Insights into the Mechanisms of CO₂ Methanation on Ni(111) Surfaces by Density Functional Theory

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Abstract

The different mechanisms of CO₂ methanation on Ni(111) surfaces have been investigated by density functional theory with and without the formation of CO as an intermediate. The most stable adsorption configurations of all reaction species (O, OH, CO, CH, CH₂, CH₃, CH₄, HCOO, C(OH)₂, CH₂O etc.) in three paths of CO₂ methanation adsorbed on the Ni(111) surface are described. The energy barriers and reaction energies for the overall processes involved in the various paths are presented. The rate-determining steps for the three mechanisms are HCOO→CO+OH for path 1, CO→C+O for path 2 and CO₂+2H→C(OH)₂ for path 3 with maximum energy barriers of 306.8 kJ/mol, 237.4 kJ/mol and 292.3 kJ/mol, respectively. Path 2 is therefore the optimum of the three mechanisms. The path starts with CO₂ dissociation into CO and O, CO decomposition into C and O species and C species hydrogenation to form CH₄: CO₂→CO→C+H→CH+H→CH₂+H→CH₃+H→CH₄.

Keywords: CO₂ methanation; Ni(111) surface; Adsorption energies; Energy barriers; Density functional theory

1. Introduction

Carbon dioxide (CO₂) is a greenhouse gas that can trap heat and cause global warming. Since

the industrial revolution, continual technological progress and a continuously improving quality of life have resulted in a significant increase in atmospheric CO₂ emissions. Global CO₂ emissions will reach 40 billion tons in 2014, mainly because of fossil fuel combustion (such as coal and petroleum) and deforestation. Atmospheric CO₂ concentrations have reached over 400 ppm, which is the highest value reached in the past 800,000 years [1]. The accumulation of atmospheric CO₂ will lead to changes in the marine chemistry environment and substantially increased global temperatures, which will lead to rises in sea level.

In the last three decades, the main CO₂ treatment has been by CO₂ capture and storage and capture and utilization [2, 3], especially chemical utilization. Much research has been devoted to exploring CO₂ recycling into other compounds, such as high energy content fuels [4, 5] or industrially important compounds [6, 7]. Among these, hydrogenation has been proposed to be an effective method for CO₂ utilization [8-10], and chemical products include methanol [11-18], carbon monoxide [14-19], formic acid [15-18, 20] and methane [13-18, 21-28].

Methane synthesis using CO₂ as a reactant would have a potential dual effect to consume greenhouse gas and produce clean fuel. CO₂ methanation occurs as:

Catalysts developed for CO₂ methanation are generally made up of transition metals, such as Ni [21, 25-27, 29-36], Fe [21, 37-39], Ru [21-23, 40-44], Rh [21, 45-51] and Pd [21, 52-54]. Although the noble metals (Ru, Rh and Pd) exhibit better activity (Ru is more active for CO₂ methanation than Ni [55]), they are too expensive for large-scale industrial application. Ni is the most feasible catalytic component for CO₂ methanation because of its well-known high activity for hydrogenation and relatively low price compared with noble metal-based catalysts [30, 31, 35].

Although CO₂ methanation is a simple reaction, many products and intermediates such as methanol, carbon monoxide, formic acid and methane are probably produced during this process [13, 56]. Experimental and theoretical studies of the mechanism of CO₂ methanation [25, 43, 57-75] have been carried out but the conclusions remain controversial. Discussions on this topic fall into two main categories [57-59]: conversion of CO₂ to CO prior to methanation (involving a CO intermediate) [60-68] and direct hydrogenation of CO₂ to methane without the formation of CO as

intermediate [25, 43, 69-75].

Mechanism of CO₂ methanation with CO intermediate

The mechanism that includes a CO intermediate for CO₂ methanation involves the conversion of CO₂ into CO directly and indirectly.

