

1     **Understanding the mechanism of CO<sub>2</sub> reforming of methane to syngas on**  
2                     **Ni@Pt surface compared with Ni(1 1 1) and Pt(1 1 1)**

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1 **Abstract:** In this contribution, we combine density functional theory (DFT) calculations,  
2 experimental kinetic study and DFT assisted kinetic analysis to elucidate the impact of the  
3 interface of monolayer Pt on the Ni surface on catalytic performance of steam methane  
4 reforming including carbon formation on core-shell (Pt@Ni) catalysts and compare to Ni and  
5 Pt catalysts. We demonstrate experimentally that core-shell structured Pt@Ni significantly  
6 lowers the carbon formation without scarifying much the activity. The DFT results  
7 demonstrate that the metal identity, core shell structure and support have significant impacts  
8 on the reaction mechanism. The direct methane activation is energetically favorable reaction  
9 pathway on Ni, while the OH\* assisted methane activation is the favorable pathway on Pt and  
10 Pt@Ni catalysts, where methane activation is the rate-determining step on all catalysts. We  
11 unambiguously reveal that the core-shell Ni@Pt catalyst modified the surface Pt electron  
12 density and shifted d-band center away from Fermi level compared with Ni(111) and Pt(111),  
13 which could lead to weakening the binding strength of adsorbates on metal surface. It  
14 resulted in a strong base of surface OH\* which actively reacts with CH<sub>x</sub> and thus enhance  
15 carbon formation resistance. From the free energy profile based on DFT-calculated energetics,  
16 a kinetic model is constructed, and the determined effective activation barriers agree well  
17 with the experimental measured ones. By taking into account the activation of steam on the  
18 support and modifying the entropy changes of the methane activation, the kinetic model can  
19 describe the experimental kinetic performance satisfactorily.

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21 Keywords: CH<sub>4</sub>/H<sub>2</sub>O reforming; OH-assisted activation; Coke formation; Kinetic study;

22 Ni@Pt

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## 1 **1. Introduction**

2 Due to the massive available in natural gas and shale gas reserves, the catalytic  
3 activation and conversion of methane is of great interest both in the catalytic community and  
4 industrial application [1–3]. This reaction is involved in some important chemical processes,  
5 such as methane total oxidation [4,5], methane partial oxidation [6,7], steam reforming of  
6 methane (*SRM*) [8,9] and dry reforming of methane (*DRM*) [10,11]. Above all, *SRM* plays a  
7 key role in the large scale of production of syngas and hydrogen from natural gas. The Ni-  
8 based catalysts are considered as a promising candidate due to their low cost and high activity  
9 [12,13]. However, carbon deposition is a serve problem for Ni catalysts, which would lead to  
10 a destruction of catalysts and reactor as well as rapid deactivation [14] due to coke formation  
11 [15]. Single component Ni catalysts hardly meet the activity and stability demands.

12 Noble catalysts have been found to be much more resistant to carbon deposition than Ni  
13 catalysts [16,17]. However, large scale application remains challenge due to their high prices.  
14 Manipulating the metal size and composition in nano-catalysis paves the way to improve the  
15 catalytic performance and replace and/or lower the precious metal usage. Bimetallic catalysts  
16 and core-shell structure are feasible and effective way to tune chemical and electronic  
17 properties on purpose [18]. However, most catalysts with better carbon resistant in methane  
18 reforming compensated by a lower activity [19,20]. Decoupling the catalysts activity and  
19 stability to develop catalysts with high activity, selectivity and stability simultaneously  
20 remains a formidable challenge. The core-shell nanoparticle is found to be an effective  
21 approach to design highly active, stable and low-cost materials with high noble metal  
22 utilization for both thermo- and electro-catalysis [21]. Such core-shell offers the promise of  
23 ultralow precious metal loadings while non-precious transition metal cores hold the promise  
24 of thermodynamic stability and access to unique catalytic activity, such as designing core-  
25 shell nanocatalysts in hydrocarbon reforming reactions for syngas production to reach high

1 stability [22–24].

2 Density functional theory (DFT) combined microkinetic modeling has gained an  
3 increasing attention in exploring mechanistic insights and catalyst rational design. Through  
4 the first-principles study, Huang et al. [25] suggested to increase resistant to carbon formation  
5 by lowering methane dissociation activity through Au/Ni surface alloys. Similarly surface  
6 alloying of Rh [26] with Ni(100) and alloying of Pd [27] as well as Au [28] with Ni(111)  
7 have been found to reduce the methane dissociation and thus reduce the carbon potential. The  
8 results showed that Pt-doped Ni(111) [29] surface is beneficial to the adsorption of CH<sub>x</sub> and  
9 H species. Moreover, Fan et al. [30] studied the origin of synergistic effect over Ni-based  
10 bimetallic surfaces (NiM; M = Cu, Ru, Rh, Pd, Ag, Pt and Au) for methane dissociation. The  
11 results proved that Pt-promoted Ni catalyst shows the best coke resistance.

12 Moreover, David and Matthew work [31] has reported that absorbed O\* and OH\* could  
13 withdraw electron density from the surface to form a negatively charged surface  
14 intermediates that serve as a Brønsted base [32,33], which can activate C–H bond during the  
15 oxidation and oxidative dehydrogenation reactions [32]. On Pt(111) surface very similar  
16 barriers was found for OH\*-assisted and direct CH<sub>4</sub> activation. Thus, Pt surface can possibly  
17 be manipulated to significantly reduce the activation barrier of methane. In addition, core-  
18 shell nanoparticles have been gaining increasing interests to improve the catalytic  
19 performance through introducing the strain to modify the electronic properties [24,34,35]. Ni-  
20 core/Pt-shell particle was found to be a stable structure due to a moderate surface segregation  
21 energy of Pt on Ni [36], thus providing a promising candidate for oxidation–reduction  
22 reactions [37] to decouple the catalyst activity and stability.

23 Here we report that Ni-core/Pt-shell particle (Ni@Pt) decouples the activity and carbon  
24 resistance to keep the activity and reduce carbon formation simultaneously in methane steam  
25 reforming. A systematical DFT study of methane activation by O\* and OH\* assisted

1 activation as well as direct deprotonation and  $\text{CH}_x$  oxidation on Ni@Pt is performed and  
2 compared to Ni(111) and Pt(111) surface. Reaction pathways are elucidated and their  
3 dependence on the surfaces is revealed. We unambiguously reveal that the core-shell Ni@Pt  
4 catalyst modified the surface Pt electron density and lowered the adsorption strength of  
5 intermediates, which resulted in a strong base of  $\text{OH}^*$  to actively react with methane and  $\text{CH}_x$   
6 and enhance carbon formation resistance without sacrificing the reaction activity. In addition,  
7 we have performed the kinetic study over Ni and Ni@Pt catalysts in SRM to compare and  
8 validate the DFT results. Temperature programmed oxidation (TPO) analysis for the catalysts  
9 after reaction was tested to obtain the coke formation rate and compare with the coke  
10 potential drawn from DFT predictions.

11

## 12 **2. Computational and experimental details**

### 13 **2.1 Computational models**

14 The (111) surface usually dominates the surfaces of metal nanoparticles [38], so pure  
15 Ni(111) and Pt(111) as well as Ni@Pt are chosen as the reaction surfaces in this paper. Based  
16 on the optimized pure Ni bulk and Pt bulk, the five atomic layers Ni(111) and Pt(111) surface  
17 models were built. The bottom two layers were fixed at their equilibrium bulk positions, and  
18 the top three layers and the adsorbates were allowed to relax. Additionally, a  $p(3 \times 3)$   
19 supercell was applied, with a coverage of adsorbates of 1/9 ML, which has been widely used  
20 in previous DFT study dealing with molecular interactions with metal surfaces [12]. The  
21 computational method results in a self-consistent lattice constant of 3.540 Å (3.52 Å [8]) for  
22 the Ni bulk and 3.982 Å (3.92 Å [39]) for the Pt bulk, respectively, which are in good  
23 agreement with the well accepted experimental value in the bracket. Ni@Pt core-shell surface  
24 was built based on the optimized Ni(111) by substituting first layer Ni atoms into Pt atoms.  
25 The metal (111) surfaces are provided in Fig. 1.

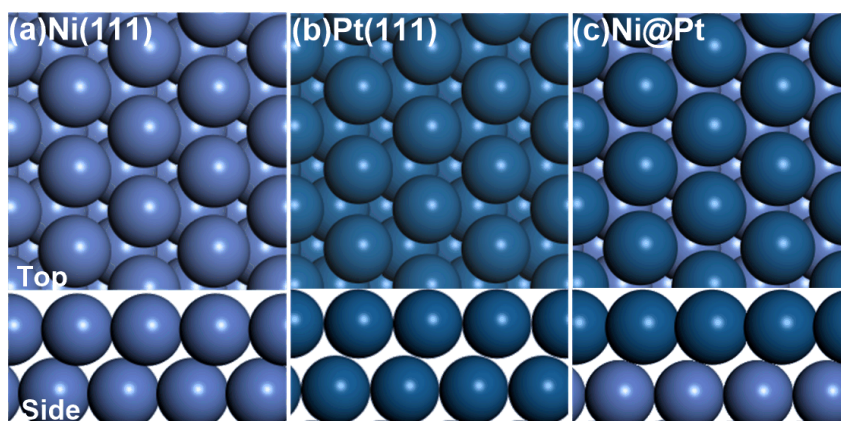


Fig. 1. Three surface models (a) Ni(111); (b) Pt(111); and (c) Ni@Pt.

## 2.2 Density functional theory (DFT) calculations

All the DFT calculations were conducted with a periodic slab model using the Vienna ab initio simulation program (VASP) [38,40]. All calculations were conducted with the generalized gradient approximation (GGA) and the Bayesian error estimation functional with van der Waals correlation (BEEF-vdW) [41], which was developed to address van der Waals interaction reasonably at an accurate description of adsorption energies of molecules on surfaces [42]. In addition, BEEF-vdW works most satisfactorily among the selected functional since it has the smallest mean absolute error by comparing results from different functions such as BEEF-vdW, RPBE, and PBE with a database of 30 adsorption reaction energies [43]. Projector augmented wave (PAW) method was used to describe the electron-ion interaction [44]. And the plane wave cutoff energy of 400 eV was utilized in the calculation of the compact convergence. DFT calculations considered spin-polarized electrons for Ni(111) and Ni@Pt surfaces, which account for the magnetic moment of Ni. A 15 Å vacuum region was used to ensure the intermolecular interaction between the slabs was negligible. In addition, a Fermi smearing of 0.2 eV was applied in our present work. Brillouin zone integration was approximated by a sum over special k-points chosen using the Monkhorst–Pack method [45]. The meshes of  $5 \times 5 \times 1$  k-points for the Ni(111), Pt(111) and Ni@Pt surfaces.

Moreover, transition states were searched by dimer method [46]. All the optimizations are converged with a force criterion of 0.03 eV/Å. The transition states in this work were verified by frequency analysis, and only one imaginary frequency was identified for each transition state, the details is provided in Supporting Information Table S1.

