A theoretical study of water adsorption and dissociation on Ni(111) surface during oxidative steam reforming and water gas shift processes

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ABSTRACT

Density functional theory (DFT) calculations were performed to investigate the adsorption of water (H$_2$O) on Ni(111) surface and the corresponding dehydrogenation reaction during oxidative steam reforming. The equilibrium configuration on top, bridge, and hollow (fcc and hcp) site was determined by relaxation of the system. The adsorption of H$_2$O on top site is favorable on Ni(111) surface, while the adsorptions of OH, H and O on hollow (fcc) site is preferred. The adsorbates are adsorbed on the nickel surface due to the interaction between p orbital of adsorbates and d orbital of nickel atoms, and the interaction is manifest on the first layer than that on any others. The dehydrogenation reaction of H$_2$O on clean and oxygen-covered nickel surface was also investigated. The results show that the dissociation energy of H atom is 72.95 kJ mol^{-1} on clean nickel surface. While dissociation energy decreases to 69.86 kJ mol^{-1} with the aid of pre-adsorbed O atom (O$_{ads}$). These phenomena indicate that the energy barrier of dehydrogenation on the pre-covered oxygen nickel surface is lower and O$_{ads}$ can promote the dehydrogenation of H$_2$O.

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1. Introduction

Water (H$_2$O) is one of the most widespread substances on our planet, which involves many chemical processes [1]. For decades some efforts have been devoted to the adsorption of H$_2$O on surfaces of metal catalyst such as Au(111) [2], Cu(110) [3], W(111) [4], Ag(100) [5], and Pd(111) [6]. Compared to these metals, nickel (Ni) has the catalytic ability of dissociating H$_2$O into OH and H [7]. In addition, its hydroxide compounds (Ni–OH) are widely used [8]. Furthermore, Ni is selected as a catalyst for some reactions, such as partial oxidation [9–11], steam reforming [12–15], methanation [16–18], water gas shift (WGS) [19–21] and oxidative steam reforming [22–26]. Furthermore, Ni is a convenient catalyst not only for the dissociation of CH$_4$ [26] and CO [27], but also for H$_2$ production through the catalytic steam reforming reaction. However, steam is added to avoid coke formation, which may lead to the catalyst deactivation. It is indicated that an additional WGS is needed to eliminate CO. For a net reaction, although it reduces the efficiency while increasing the cost of the overall alternative processes have been investigated [28]. Finally, Ni is appealing for possible hydrogen storage applications due to its ability to dissociate molecular hydrogen on an alloy surface to form a metallic interstitial hydride [29,30]. So it is necessary to investigate the dissociation of H$_2$O on Ni(111) metal surfaces. There are just a few papers in literature about DFT studies of water on Ni(111) [7]. About the dissociation products of H$_2$O, the interaction of H on metal surfaces was studied and reviewed by Christmann [31–33]. Regarding H on Ni(111), despite some papers reporting experimental studies spanning some 40 years [34], surprisingly there are just a few primary principles theoretical papers [34–38]. Available theoretical literatures for Ni(111) surfaces regarding the other water dissociation products (O, OH) are even sparser [7,35,39–42], while several experimental studies have been reported [8,41,43–46]. Nonetheless, it is striking that in none of all the above listed theoretical papers a fully consistent investigation with DFT on both H$_2$O and its dissociation products (H, O, OH) on Ni has already been presented. Therefore, knowledge about how H$_2$O participates in these processes will be helpful and prerequisite to reveal the mechanisms of these reactions.

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In this work, the adsorption site of H_2O and its dehydrogenated fragments on Ni(111) surface, and the interaction between the adsorbates and Ni atom were investigated. The dehydrogenation on clean and oxygen-covered Ni(111) surfaces was investigated to discover the mechanism of H_2O dissociation, respectively.

2. Computational methods

All density functional theory (DFT) calculations were performed using the DMol^3 package. The generalized gradient approximation (GGA) functional [47], developed by Perdew and Wang (PW91) [48], was employed. Calculations were performed using a 310 eV cut off energy and a $4 \times 4 \times 1$ k-point sampling grid. A (2×2) surface unit cell with a slab of four layers' thickness (16 Ni atoms per super cell) was selected as a model. Lattice constant of Ni slab was given as 3.53 Å versus 3.52 Å experimentally. This slab was repeated periodically with a 15 Å of vacuum region between the slabs. Only one H_2O molecule per super cell was adsorbed on one side of the slab to reduce lateral interactions between adsorbates [thus the coverage was set to 1/4 monolayer (ML)]. The geometry optimization including all degrees of freedom of the adsorbates and the two topmost metal layers were considered. Reaction energy barriers and stretch frequencies of adsorbates were also calculated. The double numeric quality (DNP) basis set with polarization functions was utilized, which corresponds to Gauss-type 6-31G** level. A Fermi smearing of 0.005 Hartree (Ha) was utilized to improve computational performance. The tolerances of energy, gradient, and displacement convergence was 2×10^{-5} Ha, 4×10^{-3} Ha/Å, and 5×10^{-3} Å, respectively. The max gradient for most of the optimized structures was less than 4×10^{-3} Ha/Å, and the k-point was set to $3 \times 3 \times 1$.