Choe et al. [60] devised a reaction mechanism where CO₂ is converted to CO directly and then to surface C before hydrogenation on a Ni(111) surface by the atom superposition and electron delocalization-molecular orbital theory. The elementary reaction steps proposed are reproduced below and consist of two mechanisms: C formation (Steps 1–3) and C methanation (Steps 4–6). CO dissociation (Step 2), which was originally proposed by Fitzharris et al. [61], was the rate-determining step based on the activation energies for every step (1.27 eV for CO₂ dissociation, 2.97 eV for CO dissociation, 0.72 eV for methylidyne, 0.52 eV for methylene and 0.50 eV for methane):

Intermediates in the indirect conversion of CO₂ into CO may be formate (HCOO) and others. Bothra et al. [62] and Vesselli et al. [63] explored the hydrogenation and methanation of CO₂ on Ni(110) surfaces by density functional theory (DFT) calculations. They believe that CO was one of the intermediates in this process by comparison of the energy barrier. They also studied other intermediates in CO₂ methanation, such as hydroxyl, carbonyl and HCOO. Peebles et al. [64] studied the methanation of CO₂ over Ni(100). Large amounts of CO were formed during the experiment, with activation energies for the formation of CH₄ and CO of 88.7 and 72.8–82.4 kJ/mol, respectively. The activation energy and reaction rates for CH₄ formation from CO₂ were close to the values for methanation of CO under identical reaction conditions. Falconer [65] studied the adsorption and methanation of carbon dioxide on a Ni/Si catalyst by temperature-programmed desorption and

temperature-programmed reduction. Their data indicate that CO₂ dissociates upon adsorption at elevated temperatures to yield CO and O atoms.

Other researchers have also studied the mechanism of CO₂ methanation involving a CO intermediate, not only on a Ni catalyst, but on other catalysts [66-68], such as Ru and Pt.

Mechanism of CO₂ methanation without CO intermediate

Mechanisms without a CO intermediate for CO₂ methanation involve the conversion of CO₂ into other intermediates with adsorbed H, and intermediate conversion to CH₄.

One of the mechanisms not involving intermediate CO formation was proposed by Medsforth [69]:

The author found that the action of promoters (such as Al and Cr) in the synthesis of methane from carbon dioxide and hydrogen in the presence of a nickel catalyst depends on the dehydration of unstable intermediate compounds. The Ni used was prepared from Ni cubes. The mechanism was developed further by Pichler [70] who proposed the following sequence:

Fujita et al. [71], Vlasenko et al. [72] and Ibraeva et al. [73] studied the mechanism of CO₂ methanation by kinetics in the transient state on a Ni catalyst. They considered that CO does not participate in the CO₂ methanation reaction. Pan et al. [25] investigated CO₂ adsorption and methanation on a Ni/Ce_{0.5}Zr_{0.5}O₂ catalyst using *in-situ* Fourier transform infrared spectra. In their study, HCOO species were found to be the main intermediate species during reaction. The adsorption and hydrogenation of formic acid was also conducted to identify the intermediate species formed during the reaction. Other researchers have explored the mechanisms of CO₂ methanation without a CO intermediate on different catalysts (CeRu [43], Pd [74] and Cu [75]).

Ni single crystals have therefore been shown to be reasonable models of practical catalysts for methanation [76, 77]. The surface science approach from model catalysts is useful for understanding mechanistic aspects of the reactions. The (111) surface was chosen because it is a lowest energy facet and usually dominates the metal nanoparticle surface [78].

From previous studies, we can know that many researchers have established different mechanisms of CO₂ methanation, but there is no consensus on kinetics and mechanisms. Therefore, in this study, we investigated three different mechanisms of total CO₂ methanation on the Ni(111) surface using the DFT method with the periodic slab model. Probable intermediates and energy barriers and reaction energies for all elementary reactions involved in this process were obtained. The entire processes of all three paths were calculated to provide insight into the mechanisms. An optimal mechanism for CO₂ methanation is expected to be confirmed on the basis of our result.

2. Computational methods

The mechanism of CO₂ methanation on the Ni(111) surface was studied using the Dmol³ program package in Materials Studio code within the generalized gradient approximation (GGA) and Perdew-Wang (PW91) functional as implemented in the Materials studio 5.5 Package [79-81]. Double numerical plus polarization (DNP) [82] basis sets were used, and all calculations were spin-unrestricted to account for the magnetic properties of Ni. The convergence criterion for the energy, maximum force and maximum displacement changes were set at 2.0×10^{-5} hartree (Ha), 4.0×10^{-3} Ha/Å and 5.0×10^{-3} Å, respectively. Self-consistent field convergence was declared when at least two of the above criteria were satisfied. A thermal smearing value of 0.005 Ha was used. A complete linear synchronous transit (LST) and quadratic synchronous transit (QST) search algorithm were used to identify the transition state of a reaction [83]. The electronic structures of the core electrons were described by the effective core potential [84, 85].

