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Mechanistic study of bio-oil catalytic steam reforming for hydrogen production: Acetic acid decomposition

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ABSTRACT

To clarify the understanding of the mechanism of bio-oil catalytic steam reforming, we selected acetic acid as a typical bio-oil model compound to study its detailed behavior in decomposition over an active stepped Ni surface by density functional theory calculations. The adsorption geometries and energies of various intermediates were reported. Linear correlations between the adsorption energy and the number of hydrogen atoms removed for CH_xCOOH , CH_xCOO , and CH_x species ($x = 1-3$) were found, with increments of -1.56 , -0.81 , and -1.80 eV, respectively. Thirty-seven possible elementary reactions of acetic acid decomposition were proposed, and their activation energies, reaction energies, rate constants, and equilibrium constants were calculated. Acetic acid dissociation likely started via α -carbon dehydrogenation, OH dehydrogenation, and dehydroxylation. Combined with microkinetic modeling, the most preferable decomposition pathway was suggested as $\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{CO} \rightarrow \text{CO} + \text{CH}_3$. The rate-determining step was CH_3COOH dehydroxylation to CH_3CO with an activation energy of 0.68 eV and a rate constant of $3.82 \times 10^8 \text{ s}^{-1}$. The formation of CH_3COO was dominant at high temperatures, whereas its decomposition occurred with difficulty.

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Introduction

Catalytic steam reforming of bio-oil is a prospective technology for renewable biomass-derived hydrogen production [1–4]. The liquid bio-oil is produced by fast pyrolysis of biomass with a high yield of 75 wt% [5]. Due to the easy transportability and storage of bio-oil, the hydrogen production can hopefully be centralized and scaled up, decreasing the cost of the hydrogen [6].

Numerous studies have been carried out on bio-oil catalytic steam reforming, especially focusing on the screening of the catalysts [7–10]. Ni and Co have been found to be two superior catalyst metals [11–14]. Because of high oxygen content, thermal instability, strong acidity, and complex composition of the bio-oil, the technology is constrained by the short period of stability and low efficiency of the catalysts [4,15–18]. Baviskar et al. studied the performance of Ni/Al₂O₃ catalyst for steam reforming of model bio-oil compounds 2-

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butanone, 1-methoxy-2-propanol, ethyl acetate and butyraldehyde, and found that the catalyst duration was less than 7 h even under high steam/carbon ratios in feed (15–25 mol/mol) [19]. Wu et al. reported that the catalyst deactivation caused by coke formation was a bottleneck in steam reforming of bio-oil [6]. Uncertainty of the reaction mechanism is one of the crucial factors to limit the development of catalysts.

Acetic acid (CH_3COOH) is a major component of bio-oil, which has an acetic acid content as high as 32 wt% [20]. Acetic acid is a simple chemical that contains all the types of C–C, C–O, C=O, C–H, and O–H bonds and is used as a probe molecule in many catalytic reactions [21–23]. Pu et al. carried out acetic acid steam reforming to test the performance of a series of ceria-promoted $\text{Ni@Al}_2\text{O}_3$ core-shell catalysts [24]. Wang et al. explored the effect of La_2O_3 replacement on Al_2O_3 supported Ni catalysts via acetic acid steam reforming [25]. Therefore, we selected CH_3COOH as a bio-oil model compound to carry out the mechanistic study.

Steam reforming of oxygenated organic molecules obeys a bifunctional mechanism on the metal-supported catalysts [20,26,27]. Organic molecules adsorb on the metal crystalline surface sites, followed by decomposition to carbonaceous residue via bond breaking. Water molecules adsorb on the support surface and dissociate into hydroxyl groups. Hydrogen is produced via the dehydrogenation of organics and the reforming of the carbonaceous residue with hydroxyl groups occurring at the metal-support boundary sites. Therefore, gaining insight into the detailed behavior of organic molecule decomposition on the metal surface is a key and first step in creating a clearer understanding of the overall mechanism of catalytic steam reforming.

