 and 0.53 eV, respectively. Along the pathway *via* HCOH intermediate, HCOH can be hydrogenated to CH₂OH with an activation barrier of 0.87 eV; similarly, along the pathway *via* CH₂O intermediate, CH₂O can hydrogenate to CH₂OH and CH₃O with the activation barriers of 1.06 and 0.65 eV, respectively.

Summarizing the activation barriers and the reaction energies of CH₄ and H₂O formation, the reaction network obtained from our studies on Ni(111) surface will help us to better understand the mechanism of CH₄ formation from syngas. Fig. 8 presents the potential energy profile of CH₄ and H₂O formation. We can obtain the following six pathways: the first pathway proceeds as follows: $CO \rightarrow HCO \rightarrow CH \rightarrow CH_2 \rightarrow CH_3$ \rightarrow CH₄ with the highest barrier of 2.33 eV, as shown in Fig. 8(a), the rate-limiting step of this pathway is CO hydrogenation to HCO. The second pathway is that $CO \rightarrow HCO \rightarrow HCOH \rightarrow CH$ \rightarrow CH₂ \rightarrow CH₃ \rightarrow CH₄ with the highest barrier 2.30 eV, as shown in Fig. 8(b), the rate-limiting step is CO hydrogenation to HCO. The third pathway proceeds as follows: CO \rightarrow HCO \rightarrow HCOH \rightarrow CH₂OH \rightarrow CH₂ \rightarrow CH₃ \rightarrow CH₄ with the highest barrier of 2.61 eV, as shown in Fig. 8(c), the rate-limiting step is CO hydrogenation to HCO. The fourth is likely to proceed via $CO \rightarrow HCO \rightarrow CH_2O \rightarrow CH_2 \rightarrow CH_3 \rightarrow CH_4$ with the highest barrier of 2.82 eV, as shown in Fig. 8(d), the rate-limiting step is CO hydrogenation to HCO and the C-O scission of CH₂O. The fifth pathway $CO \rightarrow HCO \rightarrow CH_2O \rightarrow CH_2OH \rightarrow CH_2 \rightarrow CH_3$ \rightarrow CH₄ is observed with the highest barrier of 2.56 eV, as shown in Fig. 8(e), and CO hydrogenation to HCO is the rate-limiting step. The final pathway follows the following sequence: CO \rightarrow $HCO \rightarrow CH_2O \rightarrow CH_3O \rightarrow CH_3 \rightarrow CH_4$, as shown in Fig. 8(f), this pathway has the highest barrier of 2.58 eV, the rate-limiting step is the C-O scission of CH₃O.

On the basis of above potential energy profile for the overall reaction of CH_4 formation from syngas, we can obtain that the highest barriers of these six pathways are 2.33, 2.30, 2.61, 2.82, 2.56 and 2.58 eV, respectively, suggesting that the first two pathways are the energetically feasible pathways *via* the C–O scission of either HCO or HCOH intermediates to form CH species, and eventually produces CH_4 by the successive hydrogenations of CH intermediate, which may be two parallel pathways of methane synthesis from syngas on Ni(111).

3.2.6 Comparison of CH_4 formation with CH_3OH and CH_2O . Our results show that the energy that CH_2O desorb from the Ni(111) surface is 0.84 eV, CH_2O hydrogenation to CH_2OH and CH_3O on Ni(111) surface have the corresponding activation barriers of 1.06 and 0.65 eV, respectively, suggesting that the adsorbed CH_2O prefers to be hydrogenated to CH_3O rather than being desorbed from Ni(111) surface, as a result, CH_2O formation is unfavorable compared to CH_2O hydrogenation to CH_3O .

Starting from CH₃O species, CH₃O dissociation into CH₃ + O has an activation barrier of 1.53 eV with reaction energy of -0.04 eV, whereas CH₃O hydrogenation to CH₃OH has an activation barrier of 1.31 eV with reaction energy of 0.46 eV. That is, CH₃O kinetically prefers to be hydrogenated to CH₃OH rather than forming CH3 by CH3O dissociation on Ni(111) surface. Therefore, it can be concluded that CH₃O dissociation to CH₃ is not the dominant pathways responsible for CH₄ formation in kinetics. As a matter of fact, our results have also shown that CH is the most favorable existence form among all CH_x (x = 1-3) species from syngas on Ni(111) surface, which is dominantly responsible for CH₄ formation. As presented in Fig. 8(f), the potential energy profile for the most favorable pathway of CH₃OH formation clearly show that the highest barrier of CH₃OH formation is 2.36 eV with an endothermicity of 1.51 eV, whereas CH formation need to overcome the highest barrier of 2.33 and 2.30 eV with the endothermicity of 0.89 and 1.04 eV, respectively, indicating that CH_3OH and CH formations are competitive kinetically on Ni(111) surface, however, CH formation with two parallel pathways is more favorable thermodynamically than CH_3OH formation.