The adsorption energy of the adsorbate is given by:

$$E_{ads} = E_{adsorbate/surface} - E_{adsorbate} - E_{surface} \quad (1)$$

where  $E_{adsorbate/surface}$  is the total energy of the surface with the adsorbate adsorbed,  $E_{adsorbate}$  is the total energy of the isolated adsorbate, and  $E_{surface}$  is the total energy of the bare surface. A negative value for the adsorption energy indicates that the adsorption process is exothermic.

The activation barrier ( $E_a$ ) of forward reaction is given by:

$$E_a = E^{TS} - E^{IS} \quad (2)$$

where  $E^{TS}$  is the total energy of transition state, and  $E^{IS}$  is the total energy of initial state.

The reaction heat ( $\Delta H$ ) of an elementary reaction is given by:

$$\Delta H = E^{FS} - E^{IS} \quad (3)$$

where  $E^{FS}$  is the total energy of final state.

### 2.3 Thermodynamic analysis

All the thermodynamic properties were calculated at a temperature of 1000 K firstly. Moreover, 773 K, 798 K, 823 K and 848 K applied for kinetic relevant steps to compare with the experimental results. The Gibbs free energy (G) of gas phase species was estimated by taking into account transitional, rotational and vibrational contributions. For the surface adsorbed species, only vibrational contribution was considered, including zero-point energy (ZPE), vibrational thermal energy and vibrational entropy [14, 20]. The standard molar Gibbs free energy for each species in methane dehydrogenation and reforming is calculated as [14]:

$$G^0 = E_{total} + E_{ZPE} + \gamma RT(1 + \ln \frac{P}{P^0}) + U^0 - TS^0 \quad (4)$$

1 where  $E_{total}$  is the total energy obtained from DFT calculations, and  $E_{ZPE}$ ,  $U^0$  and  $S^0$  are the  
2 correction energy from ZPE, thermal energy and entropy, respectively.  $R$  is the gas constant,  
3  $P$  is the partial pressure of the gas-phase molecule,  $\gamma$  is 0 for the surface adsorbed species and  
4 1 for gaseous molecule.

## 5 **2.4 Catalyst preparation**

6 Monometallic 12wt% Ni derived from hydrotalcite-like precursor has been prepared by  
7 co-precipitation using metal nitrites component, keeping the ratio of Ni:Mg:Al at 0.37:2.63:1 .  
8 Ni@Pt catalysts were prepared by redox reaction of the reduced Ni catalyst with the  
9 modifiers Pt in solution in the form of a precursor salt at ambient temperature. During the  
10 redox reaction, Ni atoms were gradually substituted into Pt atoms on the surface of Ni  
11 particles and  $Ni^{2+}$  formed accordingly,  $Pt^{2+} + Ni \rightarrow Pt + Ni^{2+}$ .

## 12 **2.5 Catalyst characterization**

13 In order to determine the specific surface area of nickel and nickel alloying,  
14 measurements of  $H_2$  chemisorption were performed on a Micromeritics ASAP 2010C unit at  
15 308 K. 200 mg of the freshly calcined catalysts were loaded in tubular quartz reactor,  
16 evacuated at 308 K for 1 h and reduced in a 5%  $H_2/He$  flow at 943 K for 10 hrs. in a quartz  
17 micro-reactor. After reduction, the sample was evacuated for 0.5 hrs. at 943 K and for 1 h at  
18 308 K. At this temperature, an adsorption isotherm was recorded and the metal dispersion  
19 was determined according to the quantity of hydrogen uptake.

20 The X-ray photoelectron spectroscopy (XPS) analyses were performed, where a  
21 monochromatized Al  $K\alpha$  X-ray source (GammaData Scienta) was used to get the exciting  
22 radiation in a hemispherical SCIENTA SES 2002 electron energy analyzer. The total energy  
23 resolution for XPS was estimated to be about 0.4 eV. All spectra were measured in angle  
24 integrated mode around normal emission. Transmission electron scanning (TEM) images  
25 were taken and analyzed using a JEOL-2010F, with an accelerating voltage of 200 kV. The



1 samples were prepared by ultrasonic dispersion of the reduced catalysts in ethanol. Drops of  
2 samples were put on a copper grid supported with a carbon film.

### 3 **2.6 Methane reforming**

4 Kinetic study of methane steam reforming was performed in a fixed-bed reactor at  
5 atmospheric pressure. The catalyst bed consisted of 10 mg of Ni catalyst (50-150  $\mu\text{m}$ ) diluted  
6 with inert  $\alpha\text{-Al}_2\text{O}_3$  (100 mg). Product concentrations were measured online with a micro-gas  
7 chromatograph. The catalysts were heated from room temperature to 670  $^\circ\text{C}$  at 2  $^\circ\text{C}/\text{min}$  in a  
8 mixture of 1/1  $\text{H}_2/\text{Ar}$  (total flow of 200  $\text{cm}^3/\text{min}$ ) and held at these conditions for 12 h  
9 reduction. The temperature dependence was  $\text{S}/\text{C}=3.5$ , and,  $\text{CH}_4/\text{H}_2=1.0$  where the  $\text{W}/\text{F}_0$  was  
10 varied to control the conversion lower than 10%. In addition, stability test was performed at  
11  $\text{S}/\text{C}=1$  at 700  $^\circ\text{C}$ , 1 atm. Coke formation on spent catalysts was investigated by a TGA-MS  
12 (TGA: Netzsch STA 449C Jupiter, MS: Netzsch Aëros QMS 403C) system under an  
13 Air/Helium (90/10  $\text{ml}\cdot\text{min}^{-1}$ ) atmosphere, heating from ambient temperature to 900  $^\circ\text{C}$ , at a  
14 ramping rate of 10  $^\circ\text{C}/\text{min}$ , and dwelling for half hour at this temperature. The amount of  
15 coke formation was estimated by the mass loss in TGA analysis, confirming by MS results.

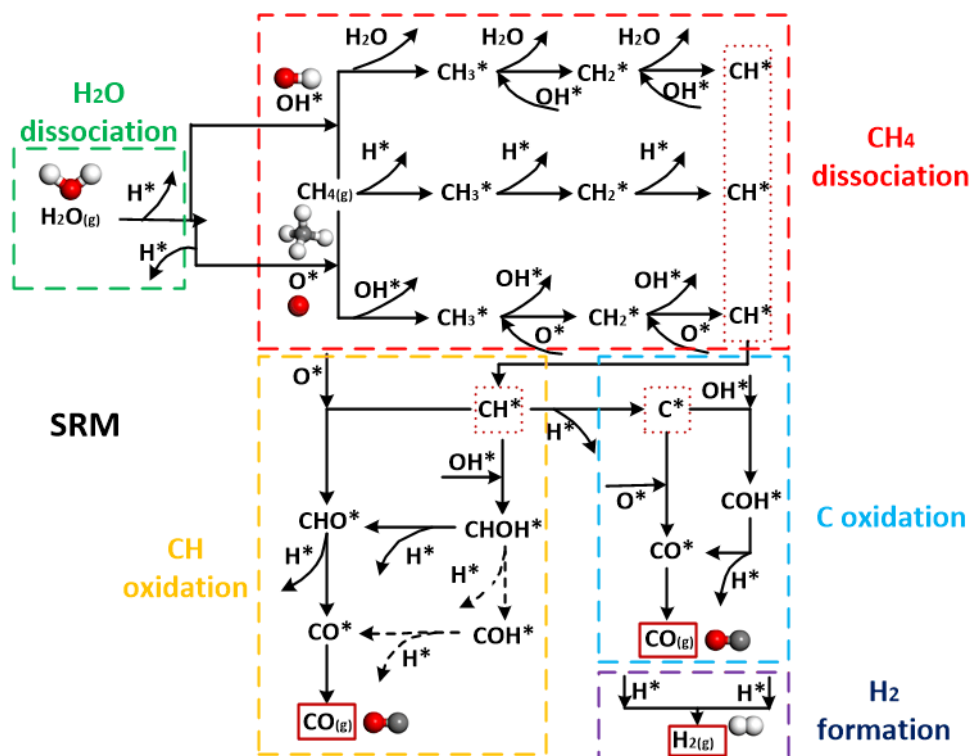
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## 17 **3. Results and discussion**

### 18 **3.1 Reaction network for methane steam reforming**

19 A reaction network for methane steam reforming considered in this work is provided in  
20 [Fig. 2](#). The whole reaction network is separated into five parts, specifically, it consists of  $\text{CH}_4$   
21 dissociation,  $\text{H}_2\text{O}$  dissociation, CH oxidation, C oxidation and  $\text{H}_2$  formation, respectively.  
22 Three pathways of  $\text{CH}_4$  activation, namely direct dissociation, O-assisted and OH-assisted  
23 activation, respectively, have been taken into account. In terms of  $\text{H}_2\text{O}$  dissociation, the  $\text{H}_2\text{O}$   
24 molecule direct dissociation into OH and H is considered. As for CH oxidation, O and OH  
25 assisted pathways have been taken into account. The intermediates of CHO, COH, CHOH are

1 formed in the CH oxidation processes and the details are shown in the CH oxidation part of  
 2 Fig. 2. In addition, C is oxidized by O and OH, and the target product of both CH and C  
 3 oxidation is CO. H<sub>2</sub> is generated from absorbed H atoms on the surface.



4  
 5 **Fig. 2.** Reaction network for methane steam reforming considered in this work. The whole network is  
 6 divided into five parts: H<sub>2</sub>O dissociation (in dashed green rectangle), CH<sub>4</sub> dissociation (in dashed red  
 7 rectangle), CH oxidation (in dashed orange rectangle), C oxidation (in dashed light blue rectangle) and H<sub>2</sub>  
 8 formation (in dashed dark blue rectangle).

### 9 3.2 Projected density of states (PDOS) and adsorption of main species

10 Fig. 3a shows the projected density of states for *d* orbital on three metal surfaces, it is  
 11 found that introducing Pt atoms into Ni surface forming Ni@Pt makes the curves of PDOS  
 12 broader and *d*-band center shifted away from Fermi level compared with Ni(111) and Pt(111),  
 13 which could lead to weakening the binding strength between adsorbates and metal surface.  
 14 The corresponding *d*-band center of three metal surfaces is calculated to be -1.31 eV  
 15 [Ni(111)], -2.00 eV [Pt(111)], and -2.59 eV [Ni@Pt], respectively.