A 3×3 slab (three layer) was chosen to represent the Ni(111) surface for CO₂ methanation. The bottom two layers of the nickel slab were fixed, whereas all other atoms were allowed to relax. The Brillouin zone was sampled by a 2×2×1 array of k-points in the Monkhorst–Pack grid [86]. The adsorption energy of the reaction was calculated from Eq. 2:

$$E_{ad} = E_{ads/s} - (E_{ads} + E_s) \quad (2)$$

where E_{ads} and E_s are the total energies of the isolated adsorbates in vacuum and the clean surface, respectively. $E_{ads/s}$ is the total energy of the adsorption system.

3. Results and discussion

3.1. H₂ adsorption

The dissociation of H₂ into H is a crucial step for every mechanism of CO₂ methanation. The structure of H₂ and H adsorption on the Ni(111) surface is presented in [Tables 1 and 2](#).

According to the results in Table 1, the best adsorption site of H₂ on Ni(111) is face-centred cubic (fcc) with an adsorption energy of −69.6 kJ/mol and the length of the H-H bond is 0.755 Å, which is in agreement with the experimental value of 0.74 Å and the calculated results of Watwe [\[76\]](#).

According to Table 2, the calculated adsorption energy of H on the Ni(111) surface at the top, bridge, hexagonal-close packing (hcp) and fcc sites are −248.1, −263.2, −293.7 and −295.3 kJ/mol, respectively, which is in good agreement with results from previous studies [\[87-90\]](#).

[Fig. 1](#) presents the potential energy profile with the relative energy values of H₂ dissociation into H*. For the reaction of H₂ dissociation to 2H*, the energy barrier is 35.3 kJ/mol, the reaction is exothermic by 73.1 kJ/mol, which agrees well with the experimental and calculated values of 95 kJ/mol [\[94\]](#) and 86 kJ/mol [\[76\]](#), respectively. We can see that H₂ can dissociate easily into H on the Ni(111) surface.

3.2 Mechanism including CO intermediate

3.2.1. Structures of adsorbed species and energetics of adsorption

The most stable site, corresponding adsorption energies of the reactant and intermediates of the three mechanisms of CO₂ methanation adsorbed on different adsorption sites are presented in [Table 3](#). The fcc site is most stable for most species, except for HCOO, CO₂, H₂O and CH₄ species, and the adsorption structure of all species is given in [Fig. 2](#).

C atoms prefer to adsorb at the fcc site with an adsorption energy of −530.3 kJ/mol. O atoms prefer to adsorb at fcc site with an adsorption energy of −466.2 kJ/mol. CO₂ adsorbs at a bridge site with an adsorption energy of −8.3 kJ/mol. HCOO adsorbs on Ni(111) with two O atoms bound to two Ni atoms at the top site with an adsorption energy of −162.8 kJ/mol. CO adsorbs at the fcc site through its C atom with an adsorption energy of −127.7 kJ/mol. OH adsorbs at the fcc site via an O atom with an adsorption energy of −231.0 kJ/mol. CH, CH₂ and CH₃ also prefer to adsorb at the fcc

site with an adsorption energy of -543.4 , -340.2 and -126.9 kJ/mol, respectively. CH_4 adsorbs on the fcc site via a C atom with an adsorption energy of -28.6 kJ/mol. The most stable adsorption configuration of intermediates involved in mechanism 1 is presented in Fig. 2.

3.2.2 Mechanism of CO_2 methanation

The mechanisms of CO_2 methanation include a CO-intermediate on the Ni(111) surface as illustrated in Schemes 1 and 2. The species with asterisk (*) are active sites that interact with the species, and * represents active sites.

