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New mechanism of the direct pathway for formic acid oxidation on Pd(1 1 1)

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ABSTRACT

By performing density functional theory calculations, we have evaluated the detailed mechanism of formic acid (HCOOH) oxidation process on Pd(1 1 1) surface, including geometric structures and energies of intermediates and transition states. Our calculations indicate that the co-adsorbed $(H_2O)_2$ or HCOOH plays an important role in influencing the initial adsorption configurations of HCOOH. For the first time, pathways of HCOOH decomposition in presence of $(H_2O)_2$ or HCOOH regarding the preference of CO_2 formation are proposed.

1. Introduction

As a promising alternative to H_2 production, the electro-catalytic oxidation of formic acid (HCOOH) on metal surfaces will play a very significant role in energy-efficient green power utilization in the future, especially in driving portable electronic appliances [1]. It is widely accepted that electrochemical oxidation of HCOOH proceeds via dual pathways, namely, direct and indirect pathways [2,3]. The former pathway starts from the O—H bond dissociation converting to CO_2 [4,5]

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$$

The latter pathway leads to CO as a reaction intermediate, which is then oxidized to CO_2 [6].

$$HCOOH \rightarrow CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$$

Generally, direct and indirect pathways may predominate, depending on the properties of catalyst used. For HCOOH oxidation on Pd catalyst, the direct pathway to yield CO_2 is well-known to be facile [7].

Nowadays, the mechanism of HCOOH decomposition on Pd system has been investigated to identify the preference of CO_2 as the dominant product. Luo et al. [8] elucidated the fundamental oxidation mechanism of a signal adsorbed HCOOH in the gas phase, and indicated the direct pathway is active on Pd(1 1 1) surface. Afterward, Zhang and coworkers [9] showed the effect of coadsorbed H_2O and its coverage on the decomposition of HCOOH on Pd(1 1 1) surface. They revealed that CO_2 is formed as the dominant product, which is largely dependent on coadsorbed H_2O. In the case of the electrocatalytic oxidation of HCOOH, however, it has been shown that dimers of HCOOH or H_2O, can affect the adsorption and decomposition of HCOOH. For example, the previous studies by Cuesta et al. [10] and Wang et al. [11] have investigated the effect of HCOOH bimolecular and H_2O dimer molecules on the electro-oxidation of HCOOH, respectively. They suggested that HCOOH can be catalyzed by H_2O dimer and formic acid itself in the gas phase, which demonstrates that oxidation process can be significantly affected by H_2O dimer and formic acid. As a result, to elucidate whether dimers of HCOOH and H_2O can effectively affect the formation of CO_2 during the electro-catalytic oxidation of HCOOH on Pd(1 1 1) surface, we investigate HCOOH decomposition in the presence of the co-adsorbed $(H_2O)_2$ and HCOOH molecules by performing density functional theory (DFT) calculations.

2. Computational details

All calculations are performed using the CASTEP code [12] with ultrasoft pseudopotentials [13] and the spin polarized generalized gradient approximation (GGA) exchange–correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE) [14]. A plane wave basis set with a cutoff energy of 400 eV is used. The first Brillouin zone is sampled using a $2 \times 2 \times 1$ Monkhorst–Pack *k*-point grid.

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For the geometry optimization, the maximum force convergence and criteria for energy used are 0.05 eV/Å and 2.0×10^{-5} eV/atom, respectively. With this setting we get the lattice constant of bulk Pd as 3.92 Å, which agrees well with the experimental finding, 3.89 Å [15]. To investigate the reaction pathways, the transition states (TSs) procedure are searched for with the linear and quadratic synchronous transit (LST/QST) complete search [16].

We define the adsorption energies as $E_{ad} = E_{surf} + E_{adsorbate} - E_{total}$, where E_{surf} is the energy of clean Pd(1 1 1), $E_{adsorbate}$ refers to the energies of free adsorbate, and E_{total} is the energy of the adsorbed system. For a CO_2 formation reaction, the activation barrier (E_a) is calculated by $E_a = E_{TS} - E_R$, respectively, where E_{TS} and E_R are the energies of transition state and reactant, respectively.

Previous work comparing 3 and 5 layer metal slabs found little change on the structural H_2O [17]. Therefore, Pd(1 1 1) surface is modeled by a periodic slab containing three atomic layers with full relaxation of the uppermost layer, while the bottom two layers are fixed at the calculated bulk positions. A $p(3 \times 3)$ unit cell with 9 metal atoms per layer is used in this study. The vacuum separation between periodically repeated slabs is 10 Å, which is large enough to avoid interactions between slabs. As shown in Fig. 1, there are four different adsorption sites on Pd(1 1 1) surface: top, bridge, hcp, and fcc, within which the adsorption and decomposition of HCOOH occurs.

