Theoretical study of the mechanism of formic acid decomposition on the PdAg(111) surface

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ABSTRACT

A deep knowledge about the mechanism of formic acid (HCOOH) decomposition on Pd-based materials is of fundamental importance to structural designs of efficient catalysts used in direct formic acid fuel cells (DFAFCs). This work presents a theoretical study of the mechanism of HCOOH decomposition on the PdAg(111) surface with the absence and presence of water molecules. The calculated results show that HCOOH preferentially decomposes to CO_2 regardless of without or with the presence of water. The energy barrier difference of the rate-determining steps for the formations of CO_2 and CO on PdAg(111) surface is found to be much larger than that on monometallic Pd(111) surface. The theoretical results indicate that bimetal PdAg(1111) surface can suppress formation of CO, which rationalize well the experimental observation that PdAg bimetal catalysts exhibit improved tolerance toward CO poisoning for HCOOH decomposition.

Introduction

Direct formic acid fuel cells (DFAFCs) are considered to be one of the most promising energy conversion devices for supplying clean and environment-friendly power sources [1,2]. In DFAFCs, the poor durability of anode catalysts is one of main bottlenecks that hinders large-scale commercialization of DFAFCs. To improve the performance of DFAFCs, an effective and low cost catalyst for formic acid oxidation is highly desirable. Pt- and Pd-based materials are the most widely used anode catalysts for HCOOH oxidation in DFAFCs [3–7]. Recent studies found that Pd catalysts show higher activity toward HCOOH oxidation than Pt ones [8–15]. Nevertheless, the catalytic performance of pure Pd catalysts is easily degraded

owing to the poisoning effect of CO generated from HCOOH dehydration pathway [16–18]. Therefore, searching for a highly selective and active catalyst that favors HCOOH dehydrogenation with formation of CO_2 [14,15] to HCOOH dehydration with formation of CO is a formidable challenge.

Recently, Pd-based bimetal catalysts, such as PdAu [8,19], PdPt [20,21], PdAl [22], and PdAg [23,24], have attracted special attention due to their unique catalytic activity and stability towards HCOOH dehydrogenation. More recently, several groups [12,25–27] have successfully prepared Ag-core/Pd-shell (Ag@Pd) bimetal nanoparticles and observed that Ag@Pd heterostructures possess enhanced catalytic activity toward HCOOH decomposition and higher tolerance to CO poisoning compared with pure Pd catalysts. Interestingly enough, the selective oxidation of HCOOH is found strongly

depending on the Pd-shell thickness [12]. Very recently, Cho et al. [26] found that the Pd monolayer on Ag(111) surface is responsible for notable enhancement of H_2 production from HCOOH oxidation. Although the excellent performance of Ag@Pd heterostructures towards the selective oxidation of HCOOH has been recognized, the relevant mechanism that elucidates the improved tolerance to CO poisoning still remains unclear. In this work, we present a systematic theoretical study for the structure-dependent oxidation of formic acid on a PdAg(111) surface in the absence and in the presence of water molecules. Based on our calculated results, we hope to explore the reason why Pd–Ag bimetal catalysts exhibit enhanced catalytic activity and improved anti-CO poisoning ability during HCOOH oxidation.

Computational details

In order to mimic the Ag–Pd core–shell structure, we designed a Pd monolayer supported on Ag(111) surface by replacing Ag atoms on the outmost layer of Ag(111) with Pd atoms. The surface was modeled by a three-layer slab with a 10 Å vacuum zone in the z direction to separate the slabs, and a $p(3 \times 3)$ unit cell with nine atoms at each layer is used in the lateral plane (Fig. 1). Pd atoms in the uppermost layer and the entire adsorbates were allowed to be fully relaxed, while the bottom two layers of Ag atoms were fixed at their bulk-truncated structures.