16 According to adsorption energy of species provided in Table S2, some features could be

1 drawn. Above all, the binding energies on the Ni@Pt surface are the weakest among three  
2 surfaces, which is in good agreement with *d*-band center of metal surface. Additionally,  
3 Pt(111) shows the strongest binding energy for most species, except for O\*, H\*, OH\* and  
4 CO\*. Specifically, as for C\*, the lowest adsorption energy occurs on Ni@Pt surface,  
5 indicating that C\* on Ni@Pt is more easier to react with other species, such as O\*/OH\*,  
6 which could lead to less carbon formation on the surface compared with Ni(111) and Pt(111).  
7 In terms of O\*, there is a big difference among three surfaces, the binding energies are –  
8 5.21eV [Ni(111)], – 4.04 eV [Pt(111)], and – 3.09 eV [Ni@Pt], respectively. For H\*, the  
9 binding energy on the Ni@Pt is lower than the others, suggesting that H<sub>2</sub> is easier to form. In  
10 addition, the most favored adsorption site on Ni(111) and Pt(111) is hollow site for OH\*,  
11 while it moves to top site on the Ni@Pt surface with the lowest binding energy. Therefore,  
12 OH-assisted dehydrogenation becomes a possible way on Ni@Pt surface, which will be  
13 discussed later. CO is one of dominant products in this reaction, binding ability on the Ni@Pt  
14 is the weakest and CO\* is more favored to desorb into gas phase on this surface.

15 **Fig. 3b** displays the main chemisorbed species involved in methane activation and  
16 reforming reactions. In conclusion, Ni(111) shows the best ability of binding oxygen atom of  
17 oxygenated species among the three surface and Pt(111) has the highest binding energy for  
18 carbon atom of hydrocarbon species, while Ni@Pt lower the adsorption of both C and O  
19 contained intermediates. In addition, strong adsorption could promote reactant initial  
20 dissociation, while weak adsorptive species is easier to join in the surface reaction, so a good  
21 catalyst for this process should have moderate adsorption strength for reactive species.

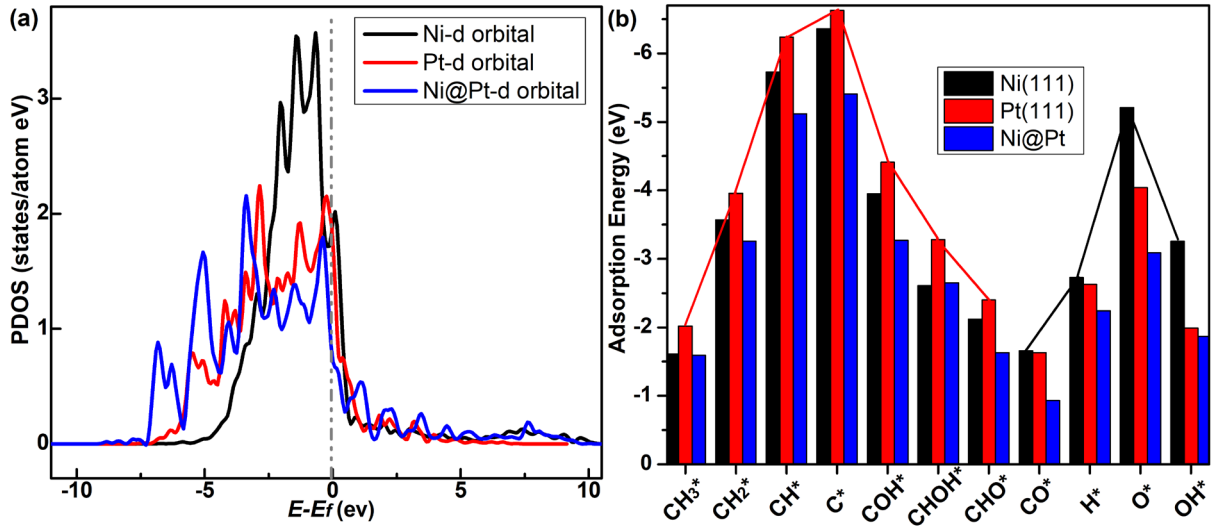


Fig. 3. (a) Projected density of states for *d* orbital; and (b) Main chemisorbed species on three metal surfaces. The dash line donates the Fermi level.

### 3.3 DFT study of CH<sub>4</sub>/H<sub>2</sub>O reforming

Table 1 provides the activation energy (*E<sub>a</sub>*) and reaction heat ( $\Delta H$ ) in CH<sub>4</sub>/H<sub>2</sub>O reforming on Ni(111), Pt(111) and Ni@Pt, respectively. The detailed discussion will be presented in the following sections.

**Table 1**

Activation energy (*E<sub>a</sub>*) and reaction heat ( $\Delta H$ ) in methane activation and reforming on Ni(111), Pt(111) and Ni@Pt.

	Ni(111)		Pt(111)		Ni@Pt	
	<i>E<sub>a</sub></i>	$\Delta H$	<i>E<sub>ads</sub></i>	$\Delta H$	<i>E<sub>ads</sub></i>	$\Delta H$
<b><i>CH<sub>4</sub> direct dissociation (A)</i></b>						
CH <sub>4</sub> + 2* $\leftrightarrow$ CH <sub>3</sub> * + H*	1.206	0.545	1.033	0.217	1.725	1.084
CH <sub>3</sub> * + * $\leftrightarrow$ CH <sub>2</sub> * + H*	0.874	0.334	1.032	0.499	1.544	1.061
CH <sub>2</sub> * + * $\leftrightarrow$ CH* + H*	0.434	-0.158	0.518	-0.191	1.224	0.732
CH* + * $\leftrightarrow$ C* + H*	1.445	0.643	1.617	0.996	1.979	1.545
<b><i>O*/OH* assisted CH<sub>4</sub> activation (B)</i></b>						
CH <sub>4</sub> + O* + * $\leftrightarrow$ CH <sub>3</sub> * + OH*	1.661	0.537	1.552	-0.119	1.424	-0.332
CH <sub>4</sub> + OH* $\leftrightarrow$ CH <sub>3</sub> * + H <sub>2</sub> O	3.389	0.859	0.699	-0.777	1.191	-0.455
CH <sub>3</sub> * + O* $\leftrightarrow$ CH <sub>2</sub> * + OH*	1.565	0.573	1.618	0.227	1.356	-0.229
CH <sub>3</sub> * + OH* $\leftrightarrow$ CH <sub>2</sub> * + H <sub>2</sub> O + *	0.931	0.58	1.068	-0.293	1.191	-0.406
CH <sub>2</sub> * + O* $\leftrightarrow$ CH* + OH*	1.023	-0.093	1.582	-0.446	1.011	-0.636
CH <sub>2</sub> * + OH* $\leftrightarrow$ CH* + H <sub>2</sub> O + *	0.865	-0.145	0.662	-0.953	0.619	-1.02
<b><i>H<sub>2</sub>O dissociation (C)</i></b>						

$\text{H}_2\text{O}^* + * \leftrightarrow \text{OH}^* + \text{H}^*$	1.003	-0.186	0.913	0.795	1.539	1.517
$\text{OH}^* + * \leftrightarrow \text{O}^* + \text{H}^*$	1.311	0.091	0.768	0.037	1.851	1.207
<b><i>CH and C oxidation (D)</i></b>						
$\text{CH}^* + \text{O}^* \leftrightarrow \text{CHO}^* + *$	1.134	0.406	1.29	-0.908	0.739	-1.965
$\text{CHO}^* + * \leftrightarrow \text{CO}^* + \text{H}^*$	0.256	-0.986	0.474	-0.566	0.562	-0.204
$\text{CH}^* + \text{OH}^* \leftrightarrow \text{CHOH}^* + *$	1.162	0.731	0.800	0.228	0.596	-1.305
$\text{CHOH}^* + * \leftrightarrow \text{CHO}^* + \text{H}^*$	0.540	-0.302	0.184	-0.105	0.84	0.609
$\text{CHOH}^* + * \leftrightarrow \text{COH}^* + \text{H}^*$	1.515	-0.155	1.612	-0.305	1.482	0.773
$\text{COH}^* + * \leftrightarrow \text{CO}^* + \text{H}^*$	1.071	-0.954	1.075	-0.265	1.157	-0.281
$\text{C}^* + \text{O}^* + * \leftrightarrow \text{CO}^* + *$	1.300	-1.723	1.354	-2.406	0.902	-3.774
$\text{C}^* + \text{OH}^* \leftrightarrow \text{COH}^* + *$	1.141	-0.605	0.729	-1.645	0.396	-2.17
<b><i>C formation (E)</i></b>						
$\text{CH}^* + * \leftrightarrow \text{C}^* + \text{H}^*$	1.445	0.643	1.617	0.996	1.979	1.545
$\text{COH}^* + * \leftrightarrow \text{C}^* + \text{OH}^*$	1.746	0.605	2.374	1.645	2.566	2.17
$\text{CO}^* + * \leftrightarrow \text{C}^* + \text{O}^*$	3.023	1.723	3.76	2.406	4.676	3.774
<b><i>CH consumption (F)</i></b>						
$\text{CH}^* + * \leftrightarrow \text{C}^* + \text{H}^*$	1.445	0.643	1.617	0.996	1.979	1.545
$\text{COH}^* + * \leftrightarrow \text{C}^* + \text{OH}^*$	1.746	0.605	2.374	1.645	2.566	2.17
$\text{CO}^* + * \leftrightarrow \text{C}^* + \text{O}^*$	3.023	1.723	3.76	2.406	4.676	3.774

1

2 **3.3.1 CH<sub>4</sub> direct activation**

3 Methane is a quite stable molecule owing to its large C–H bond energy and strictly  
4 symmetrical structure. Generally, the activation of first C–H bond was found to be the rate-  
5 limiting step in methane activation and reforming reactions [20,47]. Now that CH<sub>4</sub> direct  
6 activation to form surface C and H is investigated on three surface. The activation energy and  
7 reaction heat in this process are listed in Table 1A. Additionally, Fig. S1 presents top views  
8 and side views (insets) of transition states of CH<sub>4</sub> direct successive dehydrogenation.

9 For the first step of CH<sub>4</sub> dehydrogenation, Ni@Pt shows the highest barrier among the  
10 three surfaces with a value of 1.725 eV, and also it is a strong endothermic step, indicating  
11 that CH<sub>4</sub> direct dissociation is difficult to proceed on this surface. The CH<sub>4</sub> activation energy  
12 for Ni(111) is 1.206 eV, which is close to the reported values (1.18 [48], 1.21 [49], 1.23 [50]),  
13 and for Pt(111) is 1.033 eV, in good agreement with previous literature 1.06 eV from  
14 GGA/rPBE functions [31], both of them are lower than that of Ni@Pt. As for CH<sub>x</sub>(3-1)

1 dehydrogenation, the activation energy on different catalysts follows an order of the CH<sub>x</sub>  
2 adsorption heat, namely Ni(111) < Pt(111) < Ni@Pt. The activation barrier of CH  
3 dissociation on Ni@Pt remarkably increases to 1.979 eV, especially higher than that on  
4 Ni(111), suggesting that Ni@Pt structure has promising anti-carbon formation ability.

