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CH₄ dissociation on NiCo (111) surface: A first-principles study

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1. Introduction

Catalytic reforming of CH₄ with CO₂ to produce synthesis gas has attracted increasing attention in recent years [1-7]. This process not only reduces greenhouse gas emission, but also produces synthesis gas with the ratio to unit which is more preferable feeds for some liquid fuel synthesis processes. It is well known that all VIII transition metals, except osmium, can catalyze this reaction. Because of its good activity and relatively low cost, metal Ni is selected as the catalyst in the reforming reaction. However, deactivation of Ni catalysts by carbon of coke formation is a serious problem [8,9]. Carbon mainly results from CH₄ dissociation from thermodynamic viewpoint [10]. In addition, isotopic studies and forward rate measurements confirmed the mechanistic equivalence among CH₄-reforming and decomposition of CH₄ on Ni-based catalysts [11]. Therefore, it is the center to investigate CH₄ dissociation considered as a key and sole process in order to understand CH₄/CO₂ reforming in detail.

Nowadays, experimental researchers have proved the mechanism of CH_4 dissociation, *i.e.*, sequential dehydrogenation, by detecting chemisorbed CH_3 , CH_2 and CH on Ni (111) using secondary ion mass spectroscopy (SIMS) and X-ray photoelectron spectroscopy (XPS) technique [12]. Theoretical calculations about CH_4 dissociation on metal surface, which mainly focused on clean metal catalyst [13–17], also support the successive dehydrogenation mechanism.

ABSTRACT

A density-functional theory method has been conducted to investigate the adsorption of CH_x (x=0–4) as well as the dissociation of CH_x (x=1–4) on (111) facets of ordered NiCo alloy. The results have been compared with those obtained on pure Ni (111) surface. It shows that the adsorption energies of C and CH are decreased while it is increased for CH_3 on NiCo (111) compared to those on pure Ni (111). Furthermore, on NiCo (111), dissociation of CH_x prefers not to the top of Ni, but to the top of Co. The rate-determining step for CH_4 dissociation is considered as the first step of dehydrogenation on NiCo (111), while it is the fourth step of dehydrogenation on Ni (111). Furthermore, the activation barrier in rate-determining step is slightly higher by 0.07 eV on Ni (111) than that on NiCo (111). From above results, it is important to point out that carbon is easy to form on NiCo (111) although the adsorption energy of C atom is slightly decreased compared to that on Ni (111).

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In order to suppress carbon deposition many attempts have been focused on designing and preparing excellent bimetallic catalyst. Initially, a number of contributions have claimed that the Ni-M (M denotes noble metals) bimetallic alloys can affect the catalytic behavior and carbon formation [18-20]. For example, Nørskov and co-workers [19,20] reported that AuNi surface alloys should exhibit better carbon tolerance than monometallic Ni, and the reason is that the first step of CH₄ dissociation is hindered by a relatively high barrier than that on pure Ni (111). Clearly, addition of noble metals is not practical from an industrial standpoint. Recently, Ni-based bimetallic catalysts, focused on non-noble metals incorporation into Ni crystal, have been reported [21-24]. Takanabe et al. [23] found that carbon deposition is eliminated and CH₄ decomposition activity is improved on bimetallic NiCo/TiO₂ catalysts. Wang and co-workers [24] reported the same results on NiCo/MgO catalyst as that obtained by literature [23]. Obviously, the catalysts reported in literatures [23,24] are more excellent than that in literatures [19,20].

However, the underlying details regarding of the CH₄ dissociation on bimetallic NiCo alloy are still unknown. It is well known that the realistic catalyst reaction is a complex system, in which many factors (strong metal-support interaction, preparation condition and so on) have effect on the activity of the catalyst. Herein, only the active component effect on the reaction is considered, while other effects are considered in the next work.

In recent years, computational methods have become a powerful research tool for understanding the chemical reactions in microscopic view. For example, methods based on quantumchemical theory provide information at atomic/molecular level. In particular, the DFT calculations provide accurate energetic and

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Fig. 1. The surface and adsorption sites of NiCo (111)(a) topview (b) sideview.

geometries as well as reaction barriers. In this contribution, we present a systematic study on the successive dehydrogenation of methane on a well-characterized bulk alloy NiCo (111) surface using density functional theory (DFT) method. The adsorption geometries and energetics of CH₄ sequence dehydrogenation products on NiCo (111) have been investigated. Based on the optimized adsorption geometries, the decomposition of CH₄ was investigated. Then the results have been compared with those obtained on pure Ni (111) surface. Finally, the electronic properties have been plotted to explain the properties of adsorption and activation energy.

2. Computational details

2.1. Methods

Density functional theory (DFT) calculations were performed using the Cambridge Sequential Total Energy Package (CASTEP) [25,26]. All calculations were conducted with the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional [27]. Ionic cores were described by ultrasoft pseudopotential [28] and the Kohn-Sham one-electron states were expanded in a plane wave basis set up to a cutoff of 340 eV in order to obtain accurate energetics for all systems. A Fermi smearing of 0.1 eV was utilized and the corrected energy extrapolated to zero Kelvin. Brillouin zone integration was approximated by a sum over special k-points chosen using the Monkhorst-Pack method [29], and they were set up to $5 \times 5 \times 1$. Geometries were optimized until the energy had converged to 2.0×10^{-5} eV/atom and the force converged to 0.05 eV/Å and the max displacement converged to 2×10^{-3} Å. Spin polarization was considered in all calculations.