3.3 Reaction paths of surface C formation

The key to carbon deposition is the surface C formation.^{34,37,46,48-50} This requires the C–O bond dissociation. As a result, all possible reactions relevant to surface C formation are identified, as listed in Table 2 (R3, R20–R22). The potential energy profile of C formation together with the structures of initial states, transition states (TS), and final states are displayed in Fig. 9.

We first examine CO direct dissociation $CO^* + * \rightarrow C^* + O^*$ (R3) on Ni(111), suggesting that CO direct dissociation is not favored due to the large activation barrier of 3.74 eV, as shown in Fig. 4(R3). Further, $CO^* + CO^* \rightarrow CO_2^* + C^*$ (R20), $COH^* + *$ $\rightarrow C^* + OH^*$ (R21) and $CH^* + * \rightarrow C^* + H^*$ (R22) have been investigated.

R20. $CO^* + CO^* \rightarrow CO_2^* + C^*$. Starting from two CO molecules initially placed at two adjacent hcp sites with the coadsorption energy of -3.68 eV, the C–O bond scission of one CO molecule can take place *via* transition state TS20 to form C, in TS20, the detached O with the elongated C–O distance of 2.016 Å, the remaining C is adsorbed at the hcp site, the detached O is attached to the C atom of another CO molecule with the C–O distance of 1.236 Å, which leads to the formation of gas-phase CO₂, as shown in Fig. 9(R20). This step has the reaction energy of 2.06 eV with the activation barrier of 3.48 eV, which is agreement with the reported barriers (3.38 eV (ref. 35) with RPBE functional and 3.52 eV (ref. 37) with PBE functional). These results suggest that C deposition is unlikely to occur on Ni(111) through CO disproportionation, which may take place only at high CO surface coverage on metal surface.

R21. COH* + * \rightarrow C* + OH*. COH dissociation to form C + OH *via* the transition state TS21 is shown in Fig. 9(R21). COH is initially adsorbed at the hcp site with a small tilting angle, thus, C atom of final state is located at the hcp site, and the dissociated OH is located at the *para*-position of C atom, and the C-O distance is 3.201 Å. In TS21, the remaining C atom occupies the hcp site, the detaching OH radical moves to the top Ni atom, the cleaving C-O bond is stretched to 2.161 Å from 1.337 Å in COH. This step has the reaction energy of 0.66 eV with an activation barrier of 2.01 eV, which is close to the reported barriers using PBE functional (2.01 eV (ref. 17) and 2.07 eV (ref. 37)).

R22. CH* + * \rightarrow C* + H*. CO conversion to CH species *via* HCO or HCOH intermediate may be the precursors of coke and/or methane. Since previous studies have shown that the relative rate between CH dissociation and hydrogenation determines the rate of carbon deposition on catalyst particles,^{17,35,37} CH dissociation is of particular importance during CO methanation. Starting from the most stable CH configuration, C is formed *via* the transition state TS22, as shown in Fig. 9(R22). C is located at the hcp site, and H is located at the *para*-position fcc site with the C-H distance of 3.030 Å. In



Fig. 8 The potential energy profile of all possible reactions leading to CH_4 and H_2O formation involving in CO hydrogenation on Ni(111). (a) HCO dissociation to CH; (b) HCOH dissociation to CH; (c) HCOH hydrogenation to CH_2OH , then, CH_2OH dissociation to CH_2 ; (d) CH_2O dissociation to CH_2 ; (e) CH_2O hydrogenation to CH_2OH , then, CH_2OH dissociation to CH_3 . The red line represents the pathway of H_2O formation.

TS22, the detaching H is adsorbed at the top Ni atom with a C-H distance of 1.745 Å, and the remaining C is stationary at the hcp site. This step has the reaction energy of 0.46 eV with an activation barrier of 1.38 eV, which is consistent with the reported barriers using PBE functional (1.33 eV (ref. 17) and 1.32 eV (ref. 37)) and using RPBE functional (1.40 eV (ref. 35) and 1.38 eV (ref. 39)).

The potential energy profile of five possible reaction pathways leading to surface C formation upon CO adsorption is identified and presented in Fig. 9, (i) CO direct dissociation in a black line; (ii) CO disproportionation in a red line; (iii) the C–O bond cleavage of COH in a blue line; (iv) the C-H cleavage of CH formed by HCO intermediate in a green line; (v) the C-H cleavage of CH formed by HCOH intermediate in a pink line. Our results indicate that CO direct dissociation and CO disproportionation on Ni(111) surface are highly unlikely due to the large activation barriers of 3.74 and 3.48 eV, respectively. Meanwhile, the C-O bond cleavage of COH has the highest barrier of 2.93 eV. As a result, among five possible pathways of surface C formation, two parallel pathways of CO \rightarrow HCO(H-COH) \rightarrow CH \rightarrow C are mainly responsible for the surface C



Fig. 9 The potential energy profile of all possible reactions leading to surface C formation on Ni(111) together with the corresponding structures. (a) CO dissociation and CO disproportionation to C; (b) CO hydrogenation to COH, then, COH dissociation to C; (c) C formation *via* HCO intermediate; (d) C formation *via* HCOH intermediate. Bond lengths are in Å. See Fig. 2 for color coding.

formation, which have only the highest barriers of 2.33 and 2.42 eV, respectively.