5 In conclusion, this process is hard to proceed on Ni@Pt surface from both kinetically  
6 and thermodynamically, due to the large activation barrier and strong endothermic property.  
7 In addition, Ni(111) and Pt(111) have similar dehydrogenation ability for CH<sub>4</sub>. Specifically,  
8 Pt(111) shows a little better catalytic performance for methane dissociation than Ni(111),  
9 meanwhile, it enhances barrier for last dehydrogenation step, indicating that Pt metal has  
10 better anti-carbon formation ability, which is proved in both DFT calculations [49,51] and  
11 experimental work [52,53].

### 12 3.3.2 O\*/OH\*-assisted activation of CH<sub>4</sub>

13 O\* assisted and OH\* assisted C–H of CH<sub>4</sub> activation paths proceeding via reductive  
14 deprotonation over the metal-O\* or metal-OH\* site pairs [31–33] have been investigated here  
15 to compare with direct dissociation. The adsorbed O\* and OH\* serve as base sites which  
16 attack the acidic bond C–H bond in CH<sub>4</sub>. The activation energy of CH<sub>4</sub> dissociation follows  
17 an order of Ni@Pt < Pt(111) < Ni(111), which is an inverse order of O\* and OH\* binding  
18 energy, respectively. The CH<sub>4</sub> activation is more favorable to proceed under the assistance of  
19 OH\* than that with O\* assisted and direct dissociation ways on Ni@Pt. The binding energy  
20 of OH\* on Ni(111) which behaves a relatively weak base, resulted in a high activation energy  
21 for first C–H bond activation of CH<sub>4</sub>. In contrast, the strain introduced by the core-shell  
22 structure lowered the OH\* binding energy. Therefore, Ni@Pt surface possesses the lowest  
23 activation energy for CH<sub>4</sub> activation. For the O\* and OH\* assisted CH<sub>x</sub>\* activation, it follows  
24 the order of the reaction heat, while the presence of OH\* largely inhibits first C–H bond  
25 dissociation of CH<sub>4</sub> on Ni(111), which could be attributed to the strong binding energy for

1 OH on Ni(111) surface and large entropy loss in gas phase CH<sub>4</sub> adsorptive dissociation  
2 process. For the following dehydrogenation processes, the OH\* assisted pathway is superior  
3 to O\* assisted way on all three surfaces, indicating that OH\* species could promote most of  
4 dehydrogenation steps on three metal surfaces, except first C–H bond activation of CH<sub>4</sub> on  
5 Ni(111). The activation energy and reaction heat are listed in [Table 1B](#). Moreover, [Fig. S2](#)  
6 presents top views and side views (insets) of transition states of CH<sub>4</sub> dissociation through O\*  
7 and OH\*.

8 In conclusion, as for the activation of first C–H bond of CH<sub>4</sub> on three metal surfaces,  
9 direct dissociation into CH<sub>3</sub>\* and H\* proceeds more easily on Ni(111) than O\* and OH\*  
10 assisted CH<sub>4</sub> activation. However, compared with barrier of direct dissociation, the barriers of  
11 OH\* assisted CH<sub>4</sub> activation are decreased by 0.334 eV on Pt(111) and 0.534 eV on Ni@Pt,  
12 respectively. Thus, OH-assisted CH<sub>4</sub> activation in reforming process becomes an attractive  
13 alternative route on Pt(111) and Ni@Pt surface.

### 14 3.3.3 H<sub>2</sub>O dissociation

15 H<sub>2</sub>O dissociation on three surfaces is comparatively studied. The stable configurations  
16 for H<sub>2</sub>O binding on the three models are all at the top site with the molecular plane almost  
17 parallel to the surface. [Table 1C](#) gives the activation energy and reaction heat of H<sub>2</sub>O  
18 dissociation. In addition, [Fig. S3](#) displays the top views and side views (insets) of transition  
19 states in H<sub>2</sub>O dissociation. For the initial H<sub>2</sub>O dissociation into OH\* and H\*, the Ni(111) and  
20 Pt(111) show the similar activation barrier close to 1 eV, which has been reported in former  
21 literature [57], while this step requires a higher barrier on Ni@Pt surface with a value of  
22 1.539 eV. Most of previous works focus on H<sub>2</sub>O initial dissociation step. As for the OH\*  
23 further decomposition into O\* and H\*, Ni(111) shows the best performance, contrarily,  
24 Ni@Pt has a much higher energy barrier.

25 In order to see thermodynamic and kinetic details in H<sub>2</sub>O dissociation, energy profiles

1 for H<sub>2</sub>O dissociation on three surfaces are plotted. As seen from Fig. S4, both OH\* and O\*  
2 are possible to form in H<sub>2</sub>O dissociation on Ni(111), while it becomes less favored to  
3 complete the OH\* decomposition step on Pt(111) and Ni@Pt surface, especially for Ni@Pt,  
4 this step is almost impossible to proceed. As a consequence, OH\* is the dominant product of  
5 H<sub>2</sub>O dissociation on Pt(111) and Ni@Pt, while this process could provide both OH\* and O\*  
6 species as oxidant for CH<sub>x</sub> activation on Ni(111) surface.

### 7 **3.3.4 CH and C oxidation**

8 According to the previous report [18], CH is the most abundant species in methane  
9 dehydrogenation process on Pt(111) surface. Zhu et al. [47] found that only the CH oxidation  
10 and C oxidation are likely to proceed on Ni(111) surface, and also the pathway of CH  
11 oxidation is more favorable. However, CH and C oxidation pathways on Ni@Pt surface are  
12 still unknown, and the systematical comparison of reaction pathways on three surfaces are  
13 lacking.

14 All the activation energy and reaction heat in the CH and C oxidation on three metal  
15 surfaces are listed in Table 1D. As seen from table, it could be concluded that the stronger  
16 adsorption strength between the carbon/oxygen and surface are, the higher barrier for the C  
17 and CH oxidation in the reaction. The energy barriers for CH and C oxidation through  
18 oxygen are according to the following sequence: Pt(111) > Ni(111) > Ni@Pt, which is  
19 consistent with the tendency of carbon adsorption energy, while through hydroxyl assisted  
20 oxidation way for CH and C, the activation barriers follow the order: Ni(111) > Pt(111) >  
21 Ni@Pt, which has the same trend with the oxygen binding energy. In conclusion, no matter  
22 the O\* or the OH\* assisted oxidation of both CH and C, the Ni@Pt surface always shows the  
23 lowest energy barrier for these processes, thus Ni@Pt is predicted to be a good candidate in  
24 the reaction of CH and C oxidation. Moreover, Fig. S5 describes the top views and side views  
25 (insets) of transition states of CH and C oxidation on three surfaces.



1        **Fig. S6** shows the energy profiles for CH oxidation by both O\* and OH\* assisted ways  
2 on three surfaces. As for O\* assisted CH oxidation way, it forms the intermediate of CHO\*  
3 species firstly, Ni@Pt shows the lowest energy barrier for this process. Then CHO\*  
4 dissociates into CO\* and H\*, the low barrier and enthalpy decrease for the CHO\*  
5 dissociation suggest that CHO is not a stable intermediate on these surfaces, which has been  
6 mentioned in former work [14]. In summary, the Ni@Pt has the lowest energy barrier for  
7 CH\* oxidation into CO\* and H\* through absorbed oxygen atoms. On the other hand,  
8 regarding the OH\* assisted oxidation of CH, the intermediate CHOH\* appears in the  
9 beginning, in the CHOH\* forming step, it is found that Ni@Pt still presents the lowest energy  
10 barrier. Then, CHOH\* decomposes into CHO\* or COH\*, the former way proceeds more  
11 easily than the latter on all three surfaces in this work, which is in good agreement with  
12 previous studies [18,39,58]. Therefore, Ni@Pt surface exhibits the best performance for the  
13 oxidation of CH\* into CO\* and H\* by absorbed hydroxyl. The energy barrier for CH\*  
14 oxidation through OH\* follows the order: Ni(111) > Pt(111) > Ni@Pt. As a result, Ni@Pt  
15 model presents the better ability for CH\* oxidation through both O\* and OH\* assisted ways,  
16 compared with Ni(111) and Pt(111).

17        **Fig. S7** presents the energy profiles for C oxidation by both O\* and OH\* assisted ways  
18 on three surfaces. As for surface carbon oxidation through O\*, it directly goes into CO\*,  
19 while for OH\* assisted way, it forms intermediate COH\* firstly, and then COH\* splits into  
20 CO\* and H\*. The most favored path for both C + O and C + OH reactions happens on Ni@Pt  
21 surface, the activation barriers are 0.902 eV and 0.396 eV respectively, indicating that carbon  
22 oxidation is accelerated on the Ni@Pt and this surface is predicted to have good performance  
23 for carbon elimination. The energy barriers of C + OH reaction on three surfaces are all lower  
24 than the corresponding values of C + O reaction, indicating that OH species is more effective  
25 for carbon elimination than O species, which has been reported in previous literature [59].

### 1 3.3.5 Carbon formation

2 Three major reaction paths for carbon formation have been considered in this work,  
3 which are CH\* decomposition into C\* and H\*, COH\* dissociation into C\* and OH\*, CO\*  
4 cracking into C\* and O\*, respectively. The activation energy and reaction heat are provided  
5 in Table 1E. It is found that CH decomposition is the most favorable way for carbon  
6 formation on all surfaces. Furthermore, Fig. S8 presents the energy profiles for C formation  
7 on three surfaces, the barrier for CH cracking on Ni@Pt is the highest among the three  
8 surfaces with a value of 1.979 eV, suggesting that surface carbon is hard to form on this  
9 surface, thus Ni@Pt has good anti-carbon ability in methane dehydrogenation and reforming  
10 reactions.

11 As mentioned above, CH cracking reaction is the most possible reaction way for carbon  
12 formation on three surfaces. To further investigate the possibility for CH decomposition on  
13 different surfaces, the competitive pathways of CH oxidation through O\* and OH\* have been  
14 taken into comparison. Table 1F gives the activation energy and reaction heat in these  
15 processes. If the proper amount of O\* or OH\* can be supplied during the reaction, the  
16 oxidation pathways of both O\* and OH\* assisted show a lower activation barrier for CH  
17 consumption, especially for OH\* assisted oxidation. Moreover, energy profiles for CH  
18 consumption on three metal surfaces is shown in Fig. S9, Ni@Pt surface has the largest Ea  
19 difference between the CH decomposition and oxidation through OH\*, suggesting that CH  
20 prefers to be oxidized rather than cracking into surface carbon.

