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Theoretical study on the dissociative adsorption of CH₄ on Pd-doped Ni surfaces

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ABSTRACT

Density functional theory (DFT) was employed to predict the most stable structure of Pd-doped Ni(111), Ni(100), and Ni(211) surfaces, and the activity for CH₄ dissociation on pure and Pd-doped Ni surfaces. We predict that the thermodynamically most stable structures are the surface-doped Pd/Ni surfaces, where a surface Ni atom is replaced by a Pd atom; subsurface-doped Pd/Ni surfaces are thermodynamically unstable. Of the surface-adsorbed Pd/Ni surfaces, only the Pd/Ni(211) surface is thermodynamically stable. From the calculated adsorption energies of CH₄ dissociation intermediates (CH₄, CH₃, CH, C and H) on surface-doped Pd/Ni surfaces, we find Pd-doping to reduce the adsorption energy for all species except for CH₄. In addition, from the calculated activation barriers for CH₄ and CH dissociations, we predict CH₄ and CH to dissociate predominately on Ni(211) and Pd/Ni(211) step surfaces, followed by the broad Ni(100) and Pd/Ni(100) surfaces. Pd-doping raises the activation barriers for CH₄ and CH dissociations. For the most active Ni(211) surface, Pd-doping causes the CH dissociation step to have a higher activation barrier than the CH₄ dissociation step, which changes the rate limiting step, and helps reduce carbon deposition.

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1. Introduction

Because of global climate change, shrinking fossil fuel reserves, and climbing oil prices, energy has become a major worldwide concern in recent years. According to a February 2012 forecast made by British Petroleum (BP) in the “BP2030 World Energy Outlook” (2012: BP Energy Outlook 2030), natural gas will be the fossil fuel with the fastest worldwide growth in consumption from now until 2030. By then, Asia is predicted to have the largest natural gas production and consumption growth, with 56% of this growth occurring in China. China has relatively large reserves of natural gas and shale gas. With the large uncertainty in worldwide energy supply, it is of

strategic importance to develop processes for the efficient utilization of carbon resources such as natural gas.

In recent years, syngas production by dry methane reforming (DMR) has received wide interest as an efficient process for methane utilization [1,2]. It not only efficiently utilizes the greenhouse gas CO₂, but also yields syngas with a H₂/CO ratio of ~1, which is the ideal feedstock for Fischer–Tropsch and carbonylation reactions [3]. Over the past two decades, a series of precious metals and non-precious metals have been investigated as catalysts in DMR reactions [1,3–18]. At present, Ni-based catalysts are considered to be the most promising catalysts for commercialization because of their good activity and selectivity, and their relatively low price and availability.

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[2,4,19–21] However, these catalysts suffer from deactivation from coking, which is the main factor preventing their commercialization. Thus, significant efforts have been made to improve Ni-based catalysts to prevent coking in reforming reactions, and detailed investigation of the reaction mechanisms can aid design of novel catalysts and optimization of reaction conditions. Recent research showed that introducing small amounts of precious metals into Ni-based catalysts could effectively reduce coking and enhance catalyst activity and stability [6,11,12,22–34]. For instance, Besenbacher et al. [22] and Molenbroek et al. [23] found that the addition of a small amount of Au into the Ni catalyst (hereafter termed Au/Ni) can effectively reduce coking. Experiments also confirmed that Pt/Ni bimetallic catalysts prevent coking [12,35]. Besenbacher et al. [31] used a variety of spectroscopic techniques to systematically study the Pd/Ni catalyst's DMR performance. They found that the catalytic performance of the Pd/Ni bimetallic system depends on the catalyst support, and the bimetallic system displayed superior activity to pure Ni or Pd catalysts. With a reaction temperature of 700 °C, a Ni:Pd ratio of 4, and ZrO₂-La₂O₃ as the support, the conversion rates for CO₂ and CH₄ reached 78% and 73%, respectively, and the yields of CO and H₂ reached 57% and 59%.

Although a number of experimental and theoretical studies [7,19,22–24,36] investigated the coking mechanism on the Ni catalyst surface, there remain many unresolved issues. Because of experimental limitations, it is very difficult to elucidate details of the coking mechanism at the atomic level. Theoretical calculations, especially those using density functional theory (DFT), have contributed significantly to the elucidation of the structures of active centers on catalyst surfaces and microscopic reaction mechanisms [22,23], as well as to the investigation of the coking reduction mechanism on Au/Ni catalysts [36]. It was determined that the reaction barrier of the rate limiting step in CH₄ dissociation on the Au/Ni catalyst surface was higher than that on the pure Ni surface by 0.41 eV, which can effectively prevent coking.

To our knowledge, the Pd/Ni bimetallic catalyst surface structure and the CH₄ dissociation mechanism on this catalyst surface have not been previously reported. We used DFT methods and a periodic slab model to investigate the dissociation of CH₄ on different facets of the Pd/Ni catalyst surface. We analyzed the electronic structures of the thermodynamically most stable Pd/Ni catalyst surface alloy structures, and studied the kinetic effects of Pd doping on CH₄ and CH dissociations to form CH₃ and C, respectively, on the Ni catalyst surface. We chose these two elementary reactions because previous theoretical work [36] indicated that CH₄ dissociation is rate limiting on Au/Ni catalysts, and that dissociation of CH to form C is rate limiting on the pure Ni catalyst. By studying these two reactions, we hope to provide fundamental knowledge of the coking process on the Ni catalyst surface and to guide the development of novel catalysts.

2. Computational details

2.1. Computational models

We studied the (111) and (100) flat catalyst surfaces and the (211) common step surface. For the flat Pd/Ni surfaces, the model was obtained from the relevant pure Ni surface. Fig. 1 presents the cell structure of the different Pd/Ni surfaces. Three types of Pd-doped structures were investigated. In the first type (Fig. 1, 1a–c), a surface Ni atom (Ni-1st) on the flat surface (or a Ni atom at the step for the step surface) was replaced by a Pd atom. In the second Pd-doped structure (Fig. 1, 2a–c), Pd replaces subsurface Ni atoms (Ni-2nd). Finally, in the third type of structure (Fig. 1, 3a–c), Pd is adsorbed on top of the flat surface or the step corner. Ni atoms in the third layer are referred to Ni-3rd.

