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Importance of Pd monomer pairs in enhancing the oxygen reduction reaction activity of the AuPd(1 0 0) surface: A first principles study

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ABSTRACT

Based on density functional theory calculations, we present that pairs of 1st nearest Pd monomers play an important role in significantly enhancing the oxygen reduction reaction (ORR) on the AuPd(1 0 0) surface. While the catalytic ORR activity tends to be sensitive to the surface atomic ordering, we find that the Pd monomer pairs lead to a substantial reduction in the activation barrier for O/OH hydrogenation with no significant suppression of O–O bond scission, thereby considerably lowering the overall activation energy for the ORR as compared to the case of pure Pd(1 0 0). On the other hand, an isolated Pd monomer tends to greatly suppress the O–O bond cleavage reaction, which in turn slows down the ORR kinetics. Unlike the monodentate adsorption of O_2 on an isolated Pd monomer, the pairing of Pd monomers allows O_2 adsorption in a bidentate configuration and consequently facilitating O–O bond scission. However, the barrier for OH hydrogenation at each Pd site shows no significant change between the isolated and paired cases, while it is noticeably lower than the pure Pd case.

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1. Introduction

Bimetallic gold-palladium (AuPd) catalysts have been tested and used for various chemical reactions such as production of vinyl acetate monomer [1], low temperature oxidation of carbon monoxide [2–5], selective oxidation of formic acid [6–8], and selective production of hydrogen peroxide (H_2O_2) from molecular O_2 and H_2 [6,9–11]. Recent studies suggest that the surface activity of AuPd is governed by the various alloying effects such as the so-called electronic (ligand) effects [4,6,12–15] (electronic state change by metal–metal interactions) and ensemble (geometric) effects (modification of catalytic activity by the unique arrangement of surface atoms) [16–20]. However, the underlying mechanism of AuPd alloy catalysis still remains unclear.

It has been theoretically and experimentally found that an isolated Pd monomer surrounded by Au atoms is a good site for increasing the rate of O/OH hydrogenation reaction but significantly slowing down the kinetics of O_2 bond cleavage, thereby yielding the significant enhancement of selective H_2O_2 formation [21–25]. The reactivity of Pd monomer in the AuPd catalyst can be also altered due to additional geometrical factors. For instance, it tends to be changed by the presence of low-coordination surface atoms and the strain imposed on the outer-layer atoms, in association with the size and shape of nanoparticle catalysts and the lattice parameter mismatch between the substrate and the adlayer [13,26–28]. The different surface facets such as (1 1 1) and (1 0 0) [29] may also affect the reactivity of isolated Pd monomers, leading probably to the change in catalysis of the oxygen reduction reaction (ORR). For example, according to a recent density functional theory (DFT) calculation [23], ORR strongly depends on the surface arrangement of Au and Pd atoms Pd(1 1 1). In particular, on Pd monomers surrounded by less active Au atoms, H_2O_2 is selectively produced, while on Pd dimer, the reactivity to H_2O is predicted to be enhanced compared to pure Pd(1 1 1). But there has been little investigation concerning the interplay between different facet and Pd ensemble.

In this paper, we investigate the arrangement of Pd atoms and its effect on ORR on the AuPd(1 0 0) surface, particularly the role of pairs of 1st nearest Pd, using periodic density functional theory (DFT) calculations. Here, we only consider small-sized Pd ensembles including monomer, monomer pair, and dimer which are experimentally found to be energetically favorable when the surface coverage of Pd is sufficiently low [30,31]. We first examine the relative stabilities among those small Pd ensembles

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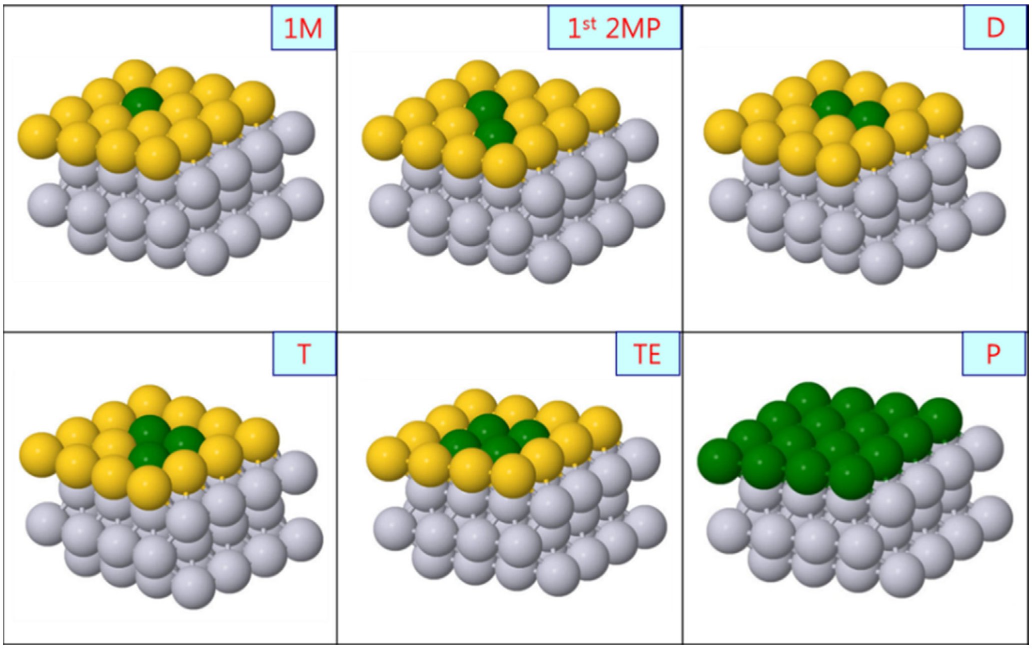