21 On the one hand, carbon is difficult to form from CH cracking reaction on Ni@Pt, even  
22 if a small amount of carbon deposition is accumulated during in the reaction on this surface,  
23 it could be easily oxidized into CO\* and COH\*, which has been demonstrated in the former  
24 C oxidation sections. In conclusion, we propose a descriptor of carbon formation possibility,  
25 from two sides of CH cracking into surface carbon possibility and the ability of surface

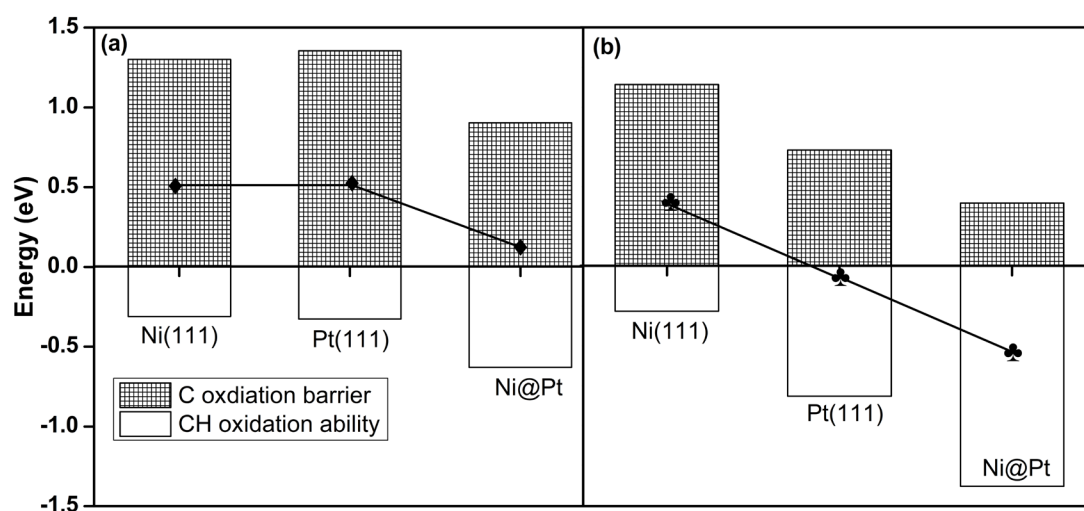
1 carbon to be oxidized. Table 2 provides the  $E_a$  difference between CH decomposition and  
 2 oxidation through  $O^*$  and  $OH^*$ , respectively, and also gives the barrier for surface carbon  
 3 oxidation on three catalyst models. According to the results and discussion, we plot the  
 4 relationship between carbon formation possibility and related reaction barriers, as depicted in  
 5 Fig. 4. We define the C oxidation barrier from  $E_a(C+O/OH \leftrightarrow CO/COH)$ , and CH oxidation  
 6 ability from  $[E_a(CH \leftrightarrow C + H) - E_a(CH+O/OH \leftrightarrow CHO/CHOH)]$ . And we assume that the  
 7 center lever of total rectangular region on each surface represents the possibility of carbon  
 8 formation. From both  $O^*$  and  $OH^*$  assisted oxidation pathways, Ni@Pt always keeps the  
 9 lowest center lever of total rectangular region. Consequently, Ni@Pt model shows the lowest  
 10 possibility of surface carbon formation in methane dehydrogenation and reforming reactions.

11 **Table 2**

12  $E_a$  difference between CH decomposition and oxidation through  $O^*$  and  $OH^*$ , and barriers for surface  
 13 carbon oxidation on three catalysts.

	Ni(111)	Pt(111)	Ni@Pt(111)
$E_{a(CH \leftrightarrow C + H)} - E_{a(CH+O \leftrightarrow CHO)}$	0.311	0.327	0.629
$E_{a(CH \leftrightarrow C + H)} - E_{a(CH+OH \leftrightarrow CHO)}$	0.283	0.817	1.383
$E_{a(C+O \leftrightarrow CO)}$	1.300	1.354	0.902
$E_{a(C+OH \leftrightarrow COH)}$	1.141	0.729	0.396

14



15

16 **Fig. 4.** Carbon formation possibility from both (a)  $O^*$  and (b)  $OH^*$  assisted ways on three surfaces. C  
 17 oxidation barrier:  $E_a(C+O/OH \leftrightarrow CO/COH)$ ; CH oxidation ability:  $E_a(CH \leftrightarrow C + H) - E_a(CH+O/OH \leftrightarrow$

### 3.3.6 H<sub>2</sub> and CO formation

For the H<sub>2</sub> formation from adsorbed H atoms, the barrier on Ni@Pt is the lowest among the three surfaces with a value of 0.361 eV. In addition, this process is exothermic on Ni@Pt, while is endothermic on the other two surfaces. The exothermic reaction with low activation barrier suggests that H<sub>2</sub> is much easier to form on Ni@Pt surface. Energy profiles for H<sub>2</sub> formation on three surfaces are shown in Fig. 5a. CO is the other dominant final product in methane dehydrogenation and reforming process. The CO adsorption site and adsorption heat are shown in Fig. 5b. Compared with the Ni(111) and Pt(111) surface, the lowest CO adsorption heat occurs on Ni@Pt, indicating that CO is more likely to desorb on this surface. Therefore, the Ni@Pt structure is a good catalyst candidate beneficial for both H<sub>2</sub> and CO formation.

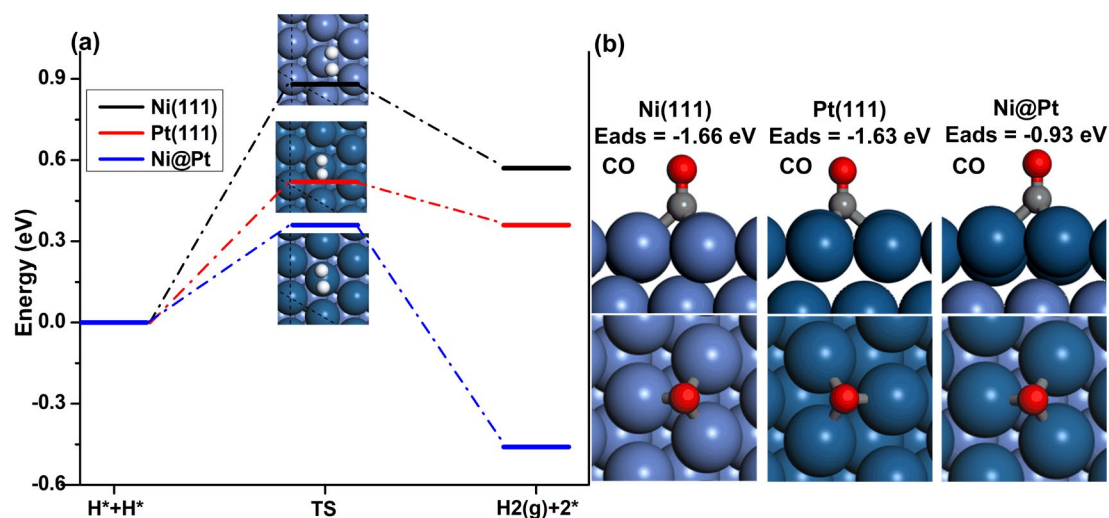
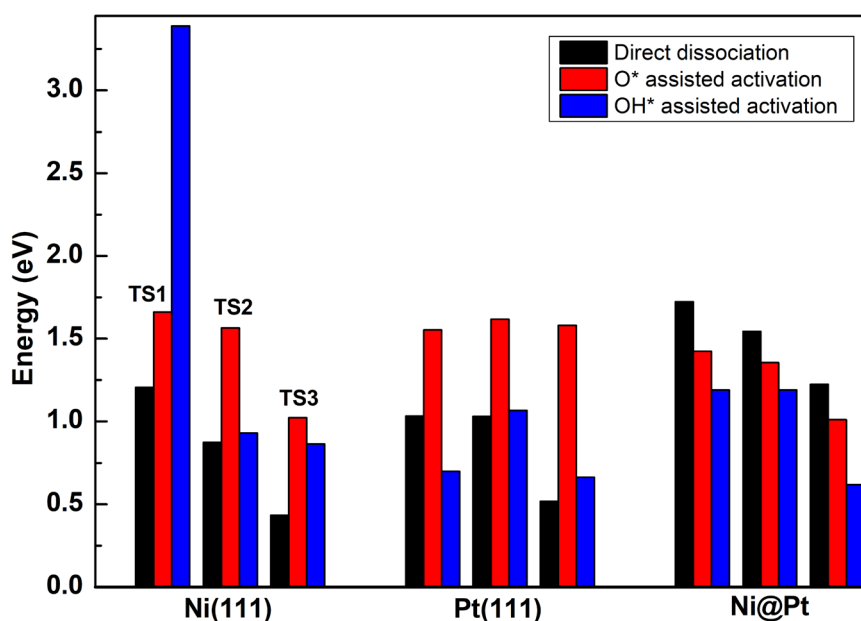


Fig. 5. (a) Energy profiles for H<sub>2</sub> formation and (b) CO adsorption on Ni(111), Pt(111) and Ni@Pt.

### 3.3.7 Reaction pathways

The dependence of the reaction pathways has been investigated by analyzing the free energy profiles of various pathways. There are many possible reaction pathways, which can be classified into the activation of CH<sub>x</sub> (x = 2-4) by direct dissociation, O\* and OH\* activation. Here we screen out the possible reaction pathways first by a simple analysis of the

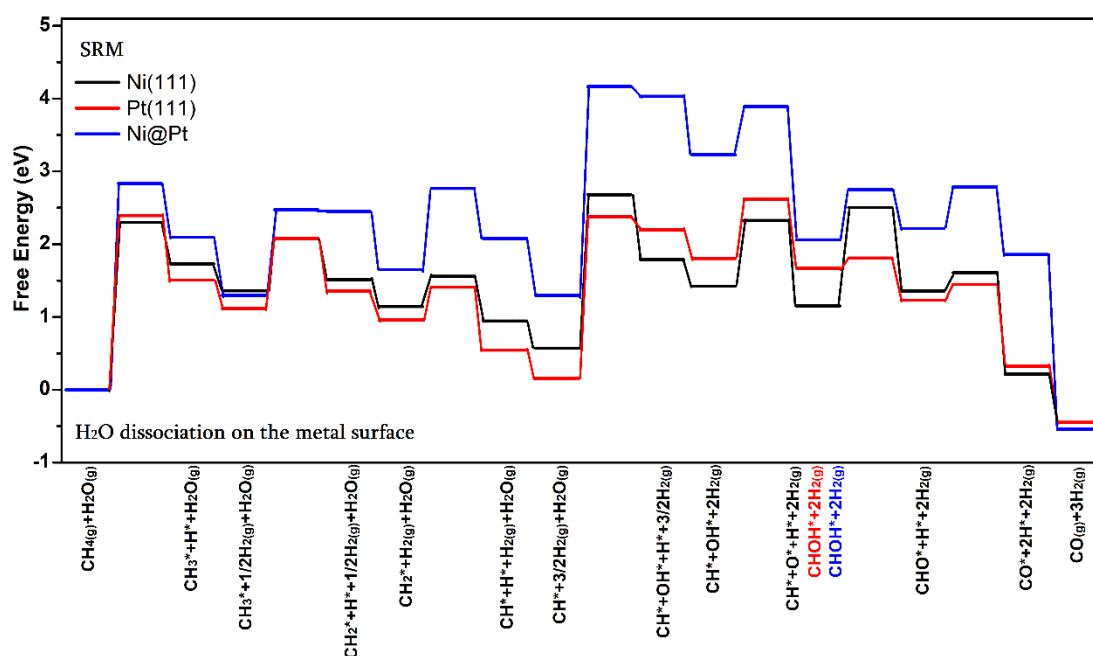
1 activation energies of the corresponding elemental steps, as shown in Fig. 6. We found that  
 2 on Ni(111), direct dissociation way is most favorable in three dehydrogenation steps, while  
 3 on Ni@Pt, OH\*-assisted CH<sub>4</sub> activation into CH proceeds more easily in three  
 4 dehydrogenation steps. On Pt(111), for the first C–H bond activation, OH-assisted way  
 5 presents the lowest energy barrier, while for the second and third C–H bond activation, direct  
 6 dehydrogenation way shows a little bit lower energy barrier. In addition, OH\* assisted  
 7 activation of CH<sub>x</sub> is energetically more favorable compared to O\* assisted activation.  
 8 Therefore, the O\* assisted activation pathways were excluded in the next analysis.