2.2. Computational methods

All calculations were carried out at the DFT level with the Vienna ab initio simulation package (VASP) [37, 38]. We used the Perdew-Burke-Ernzerhof (PBE) [39] exchange-correlation functional in the generalized gradient approximation (GGA) and the all electron projector-augmented wave (PAW) potential [40]. The cutoff energy for the plane wave basis set was 400 eV. The Brillouin zone was sampled with the Monkhorst-Pack k-point grid [41]. A five-layer p(2×2) supercell model was used to simulate the (111) and (100) surfaces, where one surface or subsurface Ni atom was replaced with one Pd atom or one Pd atom was adsorbed on the surface to simulate a 0.25 monolayer (ML) coverage. For the (211) surface, a five-layer p(2×1) supercell was used, where one Ni atom was replaced by one Pd atom or one Pd atom was adsorbed to simulate a 0.5 ML coverage. The k-point grids used for the (111), (100), and (211) surfaces were (4×4×1), (4×4×1), and (4×5×1), respectively. A 1.5 nm vacuum region was used between slabs to ensure intermolecular interaction between the slabs was negligible. Adsorbates were only placed on one side of the slab, and the dipole correction was applied to eliminate interactions between slabs in the z direction. During structural optimization, the top three layers of atoms and the adsorbates were relaxed to reduce the force on each atom to below 0.2 eV/nm, while the other atoms were fixed. For isolated gas phase species, a unit cell of the size 1.5×1.525×1.55 nm³ was used, where the isolated species was placed at the center of the cell along the z direction. One k-point was used to sample the Brillouin zone and spin correction was applied. Because Ni is ferromagnetic, spin polarization was applied for all calculations. Test calculations showed that using thicker slab models and denser k-point grids only minimally affected the obtained adsorption energies, and had even less influence on the reaction barriers. Thus, the parameters we chose for the calculations were reasonable.

The stability of the catalyst surface is determined by its formation energy:

$$\Delta H = E_{\text{Pd/Ni,slab}}^{\text{tot}} - E_{\text{Ni,slab}}^{\text{tot}} + E_{\text{Ni,atom}}^{\text{bulk}} - E_{\text{Pd,atom}}^{\text{bulk}} \quad (1)$$

where $E_{\text{Pd/Ni,slab}}^{\text{tot}}$ and $E_{\text{Ni,slab}}^{\text{tot}}$ are the total energies of the Pd/Ni and pure Ni surfaces, and $E_{\text{Ni,atom}}^{\text{bulk}}$ and $E_{\text{Pd,atom}}^{\text{bulk}}$ are the Ni and Pd atomic energies in the bulk phase. A negative value for ΔH indicates that the formation of the Pd/Ni surface from the corresponding Ni surface is exothermic and that the

Fig. 1. Top view and side view of Pd-doped Ni surface structures.

resulting Pd/Ni surface is relatively stable.

The adsorption energy for the adsorbates, E_{ads} , is calculated using:

$$E_{\text{ads}} = E_{\text{tot}} - E_{\text{slab}} - E_{\text{gas}} \quad (2)$$

where E_{tot} , E_{slab} and E_{gas} are the total energy of the system with the adsorbate, the energy of the metal surface, and the energy of the isolated adsorbate in the gas phase, respectively. A negative value for the adsorption energy indicates that the adsorption process is exothermic.

The transition states for the reactions were optimized by the Force Reversed Method (FRM) [42]. For the reaction $\text{AB} \rightarrow \text{A} + \text{B}$, the reaction barrier (E_{a}) and reaction energy (E_{R}) were calculated using:

$$E_{\text{a}} = E_{\text{TS}} - E_{\text{AB}} \quad (3)$$

$$E_{\text{R}} = E_{\text{A}} + E_{\text{B}} - E_{\text{AB}} - E_{\text{slab}} \quad (4)$$

where E_{TS} , E_{AB} , E_{A} and E_{B} are the total energy of the transition state, and the total energies of the surfaces with AB,

A, and B adsorbed, respectively. Thus, the reaction energy as defined above is for an infinitely large surface, with infinitely low surface coverage.

3. Results and discussion

3.1. Pd/Ni surface stability

Tables 1 and 2 present the formation energies and structural parameters for the three types of Pd/Ni(111), (100), and (211) surfaces. For comparison, Table 3 presents the structural parameters for the pure Ni surfaces.

We first compare the surface and subsurface Pd-doped Ni surfaces. The formation of surface Pd-doped Ni surface is always exothermic, whereas the formation of subsurface Pd-doped Ni surface is endothermic (Tables 1 and 2). The atomic radius of Pd is much larger than Ni, so subsurface Pd

Table 1

Calculated formation energies (ΔH , eV) and geometric parameters of Pd/Ni(111) and Pd/Ni(100) surfaces. $d_{\text{Ni-Ni}}^{\text{inner-11}}$ and $d_{\text{Ni-Ni}}^{\text{inter-12}}$ are the distances between the two nearest Ni atoms of the same layer and of the neighboring layers, respectively.

Type	ΔH (eV)	$d_{\text{Ni-Ni}}^{\text{inner-11}}$ (nm)	$d_{\text{Ni-Ni}}^{\text{inter-12}}$ (nm)
Pd/Ni(111)			
Surface doping	-0.23	0.249 _{×2} , 0.250 _{×2}	0.247 _{×3}
Subsurface doping	0.32	0.249 _{×2} , 0.250 _{×2}	0.248, 0.253 _{×2}
Surface adsorption	0.60	0.254, 0.244	0.247 _{×2} , 2.455
Pd/Ni(100)			
Surface doping	-0.33	0.249 _{×4}	0.246 _{×4}
Subsurface doping	0.27	0.249 _{×4}	0.249 _{×4}
Surface adsorption	0.19	0.245, 0.254	0.244, 0.248, 0.247 _{×2}

Table 2

Calculated formation energies (ΔH , eV) and geometric parameters of the Pd/Ni(211) surfaces. $d_{\text{Ni-Ni}}^{\text{step-11}}$ is the distance between two nearest Ni atoms near the step.

Type	ΔH (eV)	$d_{\text{Ni-Ni}}^{\text{step-11}}$ (nm)	$d_{\text{Ni-Ni}}^{\text{inner-11}}$ (nm)	$d_{\text{Ni-Ni}}^{\text{inter-12}}$ (nm)
Surface doping	-0.40	—	0.243 _{×2}	0.242 _{×2}
Subsurface doping	0.31	0.243, 0.256	0.249, 0.243	0.246 _{×2}
Surface adsorption	-0.19	0.251, 0.248	0.243 _{×2}	0.244, 0.243

insertion into the Ni surface introduces a much greater stress than when inserted in the exterior surface layer, which causes the subsurface-doped system to further expand, increasing its energy. This is reflected in the Ni-Ni bond distances between layers. For example, for the subsurface Pd-doped Ni(111) surface, the closest Ni-Ni bond lengths between two layers were calculated to be 0.248, 0.253, and 0.253 nm, which are longer than those for the surface Pd-doped Ni(111) surface of 0.247 nm. The same trend is seen for the Pd/Ni(100) and Pd/Ni(211) surfaces, where the closest Ni-Ni bond lengths were ~0.004 nm longer than those in the subsurface-doped Ni surfaces.