2.2. Models

NiCo alloy with Co/Ni ratio to unit showed a good performance in carbon dioxide reforming of methane [23,24]. The XRD analysis showed that uniform alloy was formed from bulk to surface [24]. Therefore, the catalyst, including of 1:1 Ni–Co binary system, was modeled by replacing half of the Ni atoms in a face-centered-cubic lattice by Co atoms in accordance with the structure of L1₀. The current calculations found that lattice constants of *a* is 3.511 Å, and *c* is 3.624 Å, which has slight change compared to the calculated lattice parameters of Ni bulk (3.541 Å) and Co bulk (3.556 Å).

Although real catalysts feature complex surface structures, it is nevertheless useful to study the mechanism of elementary reaction steps for idealized model systems, *e.g.*, single-crystal surfaces, if only for reference purposes [30]. We focused here on adsorption and reactions pertinet to CH_4 dissociation on the most stable regular (1 1 1) surface of NiCo alloy.

The surfaces were obtained by cutting alloy of NiCo along [111] direction, the thickness of each surface slab was chosen to be at least as thick as a three-layer slab, which is proved reasonable to

investigate the adsorption and reaction mechanism in previous literatures [31,32]. The vacuum region between adjacent slabs was set to 10 Å. In order to decrease the computational load, the bottom layer of slab was fixed at its equilibrium bulk phase position, while the top two layers and the adsorbates were allowed to relax freely. A (2×2) supercell was used in the calculation in order to reduce interaction between adsorbates on the surface.

The chemisorption energies, E_{ads} , were calculated, as following:

$E_{ads} = E_{adsorbates/slab} - (E_{adorbates} + E_{slab})$

where $E_{adsorbates/slab}$ is the total energies of adsorbates on NiCo (111), $E_{adsorbates}$ is the total energy of isolated adsorbates which was calculated by putting isolated adsorbates in a cubic box of $10 \text{ Å} \times 10 \text{ Å} \times 10 \text{ Å}$, E_{slab} is the total energy of NiCo (111) slab.

The reaction energy was calculated by two different definitions given as following:

$$\Delta H(s) = (E_{A/slab} + E_{B/slab}) - (E_{AB/slab} + E_{slab})$$

$$\Delta H(\mathbf{c}) = E_{\mathbf{A}+\mathbf{B}/\mathrm{slab}} - E_{\mathbf{A}\mathbf{B}/\mathrm{slab}}$$

where $E_{A/slab}$, $E_{B/slab}$ and $E_{AB/slab}$ are the total energies of adsorbates A, B and AB adsorption on NiCo (111) surface, respectively, E_{slab} is the total energy of NiCo (111) slab, $E_{A+B/slab}$ is the total energy of the coadsorption A and B on NiCo (111) surface. For reaction AB \rightarrow A + B, the positive value suggests endothermic, while the negative value suggests exothermic.

Transition states (TS) are located by using the complete LST/QST method [33]. Firstly, the linear synchronous transit (LST) maximization was performed followed by an energy minimization in directions conjugate to the reaction pathway. The TS approximation obtained in that way is used to perform quadratic synchronous transit (QST) maximization. From that point, another conjugate gradient minimization is performed. The cycle is repeated until a stationary point is located. The convergence criterion for transition state calculations was set to: root-mean-square forces on atoms tolerance of 0.25 eV/Å.

The activation energy is defined as following:

$$E_{\rm a} = E_{\rm TS} - E_{\rm R}$$

where E_{TS} is the energy of transition state, and E_R is the sum of the energies of reactants.

3. Results and discussion

There are four high-symmetry sites on the (111) surface of pure Ni: top (T), bridge (B), hexagonal-close-packed (HCP) and face-centered-cubic (FCC) threefold hollow sites. On the NiCo (111) surface, some additional sites are found because of the replacement of 50% Ni atoms by Co. These adsorption sites are presented



