Full Length Article

Density functional theory study of acetic acid steam reforming on Ni(111)

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ABSTRACT

Catalytic steam reforming of bio-oil is a promising process to convert biomass into hydrogen. To shed light on this process, acetic acid is selected as the model compound of the oxygenates in bio-oil, and density functional theory is applied to investigate the mechanism of acetic acid steam reforming on the Ni(111) surface. The most favorable pathway of this process on the Ni(111) surface is suggested as $CH_3COOH^* \rightarrow CH_3COO^* \rightarrow CH_3CO^* \rightarrow CH_2CO^* \rightarrow CH_2^* + CO^* \rightarrow CH^* \rightarrow CHOH^* \rightarrow CHO^* \rightarrow CO^*$, followed by the water gas shift reaction to produce CO_2 and H_2. CH^* species are identified as the major carbon deposition precursor, and the water gas shift reaction is the rate-determining step during the whole acetic acid steam reforming process, as $CO^* + OH^* \rightarrow cis\text{-}COOH^*$ is kinetically restricted with the highest barrier of 1.85 eV. Furthermore, the formation pathways and initial dissociation of important intermediates acetone and acetaldehyde are also investigated.

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1. Introduction

Among various processing technologies of biomass, pyrolysis is especially suitable for distributed biomass conversion to produce liquid bio-oil as the major product [1,2]. The advantage of bio-oil is that it has a much higher energy density than biomass, making bio-oil easier to be reserved and transported. However, bio-oil needs to be hydro-processed to remove the excessive amount of oxygen and improve its heating value before it can be used as transportation fuels. Thus, a part of bio-oil needs to be reformed to produce the required amount of hydrogen [3]. Concerning the feasibility of bio-oil steam reforming process, Heracleous et al. [4] found that CO_2 emission of the biomass-derived hydrogen process is 50% less than methane steam reforming. Vagia et al. [5] pointed out that the total energy consumption between the steam reforming of bio-oil and methane were nearly the same. More importantly, the energy efficiency of bio-oil steam reforming is as high as 84% [6]. In addition,

it can take full advantage of the large amount of water in bio-oil *in situ* during bio-oil steam reforming.

During the experimental studies of bio-oil steam reforming, carbon deposition that results in catalyst deactivation was found to be the main problem [7–11]. Thus, to design a catalyst that simultaneously resists carbon deposits and provides high hydrogen yield has been the main objective of research in this field. To achieve these goals, it is worth illustrating the mechanism of the involved catalytic reactions. Bio-oil consists of more than 100 oxygenated compounds, including acids, ketones, alcohols, aldehydes, phenolic derivatives, and sugars. Here, acetic acid (HOAc), as one of the major compounds in bio-oil [12,13], is selected as the model compound of bio-oil considering from the following two aspects. Firstly, it is the smallest molecule that contains abundant chemical bonds, i.e. C—O, C—C, C—H, O—H and C=O; secondly, HOAc has the same C/O ratio as C6 sugars ($C_6H_{12}O_6$), which is one of the basic building blocks of biomass. Ni-based catalyst has been widely used in bio-oil steam reforming and HOAc steam reforming processes [10,11,14–17], because Ni catalyst shows an excellent activity on bond breaking performance of C—C, C—H and O—H of oxygenates [18,19].

The overall endothermic HOAc steam reforming reaction, $CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2$; $\Delta H^o_{298k} = 131.50$ kJ/mol, seems quite straightforward, whereas it is a complicated process indeed, involving HOAc decomposition, water decomposition, water gas

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shift (WGS), and the formation of some important intermediates, such as acetone and acetaldehyde.

Cheng et al. [20] and Hu et al. [21] pointed out that acetone produced during HOAc steam reforming was a carbon deposition precursor that caused catalyst deactivation. Hoang et al. [22] considered that coke formation resulted from two aspects, i.e. deep decomposition of HOAc and acetone formation. Nevertheless, only via experimental studies, the understanding of coke is limited to the deduction based on the experimental observations. The theoretical evidence closely linked to carbon deposition is still lacking, such as the source of coke, the mechanism of coke formation and the carbon deposition precursors. Wang et al. [23] studied the mechanism of HOAc decomposition on Co(111) and found that the minimal energy pathway was $CH_3COOH^* \rightarrow CH_3COO^* \rightarrow CH_3CO^* \rightarrow CH_3^* + CO^*$. Li et al. [13] systematically studied the mechanism of HOAc decomposition on Co stepped surface, including the acetone formation reactions by density functional theory (DFT) calculations. According to their study, $CH_3COOH^* \rightarrow CH_3CO^* \rightarrow CH_2CO^* \rightarrow CH_2^* \rightarrow CH^*$ is the most favorable decomposition pathway and CH_3CO^* dehydrogenation is the rate-determining step (RDS). However, the most favorable reaction pathway of HOAc steam reforming and the coke formation mechanism encountered in this process on Ni-based catalyst have not been studied in detail.