For the surface-adsorbed Pd-doped Ni surfaces, formation of the Pd/Ni(111) and Pd/Ni(100) surfaces is endothermic by 0.60 and 0.19 eV, whereas the Pd/Ni(211) surface formation is exothermic by -0.19 eV. More energy is required to form the surface-adsorbed Pd/Ni(111) surface than the Pd/Ni(100) surface because the Ni(100) surface structure is more open than the Ni(111) surface and has a higher reactivity. Forming the surface-adsorbed Pd/Ni(211) surface is exothermic because the coordination number of the two Ni atoms at the step increases from 7 to 8, which makes the system more stable.

For the Pd-doped Ni system, and for the three types of Pd/Ni surfaces, the most readily formed doping structure is surface Pd doping, especially at the Pd/Ni step surface, which can also adsorb Pd. To understand the activity of the three

Table 3

Calculated geometric parameters of pure Ni(111), Ni(100), and Ni(211) surfaces.

Surface	$d_{\text{Ni-Ni}}^{\text{inner-11}}$ (nm)	$d_{\text{Ni-Ni}}^{\text{inter-12}}$ (nm)	$d_{\text{Ni-Ni}}^{\text{step-11}}$ (nm)
Ni(111)	0.249 _{×6}	0.244 _{×3}	—
Ni(100)	0.249 _{×4}	0.247 _{×4}	—
Ni(211)	0.249 _{×2}	0.245, 0.240 _{×2}	0.249 _{×2}

Fig. 2. Projected density of states for the surface Ni and Pd atom d orbitals for the Pd/Ni(111), Pd/Ni(100) and Pd/Ni(211) surfaces.

types of Pd/Ni surfaces, and the effect of surface Pd atoms on C–H bond activation, we calculated the projected density of states (PDOS) for the 3d orbitals (4d orbitals for Pd) of the Ni and Pd atoms at the surface and the step, (Fig. 2). The PDOS for the surface Ni 3d orbitals is shown in Fig. 2(a)–(c) for the surface Pd-doped Ni surfaces, while the surface Pd 4d orbital PDOS is shown in Fig. 2(d)–(f). The d-band centers [22] for the surface Ni and Pd atoms for the Pd/Ni(100) and Pd/Ni(211) surfaces all shift towards the Fermi level compared to those for the Pd/Ni(111) surface. In general, the closer the d-band center of the active metal component is to the Fermi level, the higher the metal component activity. Therefore, the relative positions of the d-band centers for the three surfaces indicate the order of their surface activity is Pd/Ni(111) < Pd/Ni(100) < Pd/Ni(211). However, as the most readily occurring metal catalyst surfaces are those with low indices, we studied the CH₄ dissociation process on all three surface Pd doped Ni surfaces.

3.2. CH_x and H adsorption on Pd/Ni surfaces

The energy and structure of adsorbed CH_x ($x = 4, 3, 1, 0$) and H species on low index Ni surfaces have been investigated both experimentally and theoretically [36,43–46]. For comparison, we calculated the most stable adsorption structures on the

Table 4

Adsorption site and adsorption energy (eV) for CH_x and H species on Ni(111), Ni(100), and Ni(211) surfaces.

Adsorbate	Ni(111)		Ni(100)		Ni(211)	
	Site	E_{ads} (eV)	Site	E_{ads} (eV)	Site	E_{ads} (eV)
CH ₄	top	-0.01	top	-0.01	top-step-edge	-0.02
CH ₃	fcc	-1.88	bridge	-1.81	bri-step-edge	-2.23
CH	hcp	-6.47	hollow	-7.05	step-corner	-6.79
C	hcp	-6.86	hollow	-8.19	step-corner	-7.85
H	fcc	-2.88	hollow	-2.83	near-edge-hcp	-2.89

Ni(111), Ni(100), and Ni(211) surfaces, and their adsorption sites and energies are given in Table 4. Our calculated adsorption energies for different adsorbates are in good agreement with those reported previously [46]. The most stable structures and their corresponding energies for CH_x and H adsorption on surface Pd doped Ni surfaces are shown in Fig. 3.

From Table 4, for all three pure Ni surfaces, CH_4 adsorbs at a top site with a low adsorption energy. This is because all the atoms in CH_4 are saturated in their coordinations, and the C–H bond has a low polarity. Thus, CH_4 shows only weak physisorption on Ni surfaces. Because its adsorption potential energy surface is quite flat, the differences in adsorption energies between the different adsorption sites are small for all Ni surfaces [44]. Except for CH_4 , the most stable adsorption site for all the CH_x and H species is either high coordination or near the step edge, and their adsorption strength follows the order $\text{CH}_4 \ll \text{CH}_3 < \text{H} \ll \text{CH} < \text{C}$. The differences in the adsorption energies of H on the three Ni surfaces are small (< 0.1 eV). The adsorption energies of CH_3 on Ni(111) and Ni(100) surfaces display small differences (< 0.1 eV). However, adsorption of C and CH on the Ni(100) surface is stronger than on the Ni(111) surface by 1.3 and 0.6 eV, respectively. Comparing the adsorption energies on the Ni(111) and Ni(211) surfaces, all species except for CH_4 and H adsorb more strongly on the step surface than on the closely packed surface. CH_3 is more strongly adsorbed on the step surface by ~ 0.4 eV than on Ni(111) and Ni(100) surfaces. CH and C adsorb more strongly on the step surface by ~ 0.3 and 1.0 eV, respectively, than on the Ni(111) surface, and are more weakly adsorbed on the Ni(100) surface by ~ 0.3 eV. These findings are consistent with the fact that coking generally first occurs at the step surface, which is also the active position for graphene growth [24,45,47].

As shown in Fig. 3, all species except CH_4 adsorb at three-fold, four-fold, and step sites on Pd-doped surfaces (similar absorption behavior occurs on pure Ni surfaces). The adsorption energies for all species except CH_4 on Pd-doped surfaces are weaker than on pure Ni surfaces. For CH_4 , the most stable adsorption site is the Pd atom top site for all three Pd/Ni surfaces; the weak absorption energy does not significantly vary between these surfaces.

There are two types of stable adsorption sites for CH_x ($x = 3, 1$, and 0) and H on the Pd/Ni(111) surfaces. One is the hcp(3Ni) site formed by three Ni atoms, and the other is the fcc(2Ni-1Pd) site formed with two Ni and one Pd atoms. CH_x preferably adsorbs on the hcp(3Ni) site, whereas H preferably adsorbs on the fcc(2Ni-1Pd) site. Compared to their adsorption energies on the pure Ni(111) surface, these species bind more weakly to the Pd/Ni(111) surface. Among them, the change in the adsorption energy of CH_3 is the largest (0.23 eV), whereas that for the other species is similar (~ 0.13 eV).