Scheme 1. One of the mechanisms of CO_2 methanation

Scheme 2. One of the mechanisms of CO_2 methanation

CO formation. For mechanisms that include CO-intermediates, the formation of CO is a significant step. In **Scheme 1** (black line), the formation of CO includes two steps, shown as **R3**, **R4** reaction in **Scheme 1** and **R3** reaction in **Scheme 2**. For the **R3** reaction in **Scheme 1**, adsorbed CO_2 reacts with H^* to produce HCOO . This elementary reaction has an activation barrier of 113.1 kJ/mol, and this reaction is exothermic by 42.5 kJ/mol. In **TS1**, a C atom adsorbs at the hcp site, and H

adsorbs at the bridge site with the distance between the C and H decreasing to 1.424 Å from 3.242 Å. The C-O bond changes to 1.222 and 1.252 Å from 1.219 and 1.289 Å, respectively, and the final C-O bond length is 1.270 Å, which agrees with previous results (1.277 Å by Pang et al. [96]). For **R4** reaction in **Scheme 1**, HCOO breaks down into CO+OH with an activation barrier of 306.8 kJ/mol. This elementary reaction is exothermic by 1.9 kJ/mol. In **TS2**, the distance between O and H is 0.974 Å, the distance between C and O changed to 1.152 Å and 2.612 Å from 1.270 Å, respectively. For the product of TS2, the C-O and O-H bond lengths are 1.197 Å and 0.982 Å, respectively.

For the **R3** reaction in **Scheme 2** (red line), CO₂ split into CO and O with an activation barrier of 93.7 kJ/mol (64.7 kJ/mol by Zhu et al. [95], 53.1 kJ/mol by Wang et al. [100]), and this reaction is exothermic by 75.6 kJ/mol (69.5 kJ/mol by Wang et al. [97]). In **TS1** of scheme 2, one of the C-O bonds breaks down with the distance of 1.936 Å changing from 1.290 Å. The other C-O bond changes to 1.166 Å from 1.219 Å. The length of the C-O bond in CO+O is 1.193 Å. The structures of the initial, transition and final states for CO formation and the energy profiles in Schemes 1 and 2 are shown in Fig. 3.

CH_x (x = 1–4) formation

CH formation. The initial, transition and final states and the potential energy profile for the formation of CH in Schemes 1 and 2 are shown in Fig. 4.

For the **R5** reaction of **Scheme 1**, CH+OH was produced by adsorbed CO reacting with 2H*. The energy barrier of this reaction is 221.4 kJ/mol with a reaction energy of 75.3 kJ/mol shown by a black line. In **TS3**, the distance of C-H is 1.111 Å, and changes from 2.704 Å. The distance of O-H is 1.006 Å.

For the **R4** reaction of **Scheme 2** (red line), adsorbed CO split directly into adsorbed C and O. The energy barrier of this reaction is 237.4 kJ/mol, which agrees well with the values of Catapan et al. (290.5 kJ/mol) [91], Zhu et al. (283.7 kJ/mol) [95] and Wang et al. (304 kJ/mol) [100]. This reaction is endothermic by 125.6 kJ/mol in the red line. In **TS2**, O atoms adsorb at the bridge site and the C-O bond breaks with the distance between C and O elongated to 1.995 Å from 1.196 Å.

The adsorbed C reacts stepwise with adsorbed H to form CH species, as shown in the **R5**

reaction of **Scheme 2**. Adsorbed C reacts with adsorbed H to produce CH*. The energy barrier of this elementary reaction is 69.2 kJ/mol with a reaction energy of -84.9 kJ/mol. The barrier of this reaction was 87.8 kJ/mol as determined by Catapan et al. [89] and 78.2 kJ/mol by Zhu et al. [95]. As presented in Fig. 4, in **TS3**, the distance between C and H shortens to 1.699 Å from 2.736 Å. The length of the C-H bond in the CH* product is 1.101 Å, and this value agrees well with the result of Watwe (1.10 Å) [76].

CH_x (x=2-4) formation. The two different mechanisms of CO₂ methanation include a CO-intermediate, and the process of CH_x (x = 2-4) formation is exactly the same. The initial, transition and final states and the potential energy profile for the formation of CH in Schemes 1 and 2 are shown in Fig. 5.