The adsorption energy (E_{ads}) was computed as the difference between the energy of the adsorbed molecule (E_A) and the sum of the free surface (E_S) and the corresponding gas-phase species (E_M) energies according to following:

$$E_{ads} = E_A - E_S - E_M \tag{1}$$

A negative value of E_{ads} indicates an exothermic chemisorption process. The transition state (TS) of the surface transformation was located on the potential energy hypersurfaces by performing a linear synchronous transit (LST) calculation [49], combined with a quadratic synchronous transit (QST) calculation and conjugate gradient refinements [50]. To complete the calculations of LST/QST, an LST optimization calculation was performed. TS approximation obtained by performing QST maximization. From that point, another conjugate gradient minimization was performed. The cycle was repeated until a stationary point was located.

Moreover, the reaction energy (ΔE) and the activation energy (E_a) are defined as follows:

$$\Delta E = E_P - E_R \tag{2}$$

$$E_a = E_{TS} - E_R \tag{3}$$

where E_P is the energy of the product in each reaction, E_R is the energy of the reactant in each reaction, and E_{TS} is the energy of the transition state in each elementary reaction.

3. Results and discussion

In order to reveal the mechanisms of dissociation and adsorption of H_2O on Ni surface, the adsorption structures of H_2O and OH were described firstly, and then the dissociation pathways of H_2O on different Ni surface were discussed in detail.

3.1. Adsorption of H_2O, OH, O and H

As shown in Fig. 1, H_2O is adsorbed at a top site on Ni(111) surface via the oxygen atom, and H_2O plane is almost parallel to Ni surface. As shown in Tables 1 and 2, compared the structural parameters of gas phase H_2O with those of adsorbed H_2O, the O—H distance changes little (the values are 0.969 and 0.979 Å, respectively), and the H—O—H angle also changes little (103.5° versus 103.6°). It can be concluded from these data that the change of adsorbed structure is negligible and the adsorption process is unactivated.

Calculated adsorption energies and equilibrium distances for the adsorption of OH on Ni(111) surface are also listed in Tables 1 and 2. The calculated adsorption energies of OH at bridge, hcp and fcc sites are −281.67, −279.72 and −295.04 kJ mol^{-1}, respectively. These results show that the fcc site is the most stable site for OH adsorbed on Ni(111) surface. As shown in Table 3, OH can obtain 0.264 e from the surface. The transferred electrons are mainly from the Ni 4s orbital because the 3d orbital are fully occupied. The fcc site is also the most stable site for O atom and H atom adsorbed on Ni(111) surface.

As shown in Table 1, on the most favorable adsorption sites, the adsorption energies for H_2O, OH, O and H, are −3.42, −295.04 and −524.01 kJ mol^{-1}, respectively, and the corresponding perpendicular distances from the O atom to the nickel surface are 2.216, 1.360 and 1.129 Å, respectively. It can be concluded that the interaction between these species and the nickel surface increase with the order of H_2O, OH, and O. Therefore, in the next sections, the most favorable adsorption sites of H_2O, OH, and O would be utilized to discuss the dissociation of H_2O molecule on Ni(111) surface.

3.2. Density of states of OH

Density of states (DOS) including partial density of states and layer-projected density of states can provide a fundamental understanding of the adsorbate−substrate interaction [51]. In Fig. 2, the partial density of states (PDOS) on the orbitals of O atom and the nearest neighbor Ni atom on the surface are illustrated. From −2125 to −1935 kJ mol^{-1}, the total DOS is mainly contributed by 2s orbital of adsorbed O(OH), while in other energy regions the total DOS is predominantly contributed by O 2p orbital. Inspecting the orbital contribution of Ni atom, from −1029 to 627 kJ mol^{-1}, the total DOS is predominantly contributed by Ni 3d orbital. There are hybridizations between Ni 4s and 3d