Density functional theory (DFT) calculation is a high-efficiency quantum chemistry tool in mechanistic study, and DFT is widely used in homogeneous and heterogeneous catalytic reactions [28–30]. We have carried out a series of DFT calculations to explore the reaction mechanisms of bio-oil steam reforming to produce hydrogen. CH_3COOH decomposition over a stepped Co surface and a flat Co(111) surface was studied, and the potential energy profiles and favorable pathways were identified [13,31]. The decomposition pathway of CH_3COOH distinguishes between the stepped surface and the flat surface. On the flat surface, CH_3COOH dissociation likely starts from dehydrogenation of the OH group to acetate CH_3COO , whereas on the stepped surface CH_3COOH dissociation prefers to start from dehydroxylation to acyl CH_3CO . Another bio-oil model compound, formic acid, was selected to study its decomposition and microkinetic behavior [32]. The effects of solvents water, methanol, and acetone on the decomposition mechanism of formic acid were also investigated [33]. Furthermore, CH_3COOH , hydroxyacetone, furfural, and phenol dissociations and their subsequent reforming reactions with hydroxyl group over a flat Ni(111) surface were systematically calculated [12]. Ran et al. also carried out a mechanistic study of CH_3COOH steam reforming over a flat Ni(111) surface via DFT calculations [34]. The decomposition mechanisms of propionic acid, which occur through decarbonylation and decarboxylation over a Pt(111) surface, have been reported by Lu et al. [35,36].

However, to the best of our knowledge, CH_3COOH decomposition over a stepped Ni surface has not been reported. It is well recognized that stepped surfaces are the most active

facets of transition-metals for heterogeneous catalytic reactions [7,37,38]. Therefore, we performed DFT calculations and microkinetic modeling for CH_3COOH decomposition over the stepped Ni surface, which provides detailed reaction mechanisms and accurate kinetic and thermodynamic parameters of the elementary reactions. This calculation and modeling are helpful to have a clearer understanding of bio-oil catalytic steam reforming mechanisms.

Computational methods

The periodic DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) [39–41]. Spin polarization was included. The exchange-correlation energy was calculated by Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA). The cutoff energy for a plane wave basis was set to 400 eV. The convergence criterion for the electronic self-consistency and the forces on all atoms were set to 1×10^{-4} eV and 0.05 eV/Å, respectively. The Brillouin zones were sampled by the Monkhorst-Pack method with k meshes of $6 \times 6 \times 6$ and $3 \times 3 \times 1$ for bulk lattice optimization and surface calculations, respectively. The Methfessel-Paxton scheme with a sigma value of 0.1 eV was used at the Fermi-level. The optimized lattice constant of Ni is 3.517 Å, which agrees well with theoretical (3.518 Å) and experimental values (3.516 Å) [42]. The construction of the stepped Ni surface was the same as the construction of the Co-stepped surface, which was described in detail in our previous work [28,31]. A vacuum space of 15 Å was used to avoid periodic interactions.

The transition state (TS) was searched by the climbing nudged elastic band (CINEB) method [43,44], in which eight images were inserted between the initial state (IS) and final state (FS) of every elementary step. Every TS was confirmed by the existence of a unique imaginary frequency along the reaction coordinate. All the calculated energies, including adsorption energy, activation energy, and reaction energy, were zero-point-energy (ZPE) corrected.

Reaction rate constants were determined by harmonic transition-state theory [45]. To eliminate the error caused by the low frequency, we shifted all the real frequencies below 200 cm^{-1} to 200 cm^{-1} . This procedure is consistent with the procedure of Lu et al., in which they reported that low frequency modes have no effect on reaction energies and barriers of surface reactions [36]. The equilibrium constants were defined as the forward rate constant divided by the backward rate constant. The microkinetic modeling was performed in an isothermal steady-state plug-flow reactor. All reactions were reversible. The detailed simulation process was reported in our previous work [32,33].

Results and discussion

Adsorption of intermediates

The most stable adsorption geometries of key intermediates on the surface are presented in Fig. 1, and their corresponding adsorption energies, configurations and geometrical parameters are listed in Table 1. Nomenclature of $\eta^i-\mu_j$ is applied to

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