The generated CH* reacts sequentially with adsorbed H to form CH₂ species. The energy barrier and reaction energy of this reaction are 68.2 and 6.3 kJ/mol, respectively. In **TS4**, as shown in Fig. 4, H atoms adsorb at the hcp site with the distance decreasing to 1.638 Å from 2.712 Å, and the length of the new C-H bond is 1.129 Å in the CH₂ species. The adsorbed CH₂ species reacts sequentially with adsorbed H to form CH₃ species. This elementary reaction has an energy barrier of 71.4 kJ/mol with a reaction energy of -34.2 kJ/mol. The barrier is slightly smaller than the result of Michaelides and Hu of 49 kJ/mol [92]. In **TS5** of Fig. 5, the H atoms adsorb at the top site with the distance between the C and H changing to 1.745 Å from 2.079 Å. The length of the new C-H bond is 1.109 Å, which is slightly shorter than previously calculated values (1.118 Å by Pang et al. [96]). In the final step of R5 in Scheme 2, adsorbed CH₃ reacts sequentially with adsorbed H to form CH₄ species. The energy barrier of this reaction is 137.4 kJ/mol with the reaction energy of -41.3 kJ/mol. In **TS6**, the H atoms adsorb at the bridge site with the distance between the C and H changing to 1.805 Å from 2.885 Å. The length of the newly generated C-H is 1.099 Å, which agrees well with the results of Watwe [76] (1.10 Å) and Kratzer (1.09 Å) [101]. The reaction barriers calculated by Wang et al. [87] and Zhu et al. [100] on each elementary reaction were 78.1 kJ/mol and 78.2 kJ/mol for TS3 in Scheme 2, 69.5 kJ/mol and 66.6 kJ/mol for TS4, 58.9 kJ/mol and 60.8 kJ/mol for TS5 and 78.2 kJ/mol and 86.8 kJ/mol for TS6.

3.3 Mechanism without CO intermediate

3.3.1. Structures of adsorbed species and energetics of adsorption

The most stable site, corresponding reactant adsorption energies and intermediates adsorbed on different adsorption sites are presented in [Table 3](#) and [Fig. 2](#).

The adsorption site and energy of OH, CH₂, CH₃, CH₄ and H₂O have been mentioned above. The stable adsorption site of C(OH)₂ is the top site via the C atom, and the adsorption energy is –220 kJ/mol. The stable adsorption site of the CH₂O species is a bridge via the C and O atoms, and the adsorption energy is –70.2 kJ/mol.

3.3.2 Mechanism of CO₂ methanation without CO intermediate

The mechanisms of CO₂ methanation without the CO intermediate on the Ni(111) surface are illustrated in Scheme 3. Species with asterisks (*) represent active sites interacting with species, whereas * represents active sites.

Scheme 3. Mechanisms of CO₂ methanation without CO intermediate

The initial, transition and final states and the potential energy profile for some reactions in Scheme 3 are shown in [Fig. 6](#).

For **R3** in **Scheme 3**, adsorbed CO₂ reacts with two H atoms to produce C(OH)₂. The energy barrier and reaction energy for this reaction are 292.3 kJ/mol and 74.5 kJ/mol, respectively. In **TS1**, the distances of two O-Hs are 1.572 Å and 1.968 Å, which change from 3.102 Å and 3.259 Å respectively. The final length of the O-H bonds of this elementary reaction are 1.012 Å and 0.996 Å, respectively. The adsorbed C(OH)₂ species react with H* to form CH₂O+OH, the energy barrier of

this reaction is 98.7 kJ/mol with a reaction energy of -27.0 kJ/mol. In **TS2**, one of the C-O bond breaks, and the distance between C and O increases to 2.987 Å from 1.339 Å. The other C-O bond changes slightly to 1.229 Å from 1.339 Å. The distance between the C and H atoms shortens to 2.805 Å from 1.893 Å, respectively, to form two C-H bonds. In the product $\text{CH}_2\text{O}+\text{OH}$, the length of the two C-H and the C-O bonds are 1.109 Å, 1.108 Å and 1.354 Å, respectively. The final distance between C and O is 3.676 Å. Adsorbed CH_2O reacts sequentially with H^* to form CH_2+OH . The energy barrier and reaction energy are 163.7 kJ/mol and 9.6 kJ/mol, respectively. In **TS3**, the distance between the C and O atoms changes to 2.722 Å from 1.340 Å, and the distance between the O and H atoms changes to 1.432 Å from 3.055 Å. The C-H bonds change slightly. In the product $\text{CH}_2 + \text{OH}$, the length of the new-generated O-H bond is 0.981 Å. The length of the C-H bonds is 1.128 and 1.100 Å.

The conditions for CH_3 and CH_4 formation are mentioned in **3.2**.