CH3@HCP-1 site	CH3@HCP-2 site	CH3@FCC-1 site	CH ₃ @FCC-2 site	CH2@FCC-Ni	CH2@FCC-Co	CH2@FCC-Ni
				site (top-Ni-H)	site (top-Co-H)	site (top-Ni-H)
E_{ads} =-1.81 eV	E_{ads} =-1.71 eV	E _{ads} =-1.90 eV	E _{ads} =-1.75 eV	E _{ads} =-4.66 eV	E_{ads} =-4.57 eV	E _{ads} =-4.52 eV
$d_{\text{C-Ni}}{=}2.140~\text{\AA}$	$d_{\text{C-Ni}}{=}2.157~\text{\AA}$	d _{C-Ni} =2.138 Å	d _{C-Ni} =2.115 Å	$d_{\text{C-Ni}}{=}1.795~\text{\AA}$	$d_{C\text{-Ni}}{=}1.962~\text{\AA}$	$d_{C-Ni}=2.157 \text{ Å}$
d _{C-Co} =2.150 Å	d _{C-Ni} =2.153 Å	d _{C-Co} =2.124 Å	$d_{\text{C-Ni}}{=}2.134~\text{\AA}$	d _{C-Co} =1.948 Å	$d_{C\text{-}Co}{=}1.946~\text{\AA}$	$d_{C\text{-Ni}}{=}1.950\text{ Å}$
$d_{C-Co}=2.132 \text{ Å}$	d _{C-Co} =2.161 Å	$d_{C-Co}=2.144 \text{ Å}$	$d_{\text{C-Co}}{=}2.154~\text{\AA}$	$d_{\text{C-Co}}{=}1.954~\text{\AA}$	$d_{\text{C-Co}}{=}2.026~\text{\AA}$	$d_{\text{C-Co}}{=}2.021~\text{\AA}$
d _{C-H} =1.118 Å	d _{C-H} =1.115 Å	d _{C•H} =1.117 Å	d _{C-H} =1.118 Å	d _{C-H} =1.156 Å	$d_{\text{C-H}}\!\!=\!\!1.100~\text{\AA}$	d _{C-H} =1.147 Å
d _{с-н} =1.119 Å	d _{C-H} =1.113 Å	$d_{C-H}=1.124$ Å	d _{C-H} =1.122 Å	d _{C-H} =1.102 Å	d _{C-H} =1.151 Å	d _{C-H} =1.102 Å
$d_{C-H}=1.122 \text{ Å}$	$d_{\text{C-H}}{=}1.120~\text{\AA}$	d _{C-H} =1.114 Å	$d_{C-H}=1.115 \text{ Å}$	$d_{\text{Ni-H}}{=}1.795~\text{\AA}$	$d_{\rm Co-H}{=}1.849~{\rm \AA}$	$d_{\rm Ni\text{-}H}{=}1.831~{\rm \AA}$



CH2@FCC-Co	CH2@HCP-1 site	CH2@HCP-1 site	CH2@HCP-2 site	CH2@HCP-2 site	CH@FCC-1 site	CH@FCC-2 site
site (top-Co-H)	(top-Ni-H)	(top-Co-H)	(top-Ni-H)	(top-Co-H)		
E_{ads} =-4.59 eV	E _{ads} =-4.56 eV	Eads=-4.64 eV	E _{ads} =-4.56 eV	Eads=-4.65 eV	E _{ads} =-6.13 eV	E_{ads} =-6.02 eV
$d_{C\text{-Ni}}{=}1.949~\text{\AA}$	$d_{\text{C-Ni}}{=}2.012~\text{\AA}$	$d_{C\text{-Ni}}{=}1.956~\text{\AA}$	$d_{\text{C-Ni}}{=}2.019~\text{\AA}$	$d_{\text{C-Ni}}{=}1.939~\text{\AA}$	$d_{\text{C-Ni}}{=}1.889~\text{\AA}$	$d_{C\text{-Ni}}{=}1.878~\text{\AA}$
$d_{\text{C-Ni}}{=}1.946~\text{\AA}$	d_{C-Co} =1.958 Å	$d_{\text{C-Co}}{=}1.948~\text{\AA}$	d_{C-Ni} =1.940 Å	$d_{\text{C-Ni}}{=}1.948~\text{\AA}$	$d_{\text{C-Co}}{=}1.879~\text{\AA}$	$d_{\text{C-Ni}}{=}1.886~\text{\AA}$
$d_{C\text{-}Co}{=}1.977~\text{\AA}$	$d_{C\text{-}Co}{=}1.950~\text{\AA}$	$d_{\text{C-Co}}{=}2.003~\text{\AA}$	d _{C-Co} =1.937 Å	d _{C-Co} =1.976 Å	$d_{\mathrm{C-Co}}{=}1.878~\text{\AA}$	$d_{C-Co}=1.860$ Å
d _{C-H} =1.162 Å	d _{C-H} =1.155 Å	d _{C-H} =1.156 Å	d _{C-H} =1.156 Å	d _{C-H} =1.101 Å	d _{C-H} =1.099 Å	d _{C-H} =1.100 Å
$d_{C-H}=1.101 \text{ Å}$	$d_{C-H}=1.104 \text{ Å}$	$d_{C-H}=1.102$ Å	d _{C-H} =1.102 Å	d _{C-H} =1.167 Å		
$d_{\mathrm{Co-H}}{=}1.787~\text{\AA}$	$d_{\text{Ni-H}}{=}1.809~\text{\AA}$	$d_{\text{Co-H}}{=}1.818~\text{\AA}$	$d_{\text{Ni-H}}{=}1.801~\text{\AA}$	d _{Со-Н} =1.772 Å		



Fig. 2. The adsorption geometries and parameters of CH_x (x = 0-4) and H on NiCo (111).

in Fig. 1. It is clear that each group of the T, HCP and FCC site is split into two subsets, while B site is split into three subsets.

3.1. Adsorption of CH_x on NiCo (111)

We first investigate the adsorption of CH_x (x=0-4) species involving CH_4 successive dehydrogenation steps. In each

subsection, the adsorption of the CH_x and H intermediates is discussed. The geometries and adsorption energies are presented in Fig. 2.