To support our choice of setting, we calculated the bond lengths for HCOOH. The theoretical values are 0.986 (0.972) Å for O—H, 1.105 (1.097) Å for C—H, 1.218 (1.202) Å for C═O and 1.354 (1.343) Å for C—O, respectively. Our results are in fairly good agreement with the corresponding experimental values displaced in the parentheses [18], indicating the acceptable accuracy and reliability of the computational method employed. HCOOH has the *trans* and the *cis* forms, depending on the orientation of the hydroxyl group (—OH). Experiment has confirmed that the *trans* conformer is the dominant in the gas phase, and the energy difference between the two conformers is about 0.17 eV [19]. In this study, the energy of the *trans* form was calculated to be 0.15 eV lower than its *cis* form, which is in good agreement with the experimental value. It should be noted that in this study our main concern is the accuracy of the relative energies involved in oxidation processes. Energy errors for the initial state and final state in a chemical process are almost the same. Therefore, they can counteract each other. Thus, we consider that our results are exact and the conclusion drawn is reliable.

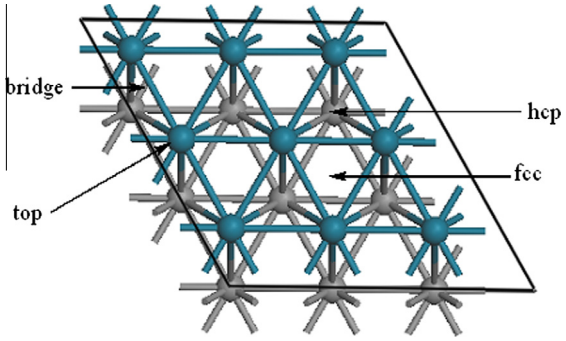

Fig. 1. Top view of the $p(3 \times 3)$ surface unit cell of Pd(1 1 1) surface with possible adsorption sites. For clarity, only two layers of Pd atoms are illustrated. The blue balls and gray balls denote the first-layer and the second-layer Pd atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. HCOOH decomposition in presence of $(H_2O)_2$

In this section, we discuss HCOOH decomposition in presence of $(H_2O)_2$. By performing extensive potential energy surface (PES) scans, we have located various intermediates and transition states along the possible pathway. Their structures with the key geometrical parameters are shown in Fig. 2. The relevant PES profiles along the reaction coordinate are depicted in Fig. 3, where the sum of the energies of the isolated reactants (HCOOH, $2H_2O$, and Pd(1 1 1) surface) is taken as zero energy.

The reaction starts by formation of IM1, where HCOOH and co-adsorbed H_2O molecules are bound via two intermolecular H bonds with the O—H···O distance being 2.034 and 2.570 Å, respectively. Previous studies reported that HCOOH prefers to stand vertical on the surface in the gas phase [8,9], while its vertical [2,20] and parallel [21,22] adsorption modes are nearly equivalent in solution. From our present calculation of HCOOH adsorption in presence of $(H_2O)_2$, it is found that HCOOH molecule is almost parallel to the surface. Once IM1 is formed, the abstraction of hydrogen can occur through two successive dehydrogenation steps. The first C—H breaking proceeds via the transition state, TS1, where the dissociating C—H bond is elongated to 1.480 Å. This process is calculated to be exothermic by 0.52 eV and needs to overcome a barrier of 0.96 eV. As the dissociated H atom moves to a fcc site in the surface, the newly formed COOH binds to the

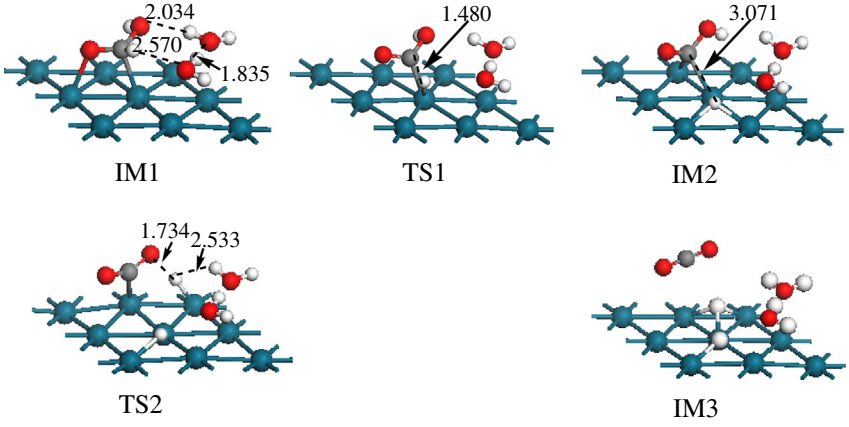

Fig. 2. Optimized geometries for the intermediates and the transition states involved during CO_2 formation in the presence of $(H_2O)_2$. The blue, red, gray and white balls denote Pd, O, C and H atoms, respectively. For clarity, only one layer of Pd atoms is illustrated. Distances are in angstroms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)