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A theoretical study on the role of water and its derivatives in acetic acid steam reforming on Ni(111)



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ABSTRACT

Catalytic steam reforming of acetic acid can be divided into two steps, i.e. acetic acid decomposition followed by water gas shift. While theoretical studies have been devoted to these two individual reactions, the role of water and its derivatives in the reforming process, especially in CH₃COOH decomposition, remains largely unknown. In this study, a thorough investigation of the effects of the solvent water and its derived O^{*}/OH^{*} species on some key dehydrogenation steps on Ni(111) is carried out using density functional theory. The involved dehydrogenation species include O–H bond scission species H₂O^{*}, CH₃COOH^{*}, *trans*-COOH^{*} and C–H bond scission species CH₃CO^{*}, CH₃C^{*}, CH₂C^{*}. The results show that the pre-adsorbed O^{*}, OH^{*}, and H₂O^{*} species not only affect the adsorption stability of these species, but also influence their dehydrogenation reactivity. O^{*} and OH^{*} species can both enhance the O–H bond scission, and the promotional effect of O^{*} is superior to OH^{*}. Nevertheless, H-abstraction from C–H bond by O^{*} and OH^{*} are both hindered except for CH₃CO^{*} dehydrogenation in the presence of OH^{*}. Furthermore, the solvent water notably weakens O–H bonds, yet exhibits negligible effect on the C–H bond breakage. Analogously, the solvent effect of CH₃COOH^{*} on O–H bond scission is also investigated.

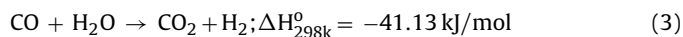
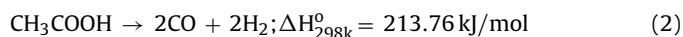
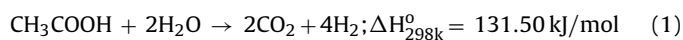
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1. Introduction

With the increasing demand for energy and growing awareness of environmental protection, the sustainable development of renewable biomass energy has attracted considerable attention in recent years. Bio-oil produced via biomass pyrolysis is highly oxygenated and requires deep hydrogenation before being used as transportation fuels. Thus large amount of hydrogen is needed and the hydrogen source becomes a research of interest [1,2]. Catalytic steam reforming of bio-oil itself can be a sustainable hydrogen source, because this process does not rely on the traditional fossil fuels as the starting materials [3–5]. Acetic acid is widely used as the model compound for studying bio-oil steam reforming, as it is one of the most abundant compounds and contains various functional groups that can represent the properties of bio-oil [6–9].

Nickel-based catalysts have been widely used in acetic acid steam reforming experimentally for its low cost, high stability and activity, and high hydrogen selectivity [10–13]. High hydrogen selectivity is always the ultimate goal of acetic acid steam reform-

ing. In fact, the efficiency of the hydrogen production depends on the activation of C–H and O–H bonds. Generally speaking, acetic acid steam reforming (1) can be basically divided into the following two reactions, i.e. acetic acid decomposition (2) and water gas shift reaction (WGS) (3) [14]:



From the total reaction Eq. (1), it is clearly understood that hydrogen originates from acetic acid and water via acetic acid decomposition and WGS, respectively. Meanwhile, two hydrogen-producing routes yield the equivalent amount of objective product H₂, indicating that the two paths are equally important. In Eqs. (2) and (3), water seems to be involved only in the WGS reaction, but unrelated to acetic acid decomposition. In fact, the role of water in the reforming system is of great significance. On the one hand, water is a key reactant, and based on our previous calculations [15], water derived O^{*} and OH^{*} species indeed play a crucial role in carbon elimination and WGS. On the other hand, water itself is fundamentally a solvent, where the solvent effect on the dissociation pathways can not be neglected.

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Regarding the effects of water derived active oxygen-containing species (O^* and OH^*) on dehydrogenation reactions, O^* and OH^* species commonly participate in the H-abstraction steps directly, yielding co-adsorbed OH^* and H_2O^* , respectively. Huang et al. [16] reported that in the presence of O^* and OH^* species, three dehydrogenation reactions are almost consistently promoted. In methanol steam reforming on Cu catalysts [17,18], the presence of co-adsorbed O^* and OH^* species not only altered the reaction pathways, but also decreased the activation barriers of some dehydrogenation steps. However, Syu et al. [19] found that surface oxygen species slightly elevated the reaction barriers of ethanol decomposition on Rh(111), either for O–H or C–H bond cleavage. Thus, the influence of water derived O^* and OH^* species on acetic acid decomposition remains ambiguous and worth studying in depth.

To our best knowledge, the role of water and its derivatives in acetic acid decomposition, especially in dehydrogenation steps, has not been systematically studied. Chang et al. [20–22] have done a series of work on the water promotion mechanism in heterogeneous catalysis. In methanol steam reforming on PdZn(111) [21], they pointed out that the solvent effect of water not only improved the adsorption stability of reaction species, but also reduced the activation energies of six dehydrogenation steps involving both O–H and C–H bond scission. Boucher et al. [23] revealed that the addition of hydrogen-bonded water complexes facilitated the O–H bond cleavage on copper catalysts, thus resulting in the conversion of methanol to formaldehyde. Nevertheless, the catalytic role of water for dehydrogenation steps has not reached a consensus. Density functional theory (DFT) calculations showed that with the presence of co-adsorbed water molecule on Rh(111), the O–H bond breakage of alcohols was favored, whereas the C–H bond breakage was inhibited [24]. The work by Zaffran et al. [25] studying polyalcohol dehydrogenation on several transition metal catalysts in the solvent water environment came to a similar conclusion. Furthermore, water just acts as a spectator without being involved in the H-abstraction reactions. The promotional role of water in dehydrogenation pathways is typically ascribed to the hydrogen bonding interaction with the dehydrogenation species.