Summary

We obtain the energy barrier and reaction energy of every elementary reaction involved in the three mechanisms of CO_2 methanation on the Ni(111) surface by DFT calculations. Fig. 7 presents a summary potential energy diagram of every elementary reaction involved in three mechanisms of CO_2 methanation on the Ni(111) surface.

For mechanism 1 (black line), the highest energy barrier for this process is 306.8 kJ/mol, so the rate-determining step for this mechanism of CO_2 methanation is the dissociation of HCOO species on the Ni(111) surface into CH and OH, i.e. $\text{HCOO} \rightarrow \text{CO} + \text{OH}$.

For mechanism 2 (red line), the formation of C has the highest energy barrier and reaction energy of 237.4 kJ/mol and 125.6 kJ/mol, and the rate-determining step for this mechanism of CO_2 methanation is the dissociation of CO species on the Ni(111) surface into absorbed C and O, i.e. $\text{CO} \rightarrow \text{C} + \text{O}$.

For mechanism 3 (blue line), the formation of $\text{C}(\text{OH})_2$ has the highest energy barrier and a reaction energy of 292.3 kJ/mol and 74.5 kJ/mol. The rate-determining step for this mechanism of CO_2 methanation is the formation of $\text{C}(\text{OH})_2$ species through the reaction of CO_2 and H, i.e. $\text{CO}_2 + 2\text{H} \rightarrow \text{C}(\text{OH})_2$.

In conclusion, the best mechanism for CO₂ methanation among the three mechanisms is mechanism 2, which is shown in Scheme 2.

3.4 H₂O formation

At the end of the mechanism of CO₂ methanation, adsorbed O or OH reacts with H* to form H₂O. The stable adsorption of O, OH and H₂O has been presented in Figs 2. The initial, transition and final states and the potential energy profile for the formation of H₂O in the three schemes is shown in Fig. 8.

For **R6** in **Scheme 2**, adsorbed O reacts with H* to form adsorbed OH species. The energy barrier of this reaction is 137.9 kJ/mol with the reaction energy of 21.9 kJ/mol. Our result differs slightly from that of Wang et al. (by 12.5 kJ/mol) [87]. In TS', the distance between the O and H atoms changes to 1.470 Å from 2.718 Å, and finally forms OH with a length of 0.982 Å.

For **R6** in **Scheme 2**, **R7** in **Scheme 1** and **Scheme 3**, adsorbed OH reacts with H* to produce H₂O. The energy barrier and reaction energy of this reaction are 124.6 and 24.7 kJ/mol, respectively. In TS'', the distance between the H and O atoms shortens to 1.665 Å from 2.760 Å. The final length of the O-H bond is 0.987 Å in product H₂O.

The barriers for the two reactions on the formation of H₂O calculated by Catapan et al. [91] and Zhu et al. [95] were 111 kJ/mol and 130.3kJ/mol for TS', and 112 kJ/mol and 128kJ/mol for TS''.

4. Conclusion

The three mechanisms of CO₂ methanation on the Ni(111) surface were investigated systematically using DFT calculations at the molecular level. The three mechanisms fall into two categories: the mechanisms include and exclude a CO intermediate. The most stable adsorption configurations of all reaction species (O, OH, CO, CH, CH₂, CH₃, CH₄, HCOO, C(OH)₂, CH₂O etc.) in the three paths of CO₂ methanation adsorbed on the Ni(111) surface are described.

In the first path, CO₂ reacts with H to produce HCOO species. HCOO then dissociates into CO and OH and CO subsequently hydrogenates to CH₄. The highest energy barrier of this path is 306.8 kJ/mol for the dissociation of HCOO, so the rate-determining step of Path 1 is HCOO→CO+OH. In the second path, CO₂ firstly decomposes into CO and O on the Ni(111) surface. Then CO decomposes into C and O and C hydrogenates to CH₄. The highest barrier of this path is 237.4

kJ/mol from the dissociation of CO into C and O species. Therefore, the elementary reaction $\text{CO} \rightarrow \text{C} + \text{O}$ is the rate-determining step in this path. In the third path, CO_2 reacts firstly with H to produce $\text{C}(\text{OH})_2$ species on the Ni(111) surface. $\text{C}(\text{OH})_2$ species then dissociate into CH_2O and OH species. CH_2O then dissociates into CH_2 species. The highest barrier of this path is 292.3 kJ/mol for the formation of $\text{C}(\text{OH})_2$ on the Ni(111) surface, so the rate-determining step of this path is the elementary reaction of $\text{CO}_2 + 2\text{H} \rightarrow \text{C}(\text{OH})_2$. Therefore, from all tested mechanisms, path 2 is the optimal mechanism.