3.1.1. CH₄ adsorption on NiCo (111)

Previous calculation results have proved that the adsorption energy of CH_4 is substantially small on transition metal surface,



Fig. 2. (Continued)

which may be negligible [34–36]. The adsorption of methane molecular on transition metal surfaces is generally classified as a process of physisorption where the attractive interaction arises from the van der Waals force. Hence only two kind of geometry of CH₄ adsorption is considered on NiCo (111) surface, that is, three H atoms point to the surface, another H points to the surface normal through Ni or Co atom. The calculated adsorption energy is -0.01 eV, which is consistent with that on pure Ni (111) [37,38]. The optimized distance of C–Ni (Co) is 3.871 Å (3.775 Å), and the bond of C–H is 1.096 Å (1.096 Å). Obviously, the addition of Co has little impact for CH₄ adsorption on different surface sites.

3.1.2. CH₃ adsorption on NiCo (111)

CH₄ dehydrogenates one H atom resulting in CH₃. For CH₃ adsorption on aforementioned sites, there are two possible configurations with different azimuthal orientations: C–H bond pointing toward the nearest-neighboring metal atom (noted as *top-H*) or toward the midway between two neighboring metal atoms (noted as *bri-H*).

As for CH₃ adsorption on top site, there are four configurations found. When CH₃ is adsorbed on the top of Ni with *top-H* azimuthal orientation, the geometry has C_{3v} symmetry with d_{C-H} of 1.100 Å and d_{C-Ni} of 1.966 Å. Similarly, CH₃ adsorption on the top of Ni with *bri-H* azimuthal orientation, the geometry also has C_{3v} symmetry with d_{C-H} of 1.099 Å and d_{C-Ni} of 1.968 Å. Their adsorption energy calculated both are -1.43 eV. Obviously, there are almost no differences in energies and geometry parameters between *top-H* and *bri-H*.

When CH₃ is adsorbed on the top of Co with *top-H* azimuthal orientation, the geometry also has C_{3v} symmetry with d_{C-H} of 1.100 Å and d_{C-C0} of 1.994 Å. Accordingly, CH₃ adsorption on the top of Co with *bri-H* azimuthal orientation, the geometry also has C_{3v} symmetry with d_{C-H} of 1.100 Å and d_{C-C0} of 1.995 Å. Their adsorption energy calculated both are -1.44 eV. Similarly, there are almost no differences in energies and geometry parameters between *top-H* and *bri-H*. This is in agreement with the results on pure Ni (1 1 1) surface obtained by Wang et al. [14]. So we only consider the configuration with *top-H* in the following investigation.

When CH_3 is adsorbed on bridge sites, only one stable configuration was found, that is, CH_3 adsorbed on B-CoCo site. The distances of C-Co are 2.184 and 2.057 Å, respectively. The adsorption energy is -1.68 eV, which is stronger than those on top sites. Whereas, no stable CH_3 adsorption on bridge site was found on pure Ni (111) [38,39].

There are four stable configurations obtained for CH₃ adsorbed on threefold hollow site. On HCP-2 and FCC-2 sites, CH₃ interacts with two Ni atoms and one Co atom, correspondingly, the adsorption energies are -1.71 and -1.75 eV, respectively, while CH₃ is bonded to two Co atoms and one Ni atom on HCP-1 and FCC-1 sites, and the adsorption energies are -1.81 eV and -1.90 eV, respectively. It is clear that the order for adsorption energy of CH₃ is as follows: FCC-1>HCP-1>FCC-2>HCP-2>B>T. In the configuration of CH₃ adsorption on FCC-1 site, the distance which is elongated to 1.124 Å is the longest in all bonds of C-H. Our calculated adsorption energies for CH₃ are -1.78 eV on HCP site and -1.81 eV on FCC site on pure Ni (111), and the longest distance of C-H is 1.121 Å in configuration of CH₃ adsorbed on FCC site. Compared with CH₃ adsorption on pure Ni (111), the adsorption energies are bigger and the distance of C-H is longer on corresponding sites on NiCo (111), which indicates that the addition of Co increases the adsorption energy of CH₃ and makes the bond of C-H more active.

3.1.3. CH_2 adsorption on NiCo (111)

CH₂ prefers to adsorb on threefold site, and nine stable structures are obtained. The adsorbed CH₂ at each site has two geometries, i.e., one H bonds to Ni (or Co) atom, the other H atom points toward the midway of the metal-metal bridge [0] (they are denoted as top-Ni-H and top-Co-H, respectively), which results in different activation characteristics of the two C-H bonds. For example, when CH₂ adsorbed on HCP-2 site, in top-Co-H, the bond of C-H in which H pointing toward Co atom is stretched to 1.167 Å, and another bond of C–H is only stretched to 1.101 Å, while the bond of C-H in which H pointing toward Ni atom is elongated to 1.156 Å and another bond of C-H is elongated to 1.102 Å in top-Ni-H. A similar configuration was also obtained on pure Ni (111) [32,38]. Our calculated bond lengths of C–H are 1.165 Å, 1.103 Å on HCP site and 1.157 Å, 1.102 Å on FCC site, respectively, and the calculated adsorption energies of CH₂ are -4.65 eV on HCP site and -4.67 eV on FCC site on Ni (111). However, on NiCo (111) surface, the adsorption energies are -4.56 eV (top-Ni-H), -4.64 eV (top-Co-H) on HCP-1, -4.56 eV (top-Ni-H), -4.65 eV (top-Co-H) on HCP-2, -4.66 eV (top-Ni-H), -4.73 eV (top-Co-H) on FCC-1, -4.52 eV (top-Ni-H), and –4.59 eV (top-Co–H) on FCC-2, respectively. It is clear that the order for adsorption energy of CH₂ is as follows: FCC-1(top-Co-H)>FCC-



Fig. 3. The LDOS of CH_x (x = 0-3) on NiCo (111) and on pure Ni (111).