Fig. 1. Tilted side view of the model PdAu surfaces considered in this work, an isolated Pd monomer (indicated by 1M), a pair of 1st nearest monomers (1st 2MP), a dimer (D), a trimer (T), a tetramer (TE) and a Pd(1 0 0) slab (P). The green, gold, and gray balls represent surface Pd, surface Au, and subsurface Pd atoms, respectively. (For interpretation of the color information in this figure legend, the reader is referred to the web version of the article.)

considered and also calculate and compare the reaction energetics and barriers for O-O bond scission and O/OH hydrogenation on the different Pd sites. Next, we analyze the surface electronic structure modifications upon O_2 adsorption to better understand the reasons underlying the activity enhancement of pairs of 1st nearest Pd monomers toward O-O scission.

2. Computational methods

The calculations reported herein were performed on the basis of spin polarized DFT within the generalized gradient approximation (GGA-PW91) [32], as implemented in the Vienna Ab-initio Simulation Package (VASP) [33]. The projector augmented wave (PAW) method [34] with a plane-wave basis set was employed to describe the interaction between core and valence electrons. The valence configurations employed to construct the ionic pseudopotentials are: $5d^{10}$ $6s^1$ for Au, $4d^9$ $5s^1$ for Pd, and $2s^2$ $2p^4$ for O. An energy cut-off of 350 eV was applied for the planewave expansion of the electronic eigenfunctions. For Brillouin zone sampling, we used a (3 × 3 × 1) Monkhorst-Pack mesh of k points to determine the optimal geometries and total energies of systems examined, and increased the k-point mesh size up to (8 × 8 × 1) to re-evaluate corresponding electronic structures. Reaction pathways and barriers were determined using the climbing-image nudged elastic band method (c-NEBM) [35] with eight intermediate images for each elementary step.

For a model surface, we used a supercell slab that consists of a rectangular 4 × 4 surface unit cell with four atomic layers each of which contains 16 atoms. For each AuPd surface model, the topmost surface layer that is overlaid on a three-layer Pd (1 0 0) slab contains selected Pd ensembles including an isolated Pd monomer (indicated by 1M), a pair of 1st nearest monomers (1st 2MP), a dimer (D), a trimer (T), and a tetramer (TE) (see Fig. 1). A slab is separated from its periodic images in the vertical direction by a vacuum space corresponding to seven atomic layers. While the bottom two layers of the four-layer slab were fixed at corresponding bulk positions, the upper two layers were fully relaxed using the conjugate gradient method until residual forces on all the constituent atoms become smaller than 5×10^{-2} eV/Å. The lattice constant for bulk Pd is predicted to be 3.95 Å, which is virtually identical to previous DFT-GGA calculations and also in good agreement with the experimental value of 3.89 Å. The binding energy (E_b) of O_2 is calculated by $E_b = E(M) + E(O_2) - E(O_2/M)$, where $E(O_2/M)$, $E(M)$, and $E(O_2)$ represent the total energies of the O_2/slab system, the bare slab, and an isolated triplet O_2 molecule in the gas state, respectively.

3. Results and discussion

3.1. Relative stability of small Pd ensembles

Before looking at the reactivity of various Pd ensembles toward ORR, we first examined the relative stability of Pd ensembles on the (1 0 0) surface. Table 1 summarizes the predicted formation energies per Pd atom for the 1M, 1st 2MP, D, T, and TE ensembles, given by $E_f = [E_{PdAu} - E_{Au} + N_{Pd} \times (E_{Au\text{-}bulk} - E_{Pd\text{-}bulk})]/N_{Pd}$, where E_{PdAu}, E_{Au}, $E_{Au\text{-}bulk}$, and $E_{Pd\text{-}bulk}$ represent the total energies of PdAu/Pd(1 0 0) [Pd ensembles are overlaid on a three-layer Pd (1 0 0) slab], Au/Pd(1 0 0) [Au monolayer are overlaid on a three-layer Pd (1 0 0) slab], bulk Au (per atom), and bulk Pd (per atom), respectively, and NPd indicates the number of Pd atoms on a given PdAu surface. Here, the smaller the formation energy, the higher the stability of Pd ensembles.

The calculation results suggest that 1M, D, T, and TE in order of decreasing stability; that is, Pd atoms would have a tendency to remain isolated, rather than form aggregates in the AuPd (1 0 0) surface, consistent with recent theoretical and experimental results [30,36,37]. In addition, our calculations show that the E_f of 1st 2MP is comparable to that of 1M, implying that 1st 2MP can exist stably for surface catalytic reactions. Hence, we only considered the 1M, 1st 2MP, and D sites for the study of O-O bond scission and O/OH hydrogenation, with comparison to the pure Pd(1 0 0) case.

3.2. O-O bond scission

In this study, we examined the three elementary steps (the so-called dissociative mechanism) for the ORR in acidic

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