There are also two types of stable adsorption sites for CH_x and H on the Pd/Ni(100) surface. One is the hollow(3Ni-1Pd) site formed by three Ni and one Pd atoms, and the other is the bridge(2Ni) site formed with two Ni atoms. The most stable adsorption site for CH_3 on the Pd/Ni(100) surface is the bridge(2Ni) site, similar to that on the pure Ni(100) surface, while the most stable site for the other three species is the hollow(3Ni-1Pd) site. Compared with the changes in the adsorption energies upon Pd doping for the Ni(111) surface, it has different effects for the Ni(100) surface in that the change in the CH_3 adsorption energy becomes the smallest by ~ 0.06 eV, whereas large differences of 0.71 and 0.47 eV were predicted for the CH and C adsorption energies on the Ni(100) surface. Thus, Pd-doped Ni(100) surfaces have significant effects on

Fig. 3. The most stable structures and adsorption energies of CH_x ($x = 4, 3, 1$, and 0) and H on Pd-doped Ni(111), Ni(100), and Ni(211) surfaces.

C–H bond activation.

The most stable adsorption site for CH and C on the Pd/Ni(211) surface is the step-corner(3Ni-1Pd) site formed by three Ni and one Pd atoms. The differences in the adsorption energies for CH and C from the pure Ni(211) surface are similar, 0.33 and 0.36 eV, respectively. The most stable adsorption site for CH₃ on the Pd/Ni(211) surface is the bri-step-edge (1Ni-1Pd) site formed by one Ni and one Pd atom, and its adsorption is 0.26 eV weaker than that on the pure Ni(211) surface. The most stable adsorption site for H is the near-edge-hcp(2Ni-1Pd) site formed by two Ni and one Pd atoms, and its adsorption is 0.11 eV weaker than that on the pure Ni(211) surface, which represents the smallest change among all the species except for CH₄.

3.3. CH₄ and CH dissociation on the Pd/Ni Surfaces

To investigate the influence of Pd doping on the Ni-catalyzed CH₄ dissociation reactions, we calculated reaction barriers for C–H bond dissociation on the pure and Pd-doped Ni(111), Ni(100), and Ni(211) surfaces. The energetics and structural parameters for the transition states for CH_x dissociation on each surface are given in Table 5, and the corresponding reaction coordinate diagrams are shown in Fig. 4.

Table 5

Energetics and geometric parameters of the transition states for CH₄ and CH dehydrogenation on pure and Pd-doped Ni(111), Ni(100), Ni(211) surfaces.

Surfaces	CH ₄ → CH ₃ + H			CH → C + H		
	<i>E_a</i> (eV)	<i>E_R</i> (eV)	<i>d_{C-H}</i> (nm)	<i>E_a</i> (eV)	<i>E_R</i> (eV)	<i>d_{C-H}</i> (nm)
Pd/Ni(111)	1.06	0.38	0.159	1.28	0.59	0.161
Pd/Ni(100)	0.94	0.27	0.151	0.74	−0.03	0.150
Pd/Ni(211)	0.62	0.06	0.159	0.66	−0.09	0.148
Ni(111)	0.92	0.02	0.156	1.28	0.46	0.143
Ni(100)	0.83	0.16	0.161	0.52	−0.25	0.150
Ni(211)	0.53	−0.32	0.166	0.51	−0.22	0.146

In the transition state for CH₄ dissociation reaction on pure Ni surfaces, CH₃ is adsorbed on a top site above Ni, and H is adsorbed at the bridge site. In the transition state on the Pd/Ni surfaces, CH₃ is adsorbed on the top site above Pd, and H is still adsorbed at the bridge site, as observed in Fig. 4. The reaction barriers for CH₄ dissociation on the Pd/Ni surfaces are higher than those on the pure Ni surfaces, and the increase of ~0.1 eV is similar for the different surfaces (Table 5). From the reaction barriers in Table 5, the Ni(211) surface would be the most active for catalyzing the CH₄ dissociation reaction, with the Ni(111) surface the least active. Although Pd doping lowers the activity of all the Ni surfaces, the changes in the reaction barriers are similar, so the relative activities of the different Pd/Ni

Fig. 4. Reaction coordinate diagrams and transition state structures for CH₄ and CH dehydrogenation on the Pd/Ni(111), Pd/Ni(100), and Pd/Ni(211) surfaces.

surfaces remains the same, i.e. the stepped surface is the most active, and the closely packed surface is the least active.

In the transition state of the CH dissociation reaction, C locates at its most stable adsorption site, and H adsorbs at the bridge site. Comparing the reaction barriers for CH dissociation on the three surfaces, the catalytic activity follows the order of $\text{Ni}(111) \approx \text{Ni}(100) \ll \text{Ni}(211)$, and $\text{Pd}/\text{Ni}(111) < \text{Pd}/\text{Ni}(100) \ll \text{Pd}/\text{Ni}(211)$, i.e. the step surface also has the highest activity. The effects of Pd doping on the activity of the three Ni surfaces are different. Pd doping does not change the reaction barrier for CH dissociation on the Ni(111) surface, whereas it increases the reaction barrier on Ni(100) and Ni(211) surfaces by 0.22 and 0.15 eV, respectively.

We first compare the reaction barriers for the CH_4 and CH dissociation reactions on the different Ni surfaces. For the Ni(111) surface, the reaction barrier for the CH dissociation reaction is much higher than that for the CH_4 dissociation reaction, while the opposite is true for the Ni(100) surface. The reaction barriers for the CH_4 and CH dissociation reactions are similar for the Ni(211) surface. Thus the rate limiting steps for CH_4 dissociation on these surfaces are different. On the Ni(111) surface, CH dissociation is the rate limiting step, while on the Ni(100) surface, CH_4 dissociation is rate limiting. On the Ni(211) surface, there is no single rate limiting step.

Pd doping does not significantly alter the reaction barriers and the rate limiting step does not change for CH_4 dissociation on the Ni(111) and Ni(100) surfaces, but for the Ni(211) surface, the reaction barrier for CH dissociation increases more than that for CH_4 dissociation, making CH dissociation slower. As the reaction barriers for CH_3 and CH_2 dissociation are much lower than CH_4 and CH dissociation [36,43,44], we only studied CH_4 and CH dissociation. On the pure Ni(211) surface, after CH_4 loses the first H, coking can occur easily, but by introducing Pd, coking from CH dissociation becomes kinetically slower than CH_4 dissociation. Thus Pd doping slows down the rate of coking on the surface.