1(top-Ni-H)>HCP-2(top-Co-H)>HCP-1(top-Co-H)>FCC-2(top-Co-H)>HCP-2(top-Ni-H)=HCP-1(top-Ni-H)>FCC-2(top-Ni-H).

3.1.4. CH adsorption on NiCo (111)

CH is not absorbed on top and bridge sites, but adsorbed on threefold site with the remaining H atom oriented perpendicular to the NiCo (111) surface. Four stable geometries were found. The adsorption energies are -6.12 eV on HCP-1, -6.11 eV on HCP-2, -6.13 eV on FCC-1, and -6.02 eV on FCC-2, respectively. The bond of C-H is approximately from 1.099 to 1.102 Å while it is 1.103 and 1.101 Å on pure Ni (111) calculated by us which is slightly longer. The adsorption energies are -6.24 eV and -6.15 eV on HCP and FCC sites on pure Ni (111), respectively. Clearly, it is easy to conclude that addition of Co decrease the adsorption energy of CH. The stability order for all configurations on NiCo(111) is as follows: FCC-1 > HCP-1 > HCP-2 > FCC-2.

3.1.5. C adsorption on NiCo (111)

Like CH adsorption, C only prefers to adsorb on threefold sites, and four stable geometries were found. The adsorbed C has C_{2v} symmetry. For C on HCP-1 site, the bond of C-Ni is elongated to 1.778 Å, and the bond of C-Co is elongated to 1.819 Å, and the adsorption energy is -6.82 eV. Other three adsorption energies are -6.60 eV on FCC-2, -6.74 eV on HCP-2, and -6.71 eV on FCC-1, respectively. The adsorption order is as follows: HCP-1>HCP-2>FCC-1>FCC-2. Our calculated adsorption energies of C on pure Ni (111) are -6.90 eV on HCP and -6.80 eV on FCC, which is higher than those on corresponding adsorption sites on NiCo (111), indicating that the addition of Co decrease the adsorption energy of C. It has been reported that substitutionally embedded Bi, Co and Au atoms in the pure Ni (111) surface have the same effects [39]. In addition, Nørskov and co-workers [19] believed that the decrease of C adsorption weakens the interaction between the carbon atoms and the surface, thus the formation of CO becomes more likely which prevents the building up of a graphite layer.

3.1.6. Hadsorption on NiCo (111)

H adsorbed on NiCo (111) may be at top, bridge and three fold sites. For H adsorption on top site, only a stable geometry is found with adsorption energy of -2.15 eV. There are two stable configurations for H adsorption on bridge site, namely, B-NiNi site and B-CoCo site, and the adsorption energies are both -2.58 eV, however, the geometric parameters are different (d_{H-Ni} = 1.638, 1.639 Å *vs.* $d_{H-Co} = 1.674$, 1.676 Å).

For H adsorption on threefold site, four stable geometries were found. The adsorption energies are -2.73 eV on HCP-1, -2.72 eV on HCP-2, -2.75 eV on FCC-1, and -2.72 eV on FCC-2, respectively. These adsorption energies are approximately equal. Obviously, H prefers to chemisorb on the threefold hollow sites, which is in line with that on pure Ni (111). However, on Ni (111), the adsorption energies of H are -2.74 eV on HCP site and -2.77 eV on FCC site, respectively, which are slightly higher than those on corresponding sites on NiCo (111).

3.1.7. Electronic properties of CH_x (x = 0-3)

In order to profound insight into the electronic structures of the chemisorbed CH_x (x = 0-3) on NiCo (111), the Mulliken charges and the local density of states (LDOS) of CH_x adsorbed on FCC-1 site, are shown in Table 1 and Fig. 3.

From Table 1, the Mulliken charges of all the CH_x (x=0-3) adsorbed on pure Ni (111) and NiCo (111) are both negative, indicating the electron transfer from alloy NiCo surface to CH_x upon chemisorption, in agreement with the following LDOS analysis. Similar to those on Ni (111), the adsorbates are best described as $CH_x^{\delta-}$ anions. Wang et al. [14] explained that the change from

Table 1	
The Mulliken charges of CH_{x} (x = 0-3) on pure Ni (111) and NiCo (111)).

	CH ₃	CH ₂	СН	С
On pure Ni (111)	-0.65	-0.64	-0.52	-0.45
On NiCo (111)	-0.68	-0.68	-0.57	-0.46



Fig. 4. Top view of the co-adsorption modes on NiCo (111) surface (CH_x is fixed on FCC-1 site, H sits on 1, 2, 3, 4, and 5 site, respectively).

free CH_x to chemisorbed CH_x^{$\delta-$} anions makes CH_x prefer to sit on threefold hollow site because of significant charges transfer from Ni surfaces to CH_x upon chemisorption. Therefore, CH_x also prefer to reside on threefold hollow site on NiCo (111), which is consistent with above results from adsorption energy.