9  
 10 **Fig. 6.** Energy barriers for CH<sub>4</sub> activation into CH of three pathways. TS1: CH<sub>4</sub> activation; TS2: CH<sub>3</sub>  
 11 activation; and TS3: CH<sub>2</sub> activation.

12 The rate-determining step in the methane steam reforming on metal surface is still in  
 13 debate and unclear. CH oxidation by OH\* [20] and methane dissociation [54,60,61] have  
 14 been often proposed as the rate-determining steps (*RDS*). It has been reported that the rate-  
 15 determining step depends on the temperatures [62] and pressures [12]. It is generally agreed  
 16 by DFT [60] and experimental results [54] that the methane dissociation is the rate-  
 17 determining step at relatively high temperatures. In addition, experimental observation  
 18 demonstrated that the forward rate is first order with respect to the methane partial pressure

1 and that it does not depend on the partial pressure of water in SRM, and C–H bond activation  
 2 is the sole kinetically relevant step [54]. The free energy profiles of the reaction pathway  
 3 based on the direct dissociation of  $\text{CH}_x$  and following surface oxidation of CH were plotted in  
 4 Fig. 7. The highest free energy located at the step of  $\text{H}_2\text{O}$  dissociation suggesting  $\text{H}_2\text{O}$   
 5 activation as the *RDS*, which is contrast to the experimental observation. In addition, the  
 6 results from the free energy profiles suggest that the rate-determining step depends on the  
 7 steam activation. On metal surfaces in Fig. 7, activation of steam has a large energy barrier  
 8 mostly caused by an entropy change.

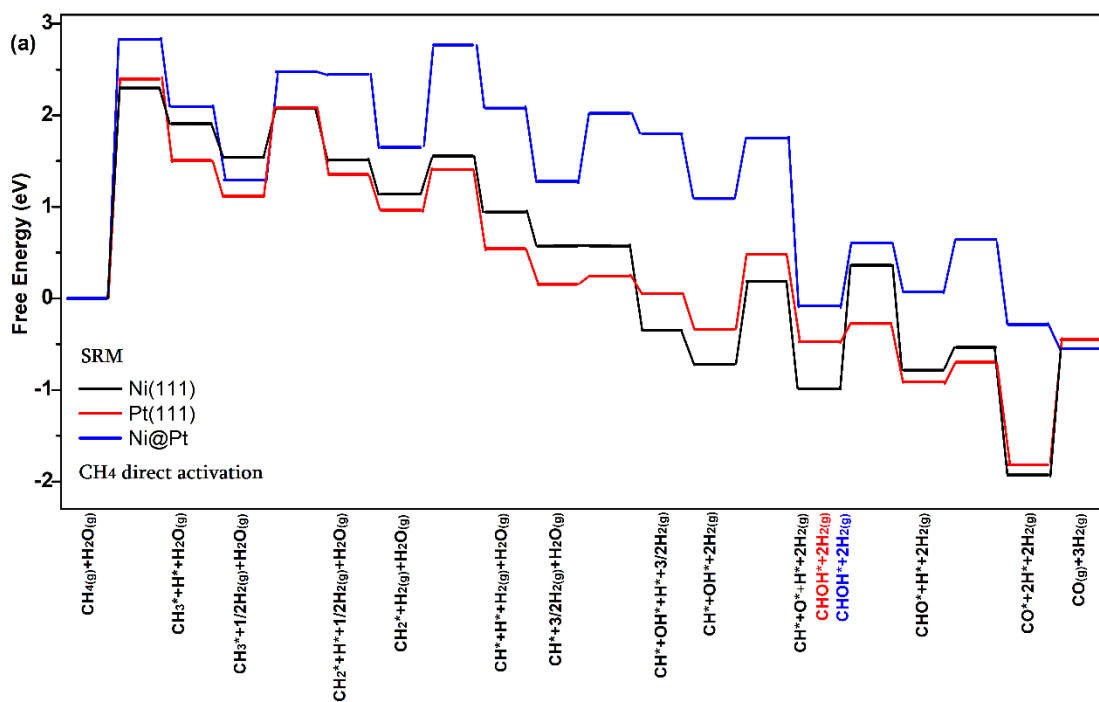


9  
 10 **Fig. 7.** Free energy landscape and dominant reaction mechanisms in SRM on Ni(111), Pt(111) and Ni@Pt,  
 11  $\text{H}_2\text{O}$  dissociation on the metal surface. Reaction conditions:  $P_{\text{CH}_4} = 0.5$  bar,  $P_{\text{H}_2\text{O}} = 0.5$  bar,  $T = 1000$  K.

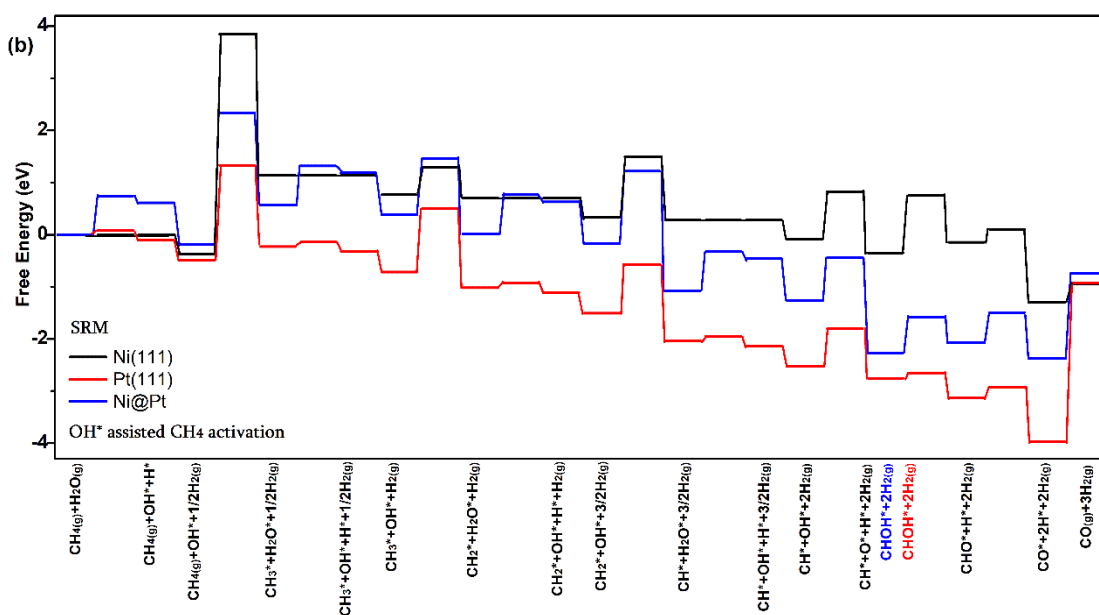
12 It should be noticed that water dissociation is more likely to proceed on the support  
 13 instead of metal surface [63–66]. In addition, DFT studies on water dissociation over  $\text{TiO}_2$   
 14 [64],  $\text{Al}_2\text{O}_3$  [65], and  $\text{MgO}$  [66] surface showed significantly lower barriers ( $< 0.3$  eV).  
 15 Moreover, surface area of support is relatively large, it is expected that  $\text{OH}^*$  is rich on the  
 16 support, which could serve as a resource immigrating to metal surface. However, this  
 17 important experimental observation has not been taken into account in any DFT assisted  
 18 mechanistic studies. Although it might be a small free energy for activation of steam on

1 support and surface diffusion to metal, here we simplify and treat it as an extreme case of  
2 zero entropy change of steam activation on metals. It means that OH\* on metal surface is  
3 possibly equilibrated with OH\* on the support, and there is no entropy changes.

4 By the assumption of steam activation on supports and zero entropy change, the free  
5 energy profiles of reaction pathways of methane direct dissociation and OH\* assisted  
6 activation in SRM on three metal surfaces at 1000 K, are plotted in Fig. 8. In the CH<sub>4</sub> direct  
7 dissociation pathway (Fig. 8a), the oxidation of CH has priority over CH decomposition on  
8 all three surfaces, according to the previous study in this paper. Thus, the dominant pathway  
9 for CH oxidation to form CO follows the mechanisms: on Ni(111), CH\* + O\* → CHO\* + \*  
10 → CO\* + H\*; on Pt(111) and Ni@Pt, CH\* + OH\* + \* → CHOH\* + 2\* → CHO\* + H\* + \* →  
11 CO\* + 2H\*. For Ni(111) and Pt(111) surfaces, the highest the free energy is the step of CH<sub>4</sub>  
12 dissociation, it suggests that the CH<sub>4</sub> adsorptive dissociation is the rate determining step,  
13 which has been confirmed in our experimental work [67], the H<sub>2</sub> reaction order is close to  
14 zero. It is interesting to note that the rate-determining step has been changed from CH  
15 oxidation to CH<sub>4</sub> adsorptive dissociation when the steam activation changed from the metal  
16 surface to supports. It reveals that the support could play an important role in determining the  
17 RDS.



1



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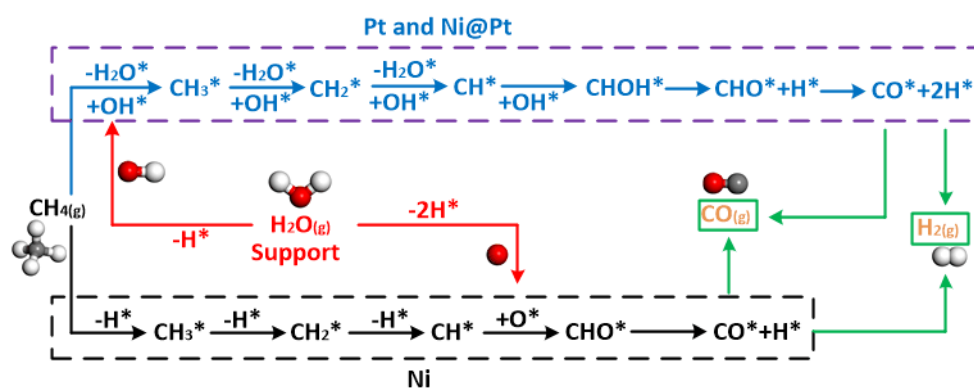
3 **Fig. 8.** Free energy landscape and dominant reaction mechanisms in SRM on three surfaces: (a) CH<sub>4</sub> direct  
 4 dissociation way; and (b) OH\*-assisted CH<sub>4</sub> activation way. Reaction conditions: P<sub>CH<sub>4</sub></sub> = 0.5 bar, P<sub>H<sub>2</sub>O</sub> = 0.5  
 5 bar, T = 1000 K.