As shown in Table 5, for Ni(211) and Pd/Ni(211) surfaces, the highest reaction barriers for CH_4 and CH dissociation reactions are 0.53 and 0.66 eV, respectively, indicating that at relatively low temperatures CH_4 can easily dissociate at the step site. The highest reaction barrier for CH_4 and CH dissociation reactions is 1.28 eV on Ni(111) and Pd/Ni(111) surfaces, so the (211) surface has much higher activity than the (111) surface. However, as shown in Table 4 and Fig. 3, C adsorption on the (211) surface is stronger than that on the (111) surface, so coking should easily occur at the step surface, resulting in catalyst deactivation. Therefore, in the DMR reaction, the majority of the catalytic activity may not be due to the step surface, but instead may result from the relatively less active closed packed surface [45]. Thus, although the step surface is able to activate CH_4 at relatively low temperatures, the DMR reaction still requires high temperatures to proceed. Our calculated reaction barrier for the CH dissociation reaction on the Ni(111) surface (1.28 eV) is consistent with the reported literature value (1.42 eV) [46], considering the differences in the model and the pseudopotential used. Thus we conclude that our calculated reaction barriers are reliable.

Pd doping raises the reaction barrier of the rate limiting step for CH_4 dissociation on (211) and (100) surfaces, but not on the (111) surface. As discussed above, the closely packed surface could be the major contributor to the DMR reaction, and therefore our calculated results cannot prove that Pd doping will reduce the catalyst activity. On the other hand, as shown in Table 4 and Fig. 3, Pd doping does reduce the adsorption strength of the various C species, which slows down coking and catalyst deactivation; thus Pd doping may actually improve the catalyst activity, which is consistent with the experimental results of Steinhauer et al. [31].

4. Conclusions

We used density functional theory to study the most stable structure of the Pd/Ni surface and the effect of Pd doping on CH_4 dissociation on several low index Ni surfaces. For the Pd/Ni system, surface Pd-doped Ni structures are the most stable. Pd doping reduces the adsorption strength of the various intermediates in CH_4 dissociation (CH_3 , CH, C, H), and increases the reaction barriers for CH_4 and CH dissociation except for CH dissociation on the (111) surface. CH_4 prefers to dissociate at surface defects (Ni(211) and Pd/Ni(211)), followed by the more open Ni(100) and Pd/Ni(100) surfaces. The CH_4 dissociation reactivity on closely packed Ni(111) and Pd/Ni(111) surfaces is the lowest. Pd doping does not change the rate limiting step for CH_4 dissociation on Ni(111) and Ni(100) surfaces, but on the Ni(211) surface the CH dissociation has a higher barrier than CH_4 dissociation, and consequently reduces the possibility for coking.

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Graphical Abstract

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Theoretical study on the dissociative adsorption of CH₄ on Pd-doped Ni surfaces

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Periodic density functional theory calculations show that CH₄ and CH dissociate predominately on the Pd/Ni(211) step surface rather than the closely packed Pd/Ni(111) surface. For the most active Ni(211) surface, Pd-doping causes CH dissociation to have a higher activation barrier than CH₄ dissociation, which changes the rate limiting step, and helps reduce carbon deposition.

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Pd掺杂的Ni催化剂表面CH₄解离吸附的理论研究

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摘要: 使用密度泛函理论研究了Pd掺杂的Ni(111), Ni(100)和Ni(211)表面最稳定的结构, 同时考察了干净的和Pd掺杂的Ni表面催化CH₄解离反应的活性. 结果表明, 由Pd原子取代最外层Ni原子而形成的表面Pd掺杂的Ni表面在热力学上最为稳定, 亚表面Pd掺杂的Ni表面在热力学上都不稳定; 而对于表面Pd吸附的Ni表面, 只有Pd/Ni(211)表面是稳定的. 表面掺杂的Pd/Ni表面上CH₄解离中间体(CH₄, CH₃, CH, C, H)吸附能的计算结果表明, Pd的掺杂在不同程度上减弱了除CH₄之外各解离中间体的吸附能. 另外, CH₄和CH均优先在Ni(211)和Pd/Ni(211)台阶面上解离, 其次是在比较开阔的Ni(100)和Pd/Ni(100)表面上. Pd的掺杂不同程度上提高了CH₄和CH解离的能垒, 对于活性最高的Ni(211)面, Pd的掺杂使得CH脱氢的能垒较CH₄脱氢的高, 改变了其速率控制步骤, 从

而抑制了积碳的生成.

关键词: 甲烷重整; 镍催化剂; 钯掺杂; 积碳; 密度泛函理论

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1. 前言

随着全球气候的变化、化石资源的日趋减少及原油价格的持续上涨, 能源问题已经成为近年来全球普遍关注的焦点之一. 根据英国石油公司(BP)2012年2月发布的《BP2030世界能源展望》预测(2012: BP Energy Outlook 2030), 从现在到2030年期间天然气将是全球使用量增长最快的化石燃料, 届时, 亚洲将是世界最大的天然气生产和消费增长地区, 中国则占其消费增长的56%. 我国是天然气和煤层气相对丰富的国家, 在当今国际能源形势急剧动荡的情况下, 开发天然气等含碳资源的高效利用技术具有重要的战略意义.

近年来, 作为甲烷高效利用的过程, 甲烷干气重整(DMR)制合成气备受重视^[1,2]. 该反应不仅能有效地利用温室气体CO₂, 同时能获得H₂/CO比约为1的合成气, 后者正是费托合成及羰基合成的理想原料^[3]. 二十几年来, 人们研究了一系列贵金属和非贵金属催化剂上的DMR反应^[1,3–18]. 到目前为止, Ni基催化剂因其具有良好的活性和选择性, 便宜易得等特点而被看作是最可能商业化的催化剂^[2,4,19–21]; 但积碳失活是阻碍其商业化的最主要原因. 因此, 人们致力于对Ni基催化剂进行改性来提高重整催化剂的抗积碳性能, 而对其反应机理的详尽研究将有助于设计新型催化剂和优化反应条件. 近期的研究发现, 将少量的贵金属引入Ni基催化剂中可以有效地降低积碳的生成和获得更高的活性和稳定性^[6,11,12,22–34]. 比如, Besenbacher等^[22]和Molenbroek等^[23]研究发现, 将少量的Au引入Ni催化剂(Au/Ni)中能有效的抑制积碳; 实验也证实了Pt/Ni双金属催化剂也具有很好的抗积碳性能^[12,35]; Steinhauer等^[31]利用X射线衍射(XRD), 电感耦合等离子光谱(ICP), X射线光电子能谱(XPS)和透射电子显微镜(TEM)等手段系统地研究了Pd/Ni催化剂在DMR反应中的性能及其对载体和反应条件的依赖关系, 发现Pd/Ni双金属体系的催化性能极强地依赖于所使用的载体, 并较Ni或Pd催化剂具有更高的活性, 在反应温度为700 °C, Ni: Pd比为4, ZrO₂-La₂O₃为载体时, CO₂和CH₄转化率分别可达78%和73%, 同时,

CO和H₂的产率也分别达到57%和59%.