3.4 Comparisons between CH₄ formation and surface C formation

Starting from CO hydrogenation, we can see from Fig. 8 that two parallel pathways are dominantly responsible for CH_4 formation, one is that $CO \rightarrow HCO \rightarrow CH \rightarrow CH_2 \rightarrow CH_3 \rightarrow CH_4$, which has the highest barrier of 2.33 eV with an endothermicity of 0.98 eV, as shown in Fig. 8(a); the other is that $CO \rightarrow HCO \rightarrow$ $HCOH \rightarrow CH \rightarrow CH_2 \rightarrow CH_3 \rightarrow CH_4$, which has the highest barrier 2.30 eV with an endothermicity of 1.13 eV, as shown in Fig. 8(b). On the other hand, as shown in Fig. 9 that two parallel pathways are responsible for surface C formation, one is that $CO \rightarrow HCO \rightarrow CH \rightarrow C$, which has the highest barrier of 2.33 eV with an endothermicity of 1.35 eV, as shown in Fig. 9(c); the other is that $CO \rightarrow HCO \rightarrow HCOH \rightarrow CH \rightarrow C$, which has the highest barrier 2.42 eV with an endothermicity of 1.50 eV, as shown in Fig. 9(d). Above results show that the CH species is the common intermediate for CH_4 synthesis and surface C formation, the relative activity between CH dissociation and hydrogenation determines the selectivity and productivity of CH_4 in CO methanation, our results are in agreement with the previous results.⁴⁷ Further, starting from CH intermediate, our results show that CH hydrogenation to CH_2 has a lower activation barrier of 0.74 eV with the reaction energy of 0.34 eV, whereas, CH dissociation to surface C has a higher activation barrier of 1.38 eV with the reaction energy of 0.46 eV.

Therefore, taking the highest barrier of CH_4 and surface C formation into consideration, we can obtain that CH intermediate is preferred to be hydrogenated to CH_2 , followed by the successive hydrogenation to CH_4 rather than being dissociated into surface C; namely, when CO methanation occurs on Ni(111) surface, CH_4 is the dominant product, meanwhile, a small quantity of surface carbon is also derived from the thermal dissociation of hydrocarbons. Our results can illustrate at the molecular level that under the realistic condition, why Nibased catalysts are chosen to be the preferred catalysts in methane synthesis from syngas.

In addition, previous studies have shown that the multiscale modeling approach can improve the performance of macroscopic processes by controlling events occurring at the atomistic, molecular and nanoscopic levels across multiple length and time scales.⁵¹⁻⁵⁴ Recently, the multiscale modeling has been widely applied to many reaction systems, for example, Mhadeshwar et al.55 have employed the microkinetic model for elucidating reaction mechanisms of methane partial oxidation and reforming, as well as for thermal decomposition of methanol and formaldehyde on Rh catalyst. Based on the hierarchical multiscale approach, Chen et al.10 have presented a predictive microkinetic model for steam reforming and carbon formation, and established a kinetic carbon potential map in the Ni catalyst pellets at different operating conditions. In this study, we haven't considered the KMC or MD simulations for CH₄ synthesis and surface C formation, which may provide the behavior of methane synthesis from syngas at a larger scale using a multi-scale modeling approach; the KMC or MD simulations will be carried out in our next work, which is very important for the quality improvement of research work.

3.5 Electronic structure analysis of the reactions related to CO and CH species

An electronic analysis of the reactions related to CO and CH species has been carried out to improve our understanding for that why CO prefers to be hydrogenated to HCO rather than CO direct dissociation, as well as CH prefers to be hydrogenated to CH_2 rather than being dissociated into C + H, which is the selectivity-controlling step. Here, the electronic interactions involved in the related reactions by plotting the projected density of states (pDOS) diagrams has been analyzed, as shown in Fig. 10.

For CH, only the 2p orbital of the C atom interact with Ni surface and accept the electrons, meanwhile, there is no electron that transfers to the C–H anti-bonding orbital, namely, there is no bond weakening. However, the electron transfers from Ni surface to the 2p orbital of C atom, which leads to the





Fig. 10 Projected density of states (pDOS) for CO, C + O, HCO, CH, C + H and CH₂ species involving in key step related to CO and CH species. Note that ¹H represents the H atom of CH and ²H represents the single H atom.

increase of its negative charge, further strengthens its attraction to the positively charged H, as a result, CH prefers to be hydrogenated to CH₂ rather than being dissociated into C on Ni(111). Similarly, for CO, the electron transfer from Ni surface to the 2p orbital of C atom increase the C negative charge, further give the stronger affinity to the positively charged H, thus, CO hydrogenation to HCO intermediate is more favorable than CO direct dissociation.