6 For OH\*-assisted CH<sub>x</sub> activation pathway (Fig. 8b), the OH\* assisted methane  
 7 dissociation on Ni(111) has a much higher maximum free energy, but a lower maximum free  
 8 energy on Pt(111) compared to methane direct dissociation pathways. It suggests that the  
 9 OH\* assisted reaction pathways is dominating on Pt(111) and methane direct dissociation is



1 dominating on Ni(111). OH\* assisted methane dissociation is the rate-determining step on  
 2 both surfaces. On Ni@Pt surface, the free energy for the reaction pathway of direct  
 3 dissociation of CH<sub>x</sub> (Fig. 8a) is significantly higher than the OH\* assisted pathway (Fig. 8b).  
 4 It suggests that the OH\* assisted CH<sub>x</sub> activation pathway is the dominating one on Ni@Pt  
 5 surface.

6 We have obtained the dominant reaction routes on three catalysts, as depicted in Fig. 9.  
 7 It is clearly seen that CH<sub>4</sub> activation proceeds in direct dissociation way on Ni, while OH-  
 8 assisted CH<sub>4</sub> activation acts the dominant way on Pt and Ni@Pt.



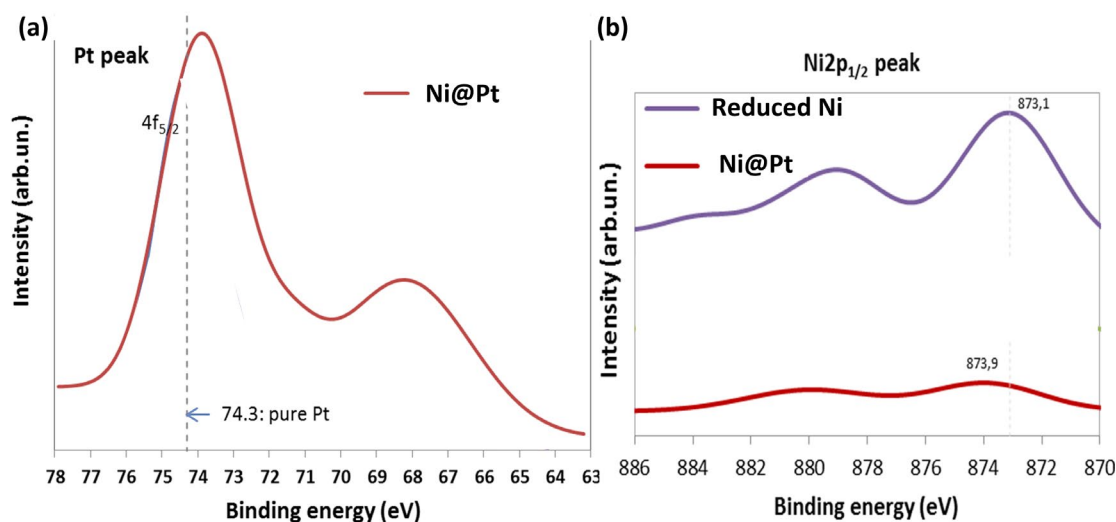
9  
10 Fig. 9. Dominant reaction routes on three surfaces.

### 11 3.4 Experimental study

#### 12 3.4.1 Characterization of catalysts

13 **XPS:** It is noteworthy that Pt electronegative elements in relation to Ni and hence Pt  
 14 atoms could produce an electron withdrawing effect from the neighboring Ni atoms bringing  
 15 about the polarization of the Pt–Ni bonds between first layer and second layer in the  
 16 bimetallic particle, which would cause a negative shift in the binding energy of the 4f<sub>5/2</sub>  
 17 signal of the Pt<sup>0</sup>. The XPS spectrum (Fig. 10a) for the bimetallic Ni@Pt catalysts clearly  
 18 shows one peak assigned to Pt4f<sub>5/2</sub> spectra of metallic Pt, in which its binding energy shifted  
 19 to the lower level of 73.9 eV. Binding energy of Ni2p<sub>1/2</sub> in Ni@Pt catalysts shifted to the  
 20 higher level. It clearly indicates charge transfer from Pt to Ni in the core-shell structured  
 21 Ni@Pt, which is in good agreement with DFT prediction that the core-shell Ni@Pt catalyst

1 modified the surface Pt electron density and shifted d-band center away from Fermi level  
 2 compared with Ni(111). Moreover, it is evidently observed of suppression of Ni2p<sub>1/2</sub> peaks in  
 3 Ni@Pt catalysts (Fig. 10b) when second metal Pt deposited on the Ni surface by replacing Ni,  
 4 suggesting Pt is mostly on the particle surface.



5  
 6 **Fig. 10.** XPS spectra of the Ni@Pt catalyst (a) Pt4f<sub>5/2</sub>; and (b) Ni2p<sub>1/2</sub>.

7 **H<sub>2</sub> chemisorption and TEM:** The active surface area of Ni and Ni@Pt catalysts was  
 8 calculated from the quantity of hydrogen uptake. Compared with pure Ni catalysts, addition  
 9 of Pt into Ni-HT catalyst causes a decreasing trend in the amount of hydrogen chemisorbed,  
 10 thus showing a decrease in metallic surface area, the details are provided in Table 3.

11 **Table 3**

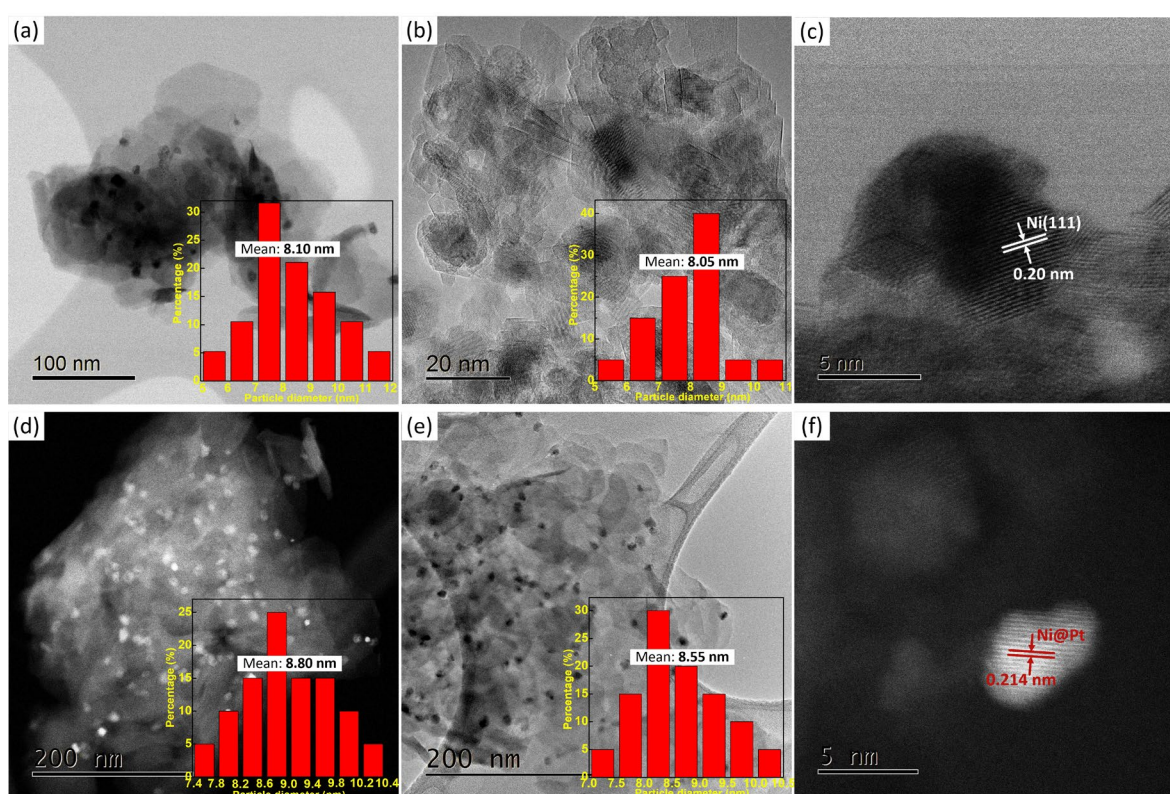
12 Metallic surface area from H<sub>2</sub> chemisorption and lattice distance from TEM images and DFT calculations.

Catalyst	Metallic Surface Area [m <sup>2</sup> /g <sub>metal</sub> ]	TEM Lattice distance [nm]	DFT Lattice distance [nm]
Ni	40.74	0.200	0.216
Ni@Pt	29.96	0.214	0.225
Pt		0.230*	0.239

13 ♣: Ref [68].

14 In addition, Fig. 11 shows the TEM images of Ni and Ni@Pt catalysts. Specifically, Fig.  
 15 11a and 11b indicate that the average particle size of Ni catalysts is around 8.10 nm, and Fig.  
 16 11d and 11e suggest that the average particle size of Ni@Pt catalysts is around 8.80 nm,

1 which is in good agreement with that the metallic surface area decrease from Ni to Ni@Pt. In  
 2 addition, fringes of 0.200 nm [69] of metallic Ni<sup>0</sup> and 0.214 nm of Ni@Pt were attributed to  
 3 (111) planes of Ni and Ni@Pt catalysts, as depicted in Fig. 11c and 11f, respectively. In  
 4 addition, it can be concluded that the lattice distance of Ni@Pt is between monometallic ones,  
 5 and the results from TEM images and DFT models are in good agreement. Combined lattice  
 6 distance from TEM images and DFT models and peak shift of XPS spectrum, it indicates that  
 7 we have successfully synthesized Ni@Pt catalysts.



8  
 9 **Fig. 11.** TEM images of Ni (a) fresh sample, (b) reduced sample, and (c) Ni surface lattice distance; and  
 10 Ni@Pt (d) (e) reduced sample, and (f) Ni@Pt surface lattice distance.