In order to unravel the role of water on acetic acid decomposition on Ni(111), the effects of water derived O^* and OH^* species and the solvent water molecule on the dehydrogenation reactions are all considered in this work. Our previous study [15] indicated that two competitive decomposition pathways of acetic acid exist on Ni(111), that is, the ketene formation path: $CH_3COOH^* \rightarrow CH_3COO^* \rightarrow CH_3CO^* \rightarrow CH_2CO^* \rightarrow CH_2^* + CO^* \rightarrow CH^*$, and CH_3C formation path: $CH_3COOH^* \rightarrow CH_3COO^* \rightarrow CH_3CO^* \rightarrow CH_3C^* \rightarrow CH_2C^* \rightarrow CHC^*$, both followed with WGS: $CO^* + OH^* \rightarrow cis-COOH^* \rightarrow trans-COOH^* \rightarrow CO_2^* + H^*$. Therefore, we choose six key dehydrogenation routes of H_2O^* , CH_3COOH^* , $trans-COOH^*$ and CH_3CO^* , CH_3C^* , CH_2C^* to represent O–H bond and C–H bond breakage, respectively. To further explore the solvent effect on dehydrogenation reactions, the solvent effect of acetic acid on H-abstraction from O–H bond is also investigated. This work provides theoretical insights in how the solvents, water and acetic acid, affect acetic acid decomposition, and helps to gain an in-depth understanding of acetic acid steam reforming on Ni-based catalysts.

2. Computational methods

All periodic DFT calculations are carried out by using Dmol³ code [26,27] as implemented in the Materials Studio program package (version 5.5) from Accelrys. The electron exchange and correlation function are calculated within the generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) functional

Table 1

Adsorption energies E_{ad} /eV of the dehydrogenation species on the clean Ni(111), O/Ni(111), OH/Ni(111) and H_2O /Ni(111) surfaces.

Species	E_{ad} /eV			
	Ni(111)	O/Ni(111)	OH/Ni(111)	H_2O /Ni(111)
H_2O	−0.40	−0.58	–	−0.63
CH_3COOH	−0.41	−0.36	−0.29	−0.45
<i>trans</i> -COOH	−2.27	−2.15	−2.44	−2.46
CH_3CO	−2.10	−2.07	−2.02	−2.19
CH_3C	−5.66	−5.66	−5.38	−5.51
CH_2C	−4.22	−4.18	−4.01	−4.23

[28,29]. The localized double numerical basis set combined with polarization functions (DNP) is employed for all the atoms to expand the Kohn–Sham orbitals. DFT semi-core pseudopotentials (DSPP) [30] is applied to treat the core electrons of metal atoms. An orbital cutoff of 4.5 Å and a thermal smearing width of 0.001 hartree (Ha) are adopted with the total energies extrapolated to 0 K.

A Ni(111) surface is modeled by a periodic 4×4 supercells, three-layer slab with a vacuum thickness of 20 Å. The top two layers together with the adsorbates are free to relax, and the bottom layer is frozen. A Monkhorst–Pack k -point grid of $3 \times 3 \times 1$ is sampled for the Brillouin zone integration [31]. Considering the magnetic property of metallic Ni and the unsaturated intermediates, spin-polarized calculations are performed. The convergence criterion of total energy, maximum displacement, and maximum force tolerances are set to the values of 2×10^{-5} Ha, 5×10^{-3} Å, and 4×10^{-3} Ha/Å, respectively. The radical species in gas phase are calculated in $20 \times 20 \times 20$ Å³ cubic boxes. The adsorption energy E_{ad} of an adsorbate is calculated as follows:

For an isolated adsorbate adsorption,

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

For the co-adsorption of adsorbate and A (O, OH, or H_2O),

$$E_{ad} = E_{(adsorbate+A)/slab} - E_{A/slab} - E_{adsorbate}$$

where $E_{adsorbate/slab}$ and $E_{(adsorbate+A)/slab}$ represent the total energies of the adsorbate on clean and O^* , OH^* , or H_2O^* pre-adsorbed Ni(111) surface, respectively; E_{slab} and $E_{A/slab}$ are the energies of clean Ni(111) surface and O^* , OH^* , or H_2O^* pre-adsorbed Ni(111) surface, respectively; $E_{adsorbate}$ means the energy of radical species in gas phase. By these definitions, a negative E_{ad} value refers to an exothermic process. More negative E_{ad} values represent stronger adsorption states on the Ni(111) surface.

For an elementary reaction, the transition state (TS) is optimized by using the complete linear synchronous transit (LST) and quadratic synchronous transit (QST) approach [32,33]. The activation energy E_a is defined as the energy difference between the TS and the initial state (IS), and the reaction enthalpy change ΔH is the energy difference between the final state (FS) and the IS.

3. Results and discussion

The most stable adsorption configurations of H_2O , CH_3COOH , CH_3CO , CH_3C , CH_2C , and *trans*-COOH on the clean Ni(111), O/Ni(111), OH/Ni(111) and H_2O /Ni(111) surfaces are investigated. The corresponding adsorption energies are displayed in Table 1. To explore the regularity of dehydrogenation reactions, two dehydrogenation reaction modes are investigated during acetic acid steam reforming, i.e., H-abstraction from O–H bond and C–H bond.

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