虽然Ni基催化剂表面积碳机理的有关实验和理论研究较多^[7,19,22–24,36], 但目前仍有很多悬而未决的问题. 由于实验工作的特殊性和实验探测手段的局限性, 在实验上很难在原子层次上阐明积碳过程. 随着计算机技术的发展, 理论计算尤其是密度泛函方法(DFT)在揭示催化剂表面活性中心的结构、微观反应机理等方面发挥了巨大的作用^[22,23]. 理论研究表明, 由于在Au/Ni合金表面上CH₄解离过程的速控步的能垒要比纯金属Ni表面高出0.41 eV, 从而有效地抑制了积碳的生成^[36].

迄今为止, Pd/Ni双金属体系的表面结构以及CH₄在该催化剂表面的解离过程鲜见报道. 本文采用DFT方法并结合周期平板模型来研究CH₄在Pd/Ni体系不同活性表面的解离. 即首先从热力学上分析Pd/Ni最可能的表面合金形式, 并分析其表面的电子结构; 然后从动力学上确定Pd的掺杂对Ni催化剂表面CH₄第一步脱氢形成CH₃的过程和最后一步由CH脱氢形成C的过程的影响. Au/Ni体系的理论研究表明, 甲烷解离的速控步是第一步, 即CH₄脱氢形成CH₃的过程, 而在纯Ni催化剂表面上则是最后一步, 即CH脱氢形成C的过程^[36]. 因此上述两个问题的研究进一步提供Ni基催化剂表面积碳过程的基础认知和信息, 为新型催化剂的开发提供理论指导.

2. 模型的选取和计算方法

2.1. 模型的选取

本文研究了(111)和(100)这两个平整的催化剂表面以及(211)这一常见的台阶面. 对于平整Pd/Ni表面, 其模型均可以由纯金属Ni的相应表面获得. 图1给出了各种Pd/Ni表面的晶胞模型. 第一种结构是以Pd原子替代纯Ni相应的平整表面最外层的或台阶表面台阶处的Ni原子(Ni-1st), 这种Pd/Ni(111), Pd/Ni(100)和Pd/Ni(211)表面分别如图1的1a, 1b和1c所示. 第二种结构是以Pd原子替代亚层的Ni原子(Ni-2nd), 这种Pd/Ni(111)、Pd/Ni(100)和Pd/Ni(211)表面分别如图1的2a, 2b和2c所示; 第三种结构是将Pd原子吸附于平整的表面与台阶边缘, 这种Pd/Ni(111), Pd/Ni(100)和Pd/Ni(211)表面分别如图1的3a,

3b和3c所示. 在图1中第三层原子用Ni-3rd表示.

2.2. 计算方法

本文所有计算都是在以DFT为基础的第一性原理分子动力学软件包VASP (Vienna ab initio simulation package)上完成的^[37,38], 计算中采用了GGA-PBE^[39]类型的交换相关泛函及全电子类型的PAW势^[40]. 平面波基组的截断能为400 eV. 总能计算中布里渊区k点积分, 采用Monkhorst-Pack特别点方法^[41]进行k点空间取样. (111)和(100)表面的计算采用p(2 × 2)超晶胞的五层平板模型, 用一个Pd原子替代一个Ni原子或者加入一个Pd原子模拟1/4的单层覆盖度; 而(211)表面的计算则采用p(2 × 1)超晶胞的五层平板模型, 用一个Pd原子替代一个Ni原子, 或者加入一个Pd原子模拟1/2的单层覆盖度. (111), (100)和(211)晶面使用的k点分别为(4×4×1), (4×4×1)和(4×5×1). 表面的模拟均选用1.5 nm真空间隔, 以确保平板间的分子间相互作用足够小. 只在金属平板模型的一端放置吸附质分子, 采用偶极校正以消除Z方向上模型之间的相互作用. 在结构优化时, 金属模型表面三层原子及吸附分子弛豫, 直至每个原子受力小于0.2 eV/nm, 其它原子固定不动. 对于孤立的气相自由基分子, 采用1.5×1.525×1.55 nm³的正交盒子, 自由基位于盒子的中心且沿z轴方向, 用1个k点取样并考虑了自旋修正. 由于Ni是有磁性的金属, 所有结构优化和反应过程均考虑了自旋极化. 另外, 本文还考察了更厚的平板模型和更密的k点对所研究的吸附物种吸附能的影响. 有关吸附能的计算结果表明, 更厚的平板模型和更密的k点对吸附能的影响非常小, 对反应能垒的影响更小, 所以我们选取的计算参数是合理的.

催化剂表面的稳定性可以由其形成热来判断:

$$\Delta H = E_{\text{Pd/Ni,slab}}^{\text{tot}} - E_{\text{Ni,slab}}^{\text{tot}} + E_{\text{Ni,atom}}^{\text{bulk}} - E_{\text{Pd,atom}}^{\text{bulk}} \quad (1)$$

其中 $E_{\text{Pd/Ni,slab}}^{\text{tot}}$ 和 $E_{\text{Ni,slab}}^{\text{tot}}$ 分别代表新形成的Pd/Ni表面和纯金属Ni相应表面的总能, $E_{\text{Ni,atom}}^{\text{bulk}}$ 和 $E_{\text{Pd,atom}}^{\text{bulk}}$ 分别代表体相Ni和Pd单个原子的总能. ΔH 数值的正(负)反映了新形成的催化剂表面相对于纯金属Ni表面的吸(放)热情况或者不稳定性(稳定性).

反应物吸附能 E_{ads} 的计算如下:

$$E_{\text{ads}} = E_{\text{tot}} - E_{\text{slab}} - E_{\text{gas}} \quad (2)$$

其中 E_{tot} , E_{slab} 和 E_{gas} 分别代表吸附后体系的总能、干净金属表面的能量以及气相吸附物种在气相中的能量. 吸附能的正负分别代表了吸附过程的吸放热.

本文对反应过渡态的搜寻采用力之反向法(FRM)计算^[42]. 解离反应 $\text{AB} \rightarrow \text{A} + \text{B}$ 能垒 E_{a} 和反应热 E_{R} 的计

算如下:

$$E_{\text{a}} = E_{\text{TS}} - E_{\text{AB}} \quad (3)$$

$$E_{\text{R}} = E_{\text{A}} + E_{\text{B}} - E_{\text{AB}} - E_{\text{slab}} \quad (4)$$

其中 E_{TS} , E_{AB} , E_{A} 和 E_{B} 分别代表反应体系过渡态的总能, 反应物AB吸附时体系的总能以及产物A和B的单独吸附体系的总能. 因本文所计算的反应热是对应于一个无限大的表面而言的, 换句话说, 是在一个覆盖度非常低的表面上的反应热.

3. 结果与讨论

3.1. Pd/Ni表面稳定性分析

表1和表2分别列出了形成三种类型Pd/Ni(111), (100)和(211)表面的形成热和结构参数. 同时, 为了对比合金形成前后表面结构的变化, 表3还给出了未掺杂Pd时纯金属Ni各个表面的结构参数.