Since the Ni(111) surface is considered as one of the most stable and catalytic active surfaces and has been studied by many researchers [24–26], DFT calculations were applied to explore the mechanism of HOAc decomposition on the Ni(111) surface. All of the possible dissociation pathways are taken into account to identify the most likely decomposition pathway, the RDS, and more importantly, to identify the carbon deposition precursors. Moreover, the mechanism of the formation of the most important intermediates acetone and acetaldehyde and their initial dissociation reactions are also investigated. Since water plays an important role in the carbon elimination and the WGS reaction during HOAc steam reforming, therefore in this paper, a systematic study on water dissociation, carbon elimination and WGS are also developed. In summary, the primary purpose of this work is to shed insight on the mechanism of HOAc steam reforming on Ni-based catalysts by mapping out the structures and energies of the relevant intermediates at the molecular level.

2. Calculation methods

DFT calculations were performed using Dmol^3 program package in Materials Studio 5.5, in which a double numerical polarization (DNP) basis set was used [27]. The Perde-Burke-Ernzerhof (PBE) within the generalized gradient approximation (GGA) [28] was applied to describe the exchange-correlation function. As Ni possesses the magnetic property and the gas phase species derived from HOAc contain unpaired electrons, spin polarization was considered during the Ni surface reactions and the gas phase radical calculations. The criterion of total energy, maximum displacement, and maximum force tolerances were converged at the values of 2×10^{-5} hartree (Ha), 5×10^{-3} Å, and 4×10^{-3} Ha/Å, respectively. The Methfessel-Paxton method [29] was applied in the calculations with a Femi smearing width of 0.001 Ha and the total energies were extrapolated to 0 K.

For surface model, a three-layer, $p(4 \times 4)$ periodic slab unit cell of the Ni(111) surface was established to represent the actual nickel-based catalyst. The bottom layer was constrained, while the top two layers were free to move. Also, a 20 Å vacuum thickness was used to avoid the interaction of adsorbates and periodic slab in the z direction. The Brillouin zone was sampled by a $3 \times 3 \times 1$ Monkhorst-Pack k-point mesh [30]. Transition state (TS) configuration was located

by a complete linear synchronous transit (LST) and quadratic synchronous transit (QST) method [31,32]. Adsorption energy E_{ad} was defined as the following equation:

$$E_{ad} = E_{adsorbate/slab} - E_{slab} - E_{adsorbate}$$

where $E_{adsorbate/slab}$ represents the total energy of adsorbate and slab, $E_{adsorbate}$ refers to the energy of gas-phase radical species, and E_{slab} means the energy of clean Ni(111) surface. According to the definition, a negative E_{ad} represents an exothermic process.

3. Results and discussion

3.1. Surface adsorption on Ni(111)

The most stable adsorption configurations of the reactants and intermediates on the Ni(111) surface were identified. Due to the multi-atomic system property of HOAc, there are many intermediates derived from different bond dissociation of HOAc and its subsequent dissociation species. The most stable adsorption geometries and the adsorption energies of these intermediates adsorbed on the Ni(111) surface are shown in Fig. 1 and Table 1.

3.1.1. H*, O* and C*

H*, O* and C*, as the single atomic species generated from HOAc dissociation, are most stably adsorbed on the fcc site of the Ni(111) surface, and the corresponding binding energies are −2.86 eV, −5.72 eV, and −6.85 eV, respectively. The computational bond lengths of adsorbed H, O, C atom with Ni atoms are 1.70 Å, 1.86 Å, and 1.77 Å, respectively, which is consistent with previous reports [26,33].

3.1.2. OH*

The hydroxyl produced via dehydroxylation of HOAc binds through O atom at the hcp site of Ni(111) forming an O−Ni bond distance of 2.00 Å. The adsorption process is greatly exothermic by 3.22 eV, which is in good agreement with reported results [34].

3.1.3. CO*

CO* prefers to bind at the fcc site with the linear CO molecule straightly perpendicular to the surface. The three C−Ni bond lengths are all 1.95 Å, and the adsorption energy is calculated to be −1.85 eV, which is close to the reported value of −1.89 eV [34].

3.1.4. CH_x^* (x = 1 - 3)

As the C−C bond cleavage products of HOAc and some C2 intermediates, CH_x^* (x = 1-3) tend to stably adsorb with C atom at the fcc site of Ni(111). With the increase of unsaturated bonds in C atom, the adsorption energies increase gradually, following the order: CH_3 (−1.98 eV) < CH_2 (−4.10 eV) < CH (−6.44 eV), and the high binding energies indicate that they are difficult to desorb from the surface. Meanwhile, the bond distances between C and Ni atoms are also gradually shortened in the order of CH_3 (2.11, 2.12, 2.13 Å) > CH_2 (1.91, 1.91, 1.98 Å) > CH (1.84, 1.84, 1.84 Å). This calculated adsorption configuration is in line with CH_x^* species from CH_4 dissociation [25].

3.1.5. H_2O^*

As shown in Fig. 1, water molecule is almost parallel to the Ni slab with its oxygen atom adsorbed on the top site of the Ni(111) surface. The optimized H−O−H angle is 104.44°, and the O−Ni bond length is 2.25 Å. The calculated binding energy is −0.40 eV, indicating water is weakly interacted with Ni catalyst and easy to desorb, which is in agreement with the previous findings [35].