By analyzing pDOS, it is clear that the 2p states of C atoms in adsorbed HCO and CH₂ shift to low energy region, indicating that the C atoms interact with Ni surface to form the new covalent bonds. Compared to the free HCO and CH₂, the C-O and C-H bond of HCO and CH2 are slightly activated. When HCO and CH₂ are adsorbed on Ni surface, the large overlap between C 2p and H 1s orbital exists, which means that the C-H

interaction mainly comes from the mixing between the C 2p and H 1s orbital. Meanwhile, there is a significant down shift of the p-orbital for the C atom of HCO and CH₂ when compared to C atom of CH and CO on Ni(111) surface, suggesting that the hybridization of p-orbitals with nearby H atom can stabilizes the p-orbital for the C atom of HCO and CH₂, shifting the p-orbital down, away from the Fermi level, as a result, HCO and CH₂ become less reactive. These results show CO and CH prefers to be hydrogenated to CH₂ and HCO rather than being dissociated into surface C.

On the other hand, the valence charges of CO, C + O, CO + H, HCO, CH, C + H, CH + H, CH₂ species adsorbed on Ni(111) surface involving in the reactions related to CO and CH species have been examined using Bader charge analysis. As shown in Table 3, in CO, C + O, CO + H, HCO, the valence charges transfer

Table 3 Charges q of the related species involving in the key steps in CO methanation on Ni(111)											
Reaction	$CO \rightarrow C + O$		$CO + H \rightarrow HCO$		$CH \rightarrow C + H$		$\rm CH + \rm H \rightarrow \rm CH_2$				
Species	СО	C + O	CO + H	HCO	СН	C + H	CH + H	CH_2			
Charge q	C (2.52) O (7.84)	C (4.54) O (6.84)	C (2.52) O (7.87) H (1.23)	C (2.96) O (7.60) H (0.88)	C (4.59) H (0.82)	C (4.55) H (1.25)	C (4.53) H (0.89) H (1.24)	C (4.61) H (0.97) H (0.85)			
Total charge	0.36	1.38	0.62	0.44	0.41	0.80	0.66	0.43			

of CO hydrogenation is calculated to be from 0.62 to 0.44, which is lower than that of CO dissociation from 0.36 to 1.38, suggesting that the valence charge transfer of CO hydrogenation between the adsorption species and Ni surface is less than that of CO dissociation, as a result, CO hydrogenation to HCO is more favorable than CO direct dissociation. In CH, C + H, CH + H, CH₂, CH hydrogenation and dissociation is similar to CO, the valence charges transfer is calculated to be from 0.66 to 0.43 for CH hydrogenation, as well as from 0.41 to 0.80 for CH dissociation, indicating that CH hydrogenation prefers to occur rather than CH dissociation.

4 Conclusions

Density functional theory calculations have been employed to investigate CO methanation and surface C formation on Ni(111) surface. The most energetically favorable configurations of the adsorbed species involved in CO methanation have been obtained. All possible pathways of CH4 formation and surface C formation have been analyzed to identify the most favorable formation pathway. Our results show that CO hydrogenation to HCO is the dominant product for the initial CO hydrogenation. Then, starting from HCO species, CH4 is formed by two parallel pathways; one is that CO \rightarrow HCO \rightarrow CH \rightarrow CH₂ \rightarrow CH₃ \rightarrow CH_4 , the other is that $CO \rightarrow HCO \rightarrow HCOH \rightarrow CH \rightarrow CH_2 \rightarrow$ $CH_3 \rightarrow CH_4$. On the other hand, surface C is also formed by two parallel pathways; one is that $CO \rightarrow HCO \rightarrow CH \rightarrow C$, the other is that $CO \rightarrow HCO \rightarrow HCOH \rightarrow CH \rightarrow C$. More importantly, CH species is the common intermediate for CH₄ formation and surface C formation, the relative activity between CH dissociation and hydrogenation determines the selectivity and productivity of CH₄ in CO methanation, however, CH intermediate is preferred to be hydrogenated to CH₂ rather than being dissociated into surface C; therefore, when CO hydrogenation occurs on Ni(111) surface, CH4 is the dominant product, meanwhile, a small quantity of surface carbon is produced by the thermal dissociation of hydrocarbons, namely, under the realistic condition, suppressing surface carbon formation can be achieved by lowering the barriers of CH hydrogenation and/or increasing that of CH dissociation.

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