The calculations were performed by the ultrasoft pseudopotential [28] density functional theory (DFT) periodic slab approach [29,30] with the spin polarized generalized gradient approximation (GGA) and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [31], as implemented in the CASTEP package [32]. The Kohn–Sham one-electron states were expanded in a plane wave basis set with a cutoff kinetic energy of 400 eV and the surface Brillouin zone was sampled with a $2 \times 2 \times 1$ k-point grid. The convergence thresholds used
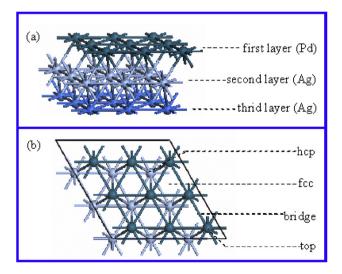

Fig. 1 – Models used in this study: (a) side and (b) top views of the PdAg(111) surface with marked adsorption sites (top site, bridge site, hexagonal-close-packed (hcp) site, and face-centered cubic (fcc) site).

for the total energy and maximum force are 2.0×10^{-5} eV/atom and 0.05 eV/Å, respectively. The transition states were searched using the linear and quadratic synchronous transit (LST/QST) procedure [33]. Our previous work [18,34,35] has demonstrated the acceptable accuracy of such a parameter set for mimicking the reactivity of HCOOH on noble metal surface, especially for the calculation of reaction barriers in heterogeneous catalysis.

The adsorption energies are determined via $E_{ad} = E_{adsorbate} + E_{surf} - E_{total}$, where E_{total} and E_{surf} are the energies of the surface with and without the adsorbate, respectively, and $E_{adsorbate}$ is the energy of free adsorbate. The barrier (ΔE_a) is defined as $\Delta E_a = E_{TS} - E_R$, where E_{TS} and E_R are the energies of the transition state and reactant, respectively.

Results and discussion

First of all, we carried out the convergence test calculations with respect to the three-layer slab and the $2 \times 2 \times 1$ k-point grid used in the present work. It is found that increasing the slab thickness to 5 layers changes the adsorption energy of HCOOH 0.06 eV, and increasing the k-point grid to $5 \times 5 \times 1$ changes the adsorption energy 0.08 eV. These small energy differences establish the acceptable accuracy of the model and parameters used. The reliability of a three-layer slab and a $2 \times 2 \times 1$ k-point for describing HCOOH adsorption on late transition metal surfaces can also be found in recent publications [36,37].

Secondly, we emphasize that the present work studies the reactivity of formic acid decomposition without considering the effect of electrocatalytic potential, although our motivation is to show its relevance to DFAFCs. Several studies [36,38,39] have indicated that the electrode operating potential has a minor effect on the reaction energy barrier, and that the barrier change resulted from the electrochemical potential shift in a typical experiment (e.g., 0.2–0.7 eV) is expected to be smaller than 0.07 eV [40]. A number of publications in literature [36,37,40,41] has established the validity of the calculation approach used in this work for evaluating the electro-catalytic performance of a catalyst. The present results can be considered as a preliminary prototype to understand the complex electrochemical oxidation of HCOOH catalyzed by PdAg bimetallic catalysts.

HCOOH adsorption on the PdAg(111) surface

We first modeled the gas phase reaction on the PdAg(111) surface as a starting point to understand the catalytic oxidation of HCOOH. In order to explore the reaction pathways of HCOOH oxidation, we considered the different structures of HCOOH adsorbed on the PdAg(111) surface based on two initial adsorption modes (vertical and parallel). For the vertical mode, three possible adsorption configurations are located, labeling as **1a**, **1b**, and **1c** in Figs. 2–4. Structure **1a** in Fig. 2 is identified as the most stable adsorption configuration of HCOOH, where the carbonyl oxygen binds to the top site of a Pd atom with a Pd–O distance of 2.218 Å and the O–H group points asymmetrically to two neighboring Pd atoms with two Pd–H distances of 2.400 and 2.419 Å, respectively. The