首先, 我们对比了最外层掺杂和亚层掺杂Pd原子的情况. 由表可见, 不论是平整的最密堆积(111)表面、更为开阔的(100)表面, 或是具有台阶缺陷的(211)面, 形成外层Pd掺杂的Pd/Ni表面均是放热反应, 而形成亚层Pd掺杂Pd/Ni表面均是吸热反应. 这是由于Pd原子半径要比Ni原子大得多. 将其嵌入到次表层中就需要承受比嵌入表层中更大的应力, 体系膨胀, 从而使得体系能量上升. 这也可以从层间Ni-Ni键长反映出来, 如次表层Pd嵌入的Pd/Ni(111)表面两层之间最邻近的Ni-Ni间键长分别为0.248, 0.253和0.253 nm, 比表层Pd嵌入的Pd/Ni(111)表面Ni-Ni间键长0.247 nm要长. Pd/Ni(100)和Pd/Ni(211)表面也出现这种情况, 层间最邻近Ni-Ni键长之间的差别约0.004 nm.

其次, 表面吸附Pd原子形成Pd/Ni(111)和Pd/Ni(100)表面是吸热反应(0.60和0.19 eV), 其中前者需要更多能量, 这是由于Ni(100)表面较Ni(111)表面更为开阔, 因而活性更高. 而形成表面Pd吸附的Pd/Ni(211)表面则是放热反应(-0.19 eV), 这是由于Pd的吸附使得台阶处两个Ni原子的配位数由原来的7变为8, 使体系更为稳定.

不难看出, 对于所考察的Pd掺杂的Pd/Ni体系的三种Pd/Ni表面而言, 最容易生成的表面掺杂形式是表层Pd掺杂, 尤其是表面Pd掺杂的Pd/Ni台阶面, 而且也可以形成表面Pd吸附的Pd/Ni台阶面. 为了深入了解三种类型Pd/Ni表面的活性, 以及解离过程中表面Pd原子对C-H键活化的影响, 本文还计算了表面和台阶处Ni, Pd原子相应的3d轨道投影态密度图(PDOS), 如图2所示. 其中2(a), 2(b), 2(c)分别给出了表面Pd掺杂的Pd/Ni(111),

Pd/Ni(100)和Pd/Ni(211)表面上Ni原子的3d轨道PDOS, 2(d), 2(e), 2(f)分别给出了相应的Pd原子的3d轨道PDOS. 可以看出, Pd/Ni(100)和Pd/Ni(211)表面Ni, Pd原子的d带中心位置相对于Pd/Ni(111)表面的d带中心^[22]都向费米能级偏移. 一般来说, 金属活性组份d带中心越接近费米能级, 金属的活性越高. 因此, 三个表面d带中心相对于费米能级的位置反映了三个表面活性顺序为Pd/Ni(111) < Pd/Ni(100) < Pd/Ni(211). 然而, 在反应过程中金属催化剂表面出现最多的是表面能较低的低指数面, 因此我们研究了这三种可能的表面Pd掺杂的Pd/Ni表面上CH₄解离过程.

3.2. CH_x和H在Pd/Ni(111), Pd/Ni(100)和Pd/Ni(211)表面上的吸附

人们对CH_x ($x = 4, 3, 1, 0$)和H在Ni的几个常见低指数表面的吸附能和吸附结构已在实验和理论上进行了详细的研究^[36,43–46]. 为了对比方便, 本文也对CH_x在Ni(111), Ni(100), Ni(211)表面最稳定吸附位进行了计算, 其最稳定吸附位及吸附能数据列于表4中, 各个物种的吸附能与文献[46]结果基本一致. CH_x和H在表面Pd掺杂的Pd/Ni的各个表面上的最稳定吸附结构及吸附能则如图3所示.

由表4可见, 在三种干净的Ni表面上, CH₄均以顶位吸附, 且吸附能极低. 这是由于CH₄中所有原子配位饱和, 且C–H键极性很小, 以物理方式微弱地吸附在Ni表面上, 它在Ni各个表面的吸附势能面均很平缓, 各个吸附位的吸附能差别也很小, 与文献[44]结果一致. 除CH₄之外, 其它CH_x和H物种最稳定的吸附位置均是高配位的或者台阶边缘, 其吸附能基本上呈现CH₄ << CH₃ < H << CH < C的趋势. 三种Ni表面上H的吸附能差别最小(<0.1 eV). Ni(111)和Ni(100)表面上CH₃的吸附能差别也很小(<0.1 eV), 而C和CH在Ni(100)表面上的吸附能比它们在Ni(111)表面上的分别要高出1.3和0.6 eV. 通过对比Ni(111)和Ni(211)表面上的吸附能发现, 除CH₄和H之外各物种在台阶面的吸附均比密堆面强. CH₃在台阶面的吸附能比在Ni(111)和Ni(100)面的高约0.4 eV, 而CH和C在台阶面处的吸附能分别高出Ni(111)面的吸附能0.3和1.0 eV, 仅比Ni(100)面低约0.3 eV. 实验发现, 积碳一般首先发生在台阶处, 也就是石墨生长活性位^[24,45,47], 与本文结果一致.

图3为各物种在不同表面Pd掺杂的Pd/Ni表面吸附数据. 可以看出, 与未掺杂的干净Ni表面一样, 除CH₄外各物种最稳定的吸附位主要还是三重配位、四重配位和台

阶处. 同时, 相对于干净的Ni表面, 除CH₄外各物种在Pd/Ni表面的吸附能都有所减小. 对CH₄而言, 它在三种Pd/Ni表面上最稳定的吸附位是表面Pd原子的顶位, 而且在三种表面上的吸附能都很低且差别很小.

Pd/Ni(111)表面CH_x ($x = 3, 1, 0$)和H的最稳定吸附位有两类: (1)由三个Ni形成的hcp(3Ni)位; (2)由两个Ni和Pd组成的fcc(2Ni-1Pd)位. CH_x均优先吸附于hcp(3Ni)位, H则优先吸附于fcc(2Ni-1Pd)位. 与Ni(111)比较而言, 这些物种在掺杂的Ni(111)上的吸附更弱. 其中CH₃的吸附能降低最多, 为0.23 eV, 其它几种物种吸附能减弱程度相当, 约为0.13 eV.

Pd/Ni(100)表面CH_x和H的最稳定吸附位也有两类: (1)由三个Ni和Pd形成的hollow(3Ni-1Pd)位和由两个Ni组成的bridge(2Ni)位. 在该表面上CH₃最稳定吸附位与平整Ni(100)表面的一样, 都是bridge(2Ni)位, 其余三个物种最稳定吸附的位置均是hollow(3Ni-1Pd)位. 对比掺杂前后各物种的吸附能可见, Pd掺杂到Ni(100)表面对于吸附能的改变情况异于其对于Ni(111)表面的改变: CH₃的吸附能改变反而是最小的, 仅为0.06 eV; 而CH和C在干净以及Pd掺杂的Ni(100)表面的吸附能差别很大, 分别为0.71和0.47 eV. 由此可以推断, Pd的掺杂势必会对C–H键在Ni(100)表面的活化产生重要影响, 这可从下文各个表面上脱氢反应的能垒上看出.