### 11 3.4.2 Kinetic study of SRM on Ni and Ni@Pt catalysts

12 The turnover frequency  $TOF_{Exp}$  is calculated from the initial reaction rate ( $r_i$ ) and Ni  
 13 dispersion (D), as shown below:

$$14 \quad r = \frac{X \cdot F}{W} = \frac{X \cdot F}{W \cdot 22414 \cdot 60} \cdot \frac{273.15}{298.15} (\text{mol} \cdot \text{s}^{-1} \cdot \text{g}_{cat}^{-1}) \quad (5)$$

$$TOF_{Exp} = \frac{r_i M_{Ni}}{f_{Ni} D} \quad (6)$$

where  $X$  is the conversion,  $F$  is the gas flow rate,  $W$  is the catalysts weight,  $M_{Ni}$  is the molecular weight of Ni,  $f_{Ni}$  is the Ni weight fraction of the catalysts. The dispersion  $D$  was estimated based on the surface area of metal measured by hydrogen chemisorption.

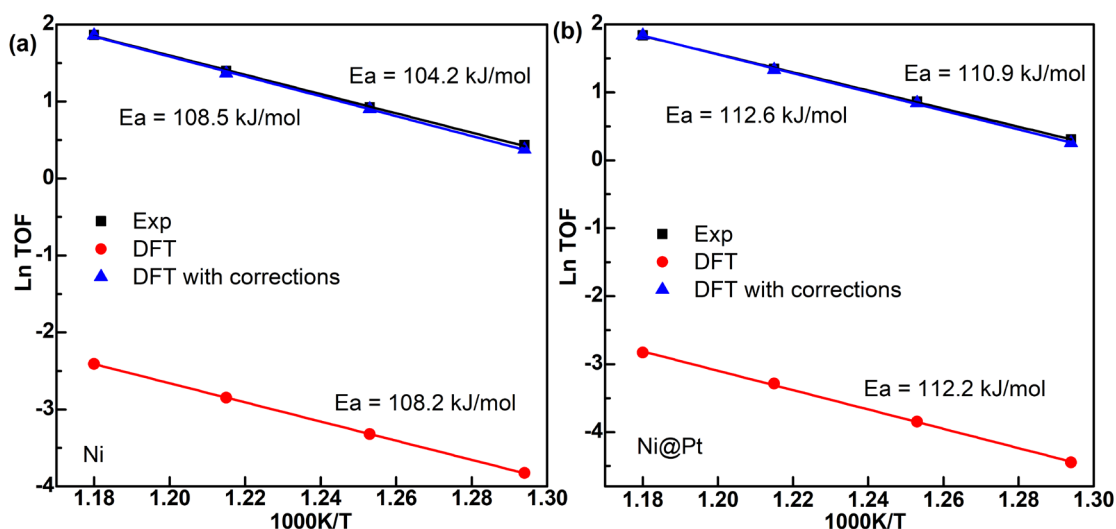
In addition, based on previous DFT calculations and G plot, we select the lowest energy pathway for SRM on Ni and Ni@Pt, namely CH<sub>4</sub> direct activation way and OH-assisted activation way, respectively, the temperatures of 773 K, 798 K, 823 K and 848 K applied for kinetic relevant steps to compare with the experiment results. The turn over frequency could also be calculated as follows based on the highest point of G plot, this point is determined by TS of CH<sub>4</sub>—CH<sub>3</sub>+H for Ni and CH<sub>4</sub>+OH—CH<sub>3</sub>+H<sub>2</sub>O for Ni@Pt in this paper, which due to CH<sub>4</sub> activation step is the *RDS*:

$$TOF_{DFT} = \frac{k_b T}{h} \exp\left(\frac{-\Delta G}{RT}\right) P_{CH_4} P_{H_2}^n \theta^{*2} \quad (7)$$

where  $k_b$  is the Boltzmann constant,  $T$  is the reaction temperature,  $h$  is the Planck constant,  $\Delta G$  is the highest point of the G plot in Fig.12,  $R$  is the gas constant,  $P_{CH_4}$  is the partial pressure of CH<sub>4</sub>, and  $P_{H_2}$  is the partial pressure of H<sub>2</sub>, due to the first C–H bond activation is regarded as the *RDS*, here reaction order for H<sub>2</sub>  $n = 0$ . The experiments are performed at relatively low pressures and high temperatures, and site vacancy ( $\theta^*$ ) is assumed close to 1.

Fig. 12 shows the Arrhenius plot and effective activation energy generated from experimental and DFT study over Ni and Ni@Pt. It can be clearly seen that two Arrhenius plots drawn from experimental and DFT studies are almost parallel on both Ni and Ni@Pt catalysts. The measured experimental effective activation energy of 104.2 kJ/mol for SRM on hydrotalcite-derived Ni catalysts in present work agrees well with the reported values of 103.6 kJ/mol at Ni/Mg(Al)O [67] and 102 kJ/mol at Ni/Al<sub>2</sub>O<sub>3</sub> [54]. The effective activation energy calculated from G plot here (108.2 kJ/mol) is rather in good agreement with the

1 experimental one (104.2 kJ/mol). Moreover, the effective activation energy is estimated from  
 2 DFT assisted kinetic analysis (112.2 kJ/mol) is also consistent with the experimental value  
 3 (110.9 kJ/mol) on the Pt@Ni catalysts.



4  
 5 **Fig. 12.** Arrhenius plot and apparent activation energy generated from experiment and DFT over (a) Ni  
 6 and (b) Ni@Pt. Reaction conditions: S/C=3.5, CH<sub>4</sub>/H<sub>2</sub>=1.0, W/F<sub>0</sub> between 0.018 and 0.037 mol.g. s<sup>-1</sup>.

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 8 The pre-exponential factors were obtained from the Arrhenius plots as shown in [Table 4](#)  
 9 based on the DFT assisted kinetic analysis. The effective entropy changes was also estimated  
 10 from the pre-exponential factors based on the transition state theory. It is clearly seen ([Table](#)  
 11 [4](#)) that effective entropy change on Ni is larger than that on Ni@Pt. The effective entropy  
 12 change is mostly related to the change between the transition state of methane activation and  
 13 the gas phase methane. The smaller effective entropy change indicates the weaker adsorption  
 14 of the transition state complex on Ni@Pt compared to Ni, which could be attributed to that  
 15 the *d*-band center of Ni@Pt is more far away from Fermi-level than that of Ni(111). It results  
 16 also in a slightly higher effective activation energy on Ni@Pt than Ni. The estimated pre-  
 17 exponential factors from DFT calculation ([Table 4](#)) are similar to the reported value [70]. The  
 18 compensation between the entropy change and the effective activation energy makes Ni@Pt  
 19 without significant scarifying activity (TOF) compared to Ni.

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**Table 4**

Entropy changes and pre-exponential factor before and after corrections at 773 K.

Catalyst	Entropy change $\Delta S$ [J/(mol·K)]	Pre-exponential factor [s <sup>-1</sup> ]	Entropy change after corrections $\Delta S$ [J/(mol·K)]	Pre-exponential factor after correction [s <sup>-1</sup> ]
Ni	- 109.80	$2.96 \times 10^7$	- 75.21	$1.90 \times 10^9$
Ni@Pt	- 82.76	$7.65 \times 10^8$	- 42.82	$9.33 \times 10^{10}$

In addition, such good agreement between DFT prediction and experimental effective activation energy could support the different mechanisms proposed by DFT calculations, namely CH<sub>4</sub> activation on Ni, while OH\* assisted CH<sub>4</sub> activation on Ni@Pt. However, there is obvious deviation of the DFT predicted TOF from the experimental ones, but the two curves in Arrhenius plots are parallel. We tune the effective entropy change as a sole parameter to fit the experimental TOSs. The corrected effective entropies for both catalysts are summarized in Table 4. The new free energy profiles after effective entropy corrections are shown in Fig. S10. The corrected kinetic model describes the experimental data satisfactorily. The corrected effective entropy is about 34 and 40 J/(mol·K) smaller than DFT predicted entropy for Ni and Ni@Pt, respectively. It should be noticed that the DFT calculation is only on ideal surface of Ni(111). Although the particle size is relatively large and Ni(111) surface is dominating, Ni(100) and Ni(211) could also contribute to the reaction. The correction of effective entropy change might include the contribution of different surfaces.

### 3.4.3 Coke formation rate on Ni and Ni@Pt catalysts

Moreover, we have performed the temperature programmed oxidation (TPO) analysis (Fig. S11) for both Ni and Ni@Pt samples to obtain the coke formation rate. The results shows that the total amount of coke formation for Ni after 4.5 hrs running is around 20 wt% of initial catalysts, while for Ni@Pt after 5.1 hrs running it is decreasing 13 wt%. Due to the

1 carbon formation is very low, here we assume that total amount of coke increases linearly as  
2 time goes by. Therefore, the coking rate for Ni catalyst is around  $0.044 \text{ mg}_{\text{coke}}/(\text{mg}_{\text{cat}}\cdot\text{h})$ ,  
3 while for Ni@Pt it is decreasing to  $0.026 \text{ mg}_{\text{coke}}/(\text{mg}_{\text{cat}}\cdot\text{h})$ , thus Ni@Pt catalyst shows the  
4 better anti-carbon formation ability compared to monometallic Ni, which is in good  
5 agreement with our DFT predictions in section 3.3.5.

6

#### 7 **4. Conclusions**

8 The mechanisms of steam reforming on Ni, Pt and single layer core-shell structured  
9 Pt@Ni catalysts are examined by combining DFT calculations, experimental kinetic study  
10 and DFT assisted kinetic analysis. The monolayer core-shell structured Ni@Pt catalyst was  
11 successfully prepared by surface redox reaction between surface Ni and Pt cations. We  
12 demonstrated experimentally core-shell structured Ni@Pt significantly lowered carbon  
13 formation without reducing very much the reaction rate. The DFT results revealed that  
14 introducing Pt atoms into Ni surface forming Ni@Pt makes the curves of PDOS broad and *d*-  
15 band center shifted away from Fermi level compared with Ni(111) and Pt(111), which could  
16 lead to weakening the binding strength between adsorbates and metal surface. It is found that  
17 CH decomposition into C + H barrier on the Ni@Pt remarkably increases to around 1.979 eV.  
18 Furthermore, Ni@Pt provides much less energy-demanding pathways for both CH and C  
19 oxidation. Therefore, CH is much energetically favored to be oxidized rather than cracking  
20 into carbon on this surface, meanwhile, Ni@Pt is beneficial for carbon elimination and shows  
21 promising anti-carbon formation performance. In addition, mechanistic study reveal a crucial  
22 role of steam activation on supports in determining favorable reaction pathways. It indicated  
23 that the mechanism with steam activated on support is in good agreement with the  
24 experimental observation. Among three methane activation pathways examined, CH<sub>4</sub> direct  
25 dissociation is energetically favorable on Ni, while OH\* assisted methane activation is the

1 dominating reaction pathway on Pt and Ni@Pt. In addition, a DFT assisted kinetic analysis is  
2 introduced to efficiently elucidate the rate-determining step and directly estimate the reaction  
3 rate from the free energy profile based DFT calculated energetics. The estimated effective  
4 activation energy is in good agreement with experimental ones on both Ni and Ni@Pt. The  
5 approach introduced in this contribution can efficiently improve the model predictions to  
6 achieve excellent agreement with experimentally measured kinetic data.

7

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