The DOS of the surface may explain the properties of the adsorbed species [40,41]. Similarly, the DOS of adsorbates also may express the adsorption properties. It is well know that p-band of the CH_x is related to its adsorption process, herein, we plot the p-band centers of them to explain the stability properties of adsorbed CH_x at FCC-1 site on NiCo (111), and then compared to those on Ni (111). As shown in Fig. 3(a), the p-band center of adsorbed CH₃ is -5.96 eV on NiCo (111) while it is -5.87 eV on pure Ni (111). Obviously, there is a larger downshift of p-band center in adsorbed CH_3 on NiCo (111) than that on pure Ni (111), indicating a more stable adsorption of CH_3 on NiCo (111) than that on pure Ni (111). However, for CH and C adsorbed on NiCo (111), the p-band centers, which are -4.21 and -3.81 eV, respectively, exhibit an upshift compared to those (-5.10 and -3.88 eV) on pure Ni (111) [shown in Fig. 3(c) and (d)], which indicates less stable adsorption on NiCo (111) than that on pure Ni (111). The change of p-band center in adsorbed CH_x is mainly caused by the addition of Co into Ni crystal. However, the change of p-band is not obvious for CH₂ adsorption on NiCo (111) compared to that on pure Ni (111).

We also examine the d-band center of clean surface Ni and surface alloy atom. Our calculated d-band center of surface Ni atom is -1.87 eV while it is -1.98 eV for surface alloy atom, which is an obvious downshift on NiCo (1 1 1) and causes the different surface activation for adsorption of CH_x.

3.2. CH₄ sequence dehydrogenation on NiCo (111)

In order to investigate CH_4 sequence dehydrogenation on NiCo $(1\ 1\ 1)$ surface, it is necessary to investigate the coadsorption of CH_x (x=0-3) and H firstly. We only consider that CH_x preadsorbs on the FCC-1 site, and H coadsorbs at all possible threefold sites, as shown in Fig. 4. In Mode **1** (**4**), CH_x resides at the FCC-1 site while H resides at the HCP-1 site, and they share one Ni (Co) in a linear way. In Mode **2** (**5**), CH_x resides at the FCC-1 site while H resides at the FCC-1 site in Mode **3**, and they share one Co atom in a zigzag way.

3.2.1. $CH_4 \rightarrow CH_3 + H$

As shown in Fig. 5, five stable coadsorption structures of CH_3 and H are found. The coadsorption energies and calculated bond parameters are present in Fig. 5. The coadsorption energies of CH_3

and H are -4.49, -4.44, -4.43, -4.49, and -4.43 eV from Modes **1–5**, respectively. These values are less negative than the sum of adsorption energies of CH₃ and H adsorption isolated in their corresponding sites, indicating repulsion interactions in CH₃ and H coadsorption geometries. These coadsorption configurations are considered as the final states (FS) of the first step in CH₄ dissociation on NiCo (1 1 1).

Based on physisorbed CH₄ and coadsorbed CH₃ and H, CH₄ dissociation is examined first, and five possible paths (FCC-1 \rightarrow Mode 1, 2, 3, 4, 5) are mapped out. The geometries and parameters of all possible transition states are present in Fig. 6. Path 1(2) is that CH_4 dissociation on top of a Ni atom into CH3 and H via TS1-1 (TS1-2) along with CH₃ moving to FCC-1 site and H moving to opposite HCP-1 (FCC-2) site. Path 3 (4 or 5) is that CH₄ dissociation on top of a Co atom into CH₃ and H via TS1-3 (TS1-4 or TS1-5) along with CH₃ moving to FCC-1 site and H moving to opposite FCC-1 (HCP-1 or FCC-2) site. The overall TS geometries are very similar to those on pure Ni (111). The energy data in Table 2 clearly show that the Paths 3, 4 and 5 have almost approximate activation energy of 1.30 eV, while Paths 1 and 2 have higher activation energies (1.40 and 1.42 eV), which indicates that dissociation of CH₄ is favorable on top of Co atom than that on top of Ni. In transition state TS1-5, the breaking C–H bond is elongated to 1.663 Å, the forming H–Co bond is 1.509 Å and C-Co bond is 2.115 Å. This reaction is endothermic by 0.26 eV and has an energy barrier of 1.29 eV, which is larger than our tested value (1.18 eV) on pure Ni (111). Therefore, the incorporation of Co into the Ni crystal hinders the activation of CH₄, similar to the effect of embedded Au and Cu atoms in Ni (111) [19,40].

3.2.2. $CH_3 \rightarrow CH_2 + H$

The coadsorption of CH_2 at FCC-1 site and H at different sites are examined, and five coadsorption geometries are also found, as shown in Fig. 5. The coadsorption energy is -7.27 to -7.42 eV while a total of adsorption of CH_2 and H is -7.40, -7.29, -7.32, -7.31 and -7.29 eV, respectively, indicating almost no effect in Modes **1** and **2**, and a attractive interaction between CH_2 and H in coadsorption Modes **3**, **4** and **5** compared to their adsorption isolated in their corresponding sites.