Pd/Ni(211)表面CH和C物种均吸附于由三个Ni和一个Pd形成的step-corner(3Ni-1Pd)处. 两者的吸附能相较于干净的Ni(211)表面降幅接近, 分别为0.33和0.36 eV. CH₃吸附于台阶处由Ni和Pd形成的bri-step-edge(1Ni-1Pd)位置, 吸附能比干净的Ni(211)表面低0.26 eV. H吸附于由两个Ni和一个Pd形成的near-edge-hcp(2Ni-1Pd)处, 吸附能比干净表面上的降低0.11 eV, 是Pd/Ni(211)表面上除CH₄外, 所有物种中吸附能降低最少的.

3.3. CH₄和CH在Pd/Ni(111), Pd/Ni(100)和Pd/Ni(211)表面上的脱氢反应

为了考察在Ni不同表面单分散Pd是如何影响CH₄解离反应的, 本文计算了干净的Ni(111), Ni(100)及Ni(211)表面上C–H键的活化能. 表5为计算的Pd掺杂Ni表面以及干净Ni表面CH_x表面脱氢反应能量数据及过渡态的结构参数, 相应的势能面见图4.

各种干净Ni表面上CH₄脱氢反应的过渡态结构中CH₃均吸附在Ni的顶位, H则均位于桥位. 由图4可见, 在Pd/Ni表面上, 这些过渡态结构中CH₃均吸附在Pd的顶

位, H仍均位于桥位. Pd/Ni表面上CH₄脱氢反应的能垒较未掺杂的Ni表面均有所升高, 且增加的幅度大致相当, 约为0.1 eV. 如表5所示, 三种干净Ni表面催化CH₄解离反应的活性以Ni(211)为最高, 而Ni(111)最低. Pd的掺杂虽然降低了各个Ni表面的活性, 但降幅大致相当, 所以各种Pd/Ni表面的相对活性不变, 仍然是台阶面最高, 密堆面最低.

对于CH脱氢生成C反应, 过渡态结构中C均位于各自吸附的最稳定位置, H均位于桥位. 从三个表面CH脱氢反应的能垒对比可以发现, 催化该反应的活性次序为Ni(111) $\approx$ Ni(100) $\ll$ Ni(211)和Pd/Ni(111) $<$ Pd/Ni(100) $\ll$ Pd/Ni(211), 即台阶面依然是活性最高的. Pd的掺杂对于三种Ni表面活性的影响也不尽相同: Pd的掺杂没有改变Ni(111)表面上CH脱氢反应的能垒, 但增加了Ni(100)和Ni(211)表面能垒, 分别为0.22和0.15 eV.

对比CH₄和CH在三种Ni表面脱氢反应的能垒可见, 在Ni(111)表面, CH脱氢反应的能垒明显比CH₄脱氢反应的要高; 在Ni(100)表面, CH₄脱氢反应的能垒则明显高于CH脱氢反应的; 而在Ni(211)表面, 两者基本相当. 所以这些表面上CH₄解离反应的速率控制步骤也不同, 在Ni(111)表面上, CH脱氢反应是反应的速控步; 在Ni(100)表面上, CH₄脱氢反应则是反应的速控步. 而在Ni(211)表面, 反应没有单一的速控步.

Pd的掺杂基本上没有改变Ni(111)和Ni(100)表面上CH₄解离反应的速控步, 而对Ni(211)表面而言, CH脱氢反应的能垒增加更多, 从而降低了CH脱氢反应的速率. 需要特别指出的是, CH₃和CH₂脱氢反应的能垒较CH₄或者CH脱氢的要低很多^[36,43,44], 因此本文中只考察了CH₄和CH的脱氢反应. 在干净的Ni(211)表面, 一旦CH₄脱掉第一个H就很容易形成积碳, 而Pd的引入使得积碳的形成过程比CH₄脱氢反应在动力学上要难一些, 从而延缓了表面积碳的生成, 在某种程度上达到抗积碳的目的, 当然这是以牺牲部分反应活性为前提的.

如表5所示, 在Ni(211)和Pd/Ni(211)表面上CH₄和CH脱氢反应的最高能垒分别为0.53和0.66 eV, 这表明在比

较低的温度下CH₄在台阶面上容易解离. 由于在Ni(111)和Pd/Ni(111)表面上CH₄和CH脱氢反应的最高能垒为1.28 eV, 因而(211)面相对于(111)面具有高得多的活性, 但如表4和图3所示, C在(211)面上的吸附能也比在(111)面上要高很多, 因而更加容易发生积碳而失活. 因此, 在干气重整反应中起主要催化作用的可能不是高活性的台阶面, 而是活性较低的紧密堆积面^[45], 所以台阶面在低温下即可活化甲烷, 但干气重整反应仍需在高温下进行. 本文算的Ni(111)面上CH解离能垒是1.28 eV, 和文献结果(1.42 eV)^[46]比较接近, 尤其是考虑到所使用的模型和赝势一些差异, 因此可以认为本文计算的反应能垒是可靠的.

另外, 虽然Pd的引入提高了(211)和(100)面上CH₄解离反应速控步的能垒, 但对(111)面上的却没有影响. 正如前所述, 紧密堆积面可能在干气重整反应中起到关键作用, 所以本文结果并不能说明Pd的引入会使得催化剂活性降低, 相反, 却不同程度地降低了各个碳物种在表面的吸附能, 从而抑制了积碳的生成, 使得催化剂表现出更高的活性, 与Steinhauer等^[31]的结果一致.

4. 结论

采用DFT研究了Pd/Ni最稳定的表面合金结构和Pd的掺杂对各种Ni的低指数表面上CH₄解离反应的影响. 结果表明, 对于Pd/Ni体系, 最优的表面掺杂形式是Pd原子取代最外层Ni原子所形成的Pd/Ni表面. Pd的掺杂在不同程度上减弱了除CH₄之外的其它CH₄解离中间体(CH₃, CH, C, H)的吸附能, 并且增加了除Pd/Ni(111)表面CH脱氢反应以外的所有表面上CH₄和CH脱氢反应的能垒. CH₄优先在Ni(211)和Pd/Ni(211)等表面缺陷处解离, 其次是在Ni(100)和Pd/Ni(100)等比较开阔的表面解离, 而Ni(111)和Pd/Ni(111)等紧密表面的反应活性最低. Pd的掺杂没有改变Ni(111)和Ni(100)表面上CH₄解离的速控步, 但它却使得Ni(211)表面上CH脱氢反应的能垒比CH₄脱氢反应的高, 从而改变了其速控步, 减少了CH脱氢积碳的可能性.