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Figure captions:

Fig. 1. Energy profile with energy changes for H₂ dissociation.

Fig. 2. Most stable adsorption configuration of reactants and intermediates involved in mechanism of CO₂ methanation. C, O, H, and Ni atoms are shown as the gray, red, white, and blue balls, respectively.

Fig. 3. Structures of initial, transition and final states with potential energy profile for CO formation in scheme 1 (black) and scheme 2 (red). Bond lengths in Å. The color coding was shown in Fig. 2.

Fig. 4. Structures of initial, transition and final states with potential energy profile for CH formation in scheme 1 (black) and scheme 2 (red). Bond lengths in Å. The color coding was shown in Fig. 2.

Fig. 5. Structures of initial, transition and final states with potential energy profile for CH_x (x = 2–4) formation in scheme 1 (black) and scheme 2 (red). Bond lengths in Å. The color coding was shown in Fig. 2.

Fig. 6. Structures of initial, transition and final states with potential energy profile for CO₂ methanation in Scheme 3. Bond lengths in Å. The color coding was shown in Fig. 2.

Fig. 7. Potential energy diagram of three mechanisms of CO₂ methanation.

Fig. 8. Structures of initial, transition and final states with potential energy profile for H₂O formation. Bond lengths in Å. The color coding was shown in Fig. 2.

Table 1Adsorption site and energy of H₂ on Ni (111) surface

Site	E _{ads} (kJ/mol)	Lit. calc
Top	−69.6	
Bridge	−69.3	
hcp	−69.62	−95.4 [87]
fcc	−69.64	−97.5 [87]

Table 2

Adsorption site and energy of H on Ni (111) surface.

Site	E_{ads} (kJ/mol)	Lit. calc
Top	-248.1	-214 [87], -221.0 [88], -214 [89], -214.3 [90]
Bridge	-263.2	-265.4 [88], -262.8 [89], -259.7 [90], -253.8 [91],
hcp	-293.7	-266 [87], -277.9 [88], -274.9 [89], -272.2 [90], -267.3 [91], -245 [92]
fcc	-295.3	-267 [87], -278.9 [88], -275.7 [89], -273.2 [90], -267.3 [91], -251 [92], -270.3 [93]

Table 3

Stable site and adsorption energies of reactants and intermediates adsorbed on Ni (111) surface.

Species	Site	E_{ads} (kJ/mol)	Lit. calc
CO ₂	^a	-8.3	-5.8 [90], -11.6 [91], -2 [95]
HCOO	Bridge ^b	-162.8	-236.4 [90], -83 [96]
CO	fcc	-127.7	-201 [91], -144.8 [93], -185.3 [95], -181 [97]
C	fcc	-530.3	-613 [76], -629 [87], -647.7 [89], -637 [91], -579 [93], -654.3 [95]
O	fcc	-466.2	-464.2 [91], -434.4 [93], -547.2 [95], -489.3 [97]
OH	fcc	-231.0	-300 [87], -322.3 [91], -241.3 [93], -330 [95]
CH	fcc	-543.4	-605 [87], -619.2 [89], -660 [91], -569.4 [93], -620.5 [95], -502.1 [98]
CH ₂	fcc	-340.2	-371 [87], -373.6 [89], -315 [92], -318.5 [93], -387 [95], -368.2 [98]
CH ₃	fcc	-126.9	-174 [87], -178.5 [89], -141 [92], -125.5 [93], -184 [95], -180 [97], -175.7 [98], -126 [99],
CH ₄	fcc ^c	-28.6	2 [95]
H ₂ O	atop	-49.0	-45.4 [91], -28 [95]
C(OH) ₂	top	-220.4	
CH ₂ O	bridge	-70.2	-59.8 [76], -72.4 [95]

^a The adsorbed site of CO₂ was shown in Fig 2

^b Two O atoms bound to two Ni atoms at atop sites

^c fcc site above Ni(111) surface without bonding with Ni atom

Fig. 1

Fig. 2

CH_2O

HCOO

C(OH)_2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8