Considered the most stable CH₃ adsorbed on FCC-1 site as the initial state (IS) and those coadsorbed configurations of CH₂ and H as the FS, the transition states of CH₃ dissociation are searched. Similarly, five possible paths (FCC-1 \rightarrow Modes 1, 2, 3, 4, 5) are designed for CH₃ dehydrogenation. The geometries and parameters of all possible transition states are present in Fig. 6. Path 1 (2) is that one H atom from adsorbed CH₃ deletes on top of a Ni atom via TS2-1 (TS2-2) along with it moving to opposite HCP-1 (FCC-2) site. Path 3(4 and 5) is that one H atom from adsorbed CH₃ deletes on top of a Co atom via TS2-3 (TS2-4 and TS2-5) along with it moving to opposite FCC-1(HCP-1 and FCC-2) site. The overall TS geometries are also very similar to that on pure Ni (111). It is clearly showed that the reaction barriers in the Paths 3, 4 and 5 are equal from Table 2, and their corresponding pathways are more favorable kinetically compared to Paths 1 and 2. In transition state TS2-5, the departing C-H bond is stretched to 1.737 Å, and the forming H-Co bond is shortened to 1.550 Å. This reaction is endothermic by 0.25 eV and has a lower energy barrier of 0.77 eV compared to those in the first step, which is approximately equal to that (0.78 eV) on pure Ni (111). Therefore, the incorporation of Co into the Ni crystal almost has no effect on the dehydrogenation of CH₃.

3.2.3. $CH_2 \rightarrow CH + H$

As shown in Fig. 5, all coadsorption configurations of CH and H have little impact on the energetics, as compared to their individual adsorption energetics. Thus they are selected as the FS of the CH₂ dehydrogenation reaction.



Fig. 5. The optimized geometries of coadsorbed CH_x (x = 0-3) and H on NiCo (111).

According to the configurations of CH₂ at FCC-1 and FS, five possible reaction paths (FCC-1 \rightarrow Modes **1**, **2**, **3**, **4**, **5**) are conceived for CH₂ dehydrogenation. The geometries and parameters of all possible transition states are present in Fig. 6. The energy data in Table 2 clearly show that the Paths **3** and **4** is more favorable kinetically. In the transition state TS3-3, the rupturing C–H bond is increased to 1.588 Å, the forming H–Co bond is shortened to 1.526 Å. This reaction is exothermic by 0.16 eV and needs to overcome a low energy barrier of 0.34 eV which is approximately equal to that (0.37 eV) on pure Ni (1 1 1).

3.2.4. $CH \rightarrow C+H$

As shown in Fig. 5, the coadsorption of C and H has more or less interaction compared to the sum of individual adsorption energies. All coadsorption configurations are considered as the FS of the CH dehydrogenation reaction.

Similar to above paths of CH_x dissociation, five possible paths (FCC-1 \rightarrow Modes **1**, **2**, **3**, **4**, **5**) are designed for CH dehydrogenation.

The geometries and parameters of all possible transition states are present in Fig. 6. One can obtain that the Paths **3** and **4** have the approximate reaction barrier and they are more favorable kinetically from Table 2. In transition state TS4-3, the breaking C–H bond is elongated to 1.664 Å, and the forming H–Co bond is 1.523 Å. This reaction is endothermic by 0.73 eV and has an energy barrier of 1.26 eV, which is lower than that (1.36 eV) on pure Ni (111). Therefore, the incorporation of Co into the Ni crystal accelerates the dissociation of CH.

3.2.5. Energetics of dissociation CH₄

According to reaction barriers (E_a) and reaction enthalpies $(\Delta H(c) \text{ and } \Delta H(s))$ of successive dehydrogenation of CH₄ on NiCo (111) and Ni (111), we plot the optimal potential energy surface, as displayed in Fig. 7. For each dehydrogenation step, the initial state is taken as a CH_x (x = 1-4) species, and the final state is CH_{x-1} (x = 1-4) species plus one coadsorbed H atom at the same unit cell and adsorbed (4-x)H atoms at infinite distance at



Fig. 5. (Continued)

stable FCC-1 site $[CH_{x-1}(x=1-4)/H$, and $CH_{x-1}(x=1-4)+(4-x)H]$. The energy of $CH_{x-1}(x=1-4)$ plus (4-x) H atoms at infinite distance $[CH_{x-1}(x=1-4)+(4-x)H]$ is consider to be the starting point for the following step.

The barriers of the first and fourth dehydrogenation steps are very close on NiCo $(1\ 1\ 1)$ from the Table 2, but the absolute energy of TS1-5 is found to be higher from Fig. 7, so one can conclude that the first step of CH₄ dissociation into CH₃ and H is the ratedetermining step in the reaction of CH₄ dissociation on NiCo $(1\ 1\ 1)$. However, it is clear that the rate-determining step is the reaction of CH dissociation on Ni (111), which is slightly higher by 0.07 eV than that on NiCo (111).

Nørskov and co-workers [19] obtained that alloying Ni surface with Au atoms leads to increase of dissociation barrier of CH_4 into CH_3 and H which is the rate-limiting step in the steam-reforming process on Ni surface, and resist the carbon formation. Conversely, addition Co to Ni crystal causes the decrease of dissociation barrier of CH_4 into CH_3 and H, so we can conclude that alloying Ni crystal with Co atoms also cannot block the carbon formation, that is, carbon is easy to form on NiCo (1 1 1).

Table 2

The reaction barriers (E_a , eV), reaction enthalpies ($\Delta H(c)$ and $\Delta H(s)$, eV) of successive dehydrogenation of CH₄ on NiCo (111).

Reaction path		Ea	$\Delta H(c)$	$\Delta H(s)$
$CH_4 \rightarrow CH_3 + H$	$CH_4(@Ni T site) \rightarrow TS1-1 \rightarrow Mode 1$	1.40	0.21	0.05
	$CH_4(@Ni T site) \rightarrow TS1-2 \rightarrow Mode 2$	1.42	0.26	
	$CH_4(@Co T site) \rightarrow TS1-3 \rightarrow Mode 3$	1.30	0.27	
	$CH_4(@Co T site) \rightarrow TS1-4 \rightarrow Mode 4$	1.30	0.21	
	$CH_4(@Co T site) \rightarrow TS1-5 \rightarrow Mode 5$	1.29	0.26	
$CH_3 \rightarrow CH_2 + H$	$FCC-1 \rightarrow TS2-1 \rightarrow Mode 1$	0.84	0.21	0.21
	$FCC-1 \rightarrow TS2-2 \rightarrow Mode 2$	0.86	0.36	
	FCC-1 \rightarrow TS2-3 \rightarrow Mode 3	0.76	0.25	0.15
	FCC-1 \rightarrow TS2-4 \rightarrow Mode 4	0.77	0.22	
	$FCC-1 \rightarrow TS2-5 \rightarrow Mode 5$	0.77	0.25	
$CH_2 \rightarrow CH + H$	$FCC-1 \rightarrow TS3-1 \rightarrow Mode 1$	0.43	-0.34	-0.22
	$FCC-1 \rightarrow TS3-2 \rightarrow Mode 2$	0.46	-0.17	
	$FCC-1 \rightarrow TS3-3 \rightarrow Mode 3$	0.34	-0.16	-0.15
	$FCC-1 \rightarrow TS3-4 \rightarrow Mode 4$	0.36	-0.28	
	$FCC-1 \rightarrow TS3-5 \rightarrow Mode 5$	0.40	-0.09	
$CH \rightarrow C + H$	$FCC-1 \rightarrow TS4-1 \rightarrow Mode 1$	1.51	0.58	0.64
	$FCC-1 \rightarrow TS4-2 \rightarrow Mode 2$	1.46	0.82	
	FCC-1 \rightarrow TS4-3 \rightarrow Mode 3	1.26	0.73	
	$FCC-1 \rightarrow TS4-4 \rightarrow Mode 4$	1.29	0.58	
	$FCC-1 \rightarrow TS4-5 \rightarrow Mode 5$	1.34	0.82	



Fig. 6. Optimized structures of the transition states of CH₄ sequence dissociation on NiCo (111).



Fig. 7. Potential energy surface of CH₄ dissociation on Ni (111) and NiCo (111) [CH_x/H (x = 0-3) denotes the co-adsorbed CH_x and H, CH_x + H denotes the adsorbed CH_x and H separately, CH₄ (g) denotes the free CH₄ molecule, respectively].

4. Conclusion

In this work, we conduct a DFT-based computational study on the adsorption and dissociation of CH_x on NiCo (111) bimetallic alloy model, and compare the results with those on pure Ni (111). DFT calculations show that the preferred site on NiCo (111) is consistent with those on pure Ni (111). Like those on pure Ni (111), CH_x and H prefer to adsorb on threefold hollow site on NiCo (111). Strictly speaking, CH_x (x = 1-3) and H prefer to bond with two Co atoms and one Ni atom at FCC-1 site, C prefer to bond with two Co atoms and one Ni atom at HCP-1 site. However, the change trend of the adsorption energies is different on NiCo (111) compared with that on pure Ni (111). It is less negative for CH and C on NiCo (111) than those on pure Ni (111), while it is more negative for CH₃ adsorption on NiCo (111), while it wo surfaces.

On the basis of the coadsorption of CH_x and H, the dissociation of CH_x (x = 1-4) is investigated. The results show that dissociation of CH₄ is favorable on top of Co atom than that on top of Ni, and the reaction barrier is almost not sensitive to the share way of coadsorbed species, but sensitive to the share atom. The activation energy in the first step of CH₄ dissociation is increased by 0.11 eV on NiCo (111) compared to that in corresponding step on pure Ni (111), while that in the last step is decreased by 0.10 eV. In addition, the activation energies in the second and the third steps are almost invariable on the two surfaces. The ratedetermining step for CH₄ dissociation is considered as the first step of dehydrogenation on NiCo (111), while it is the fourth step of dehydrogenation on Ni (111). Furthermore, the activation barrier in rate-determining step is slightly higher by 0.07 eV on Ni (111) than that on NiCo (111). Therefore, one can believe that carbon is easy to form on NiCo (111) although the adsorption energy of C is slightly decreased compared to that on Ni (111).

It is necessary to point out that our results are not in line with the above experimental results, suggesting that it is indispensable to consider other factors effect on reaction.

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