Role of Intermediate Dynamics in Controlling Hydrogenation Selectivity by Heterogeneous Catalysis

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ABSTRACT: Selectivity in heterogeneous catalysis is essential while being the most difficult parameters to obtain from theoretical simulations. Although theory holds the key for catalytic design, in the search of complex reaction networks, intermediates are considered static and different configurations for addition reactions are not considered. Here, we present the crucial role of intermediate dynamics to understand reaction selectivity of heterogeneous catalysts by studying the dynamic properties. The hydrogenation of two different intermediates hydroperoxide (OOH) and vinyl (HCCH₂) is crucial to in the direct synthesis of water peroxide and alkyne semi-hydrogenation are taken as examples on the bare and alloyed surfaces. For them, the reaction network is studied by density functional theory coupled to molecular dynamics to present the role of rotations and how they affect paths for the addition of atomic hydrogen to lead to the products. In summary, the thermodynamic selectivity can be mapped to the dynamic control in the kinetics of the process.

1. INTRODUCTION

Hydrogenation typically constitutes the addition of pairs of hydrogen atoms to a molecule, often an alkene, and plays a key role in chemical synthesis. It requires a catalyst to make the reaction proceed at a reasonable rate. Heterogeneously catalyzed hydrogenations are one of the most important processes of the chemical industry which involves both thermodynamics and kinetics. From thermodynamic point of view, the stability of the products control product distribution in a chemical reaction. Kinetics describes the relative rates of corresponding product formation and how fast equilibrium is reached, thus in turn to the relative activation energies.

Noble metal species with different size (single atoms, nanoclusters, and nanoparticles) show different catalytic behaviors for various hydrogenation reactions. Many factors including the particle size, shape, chemical composition, metal-support interaction, and metal-reactant/solvent interaction can have significant influences on the catalytic properties of noble metal catalysts. In general, the enhanced performance of noble metal catalysts may be rationalized by a combination of ligand, geometric, and/or ensemble effects. Ligand and geometric effects which describe influences of charge transfer between nearest neighbor atoms, orbital rehybridization and lattice strain generally affect the strength of interactions of reactants, intermediates, and products. In our previous work we have shown the outstanding activity, selectivity, and stability of ligand-modified Pd nanoparticles in the direct synthesis of H₂O₂. On the other hand, the ensemble effects result when more than one reactive site, composed of different metal atoms, catalyzes distinct steps in a particular reaction mechanism. Our recent study showed that the supported palladium sulfides possess unique ensembles with face- and phase-dependent geometric and electronic characteristics and high stability, demonstrating exciting potential as catalysts for the selective hydrogenation of alkenes.

Heterogeneous bimetallic catalysts, formed by adding a second metal to a host metal, garnered much research attention recently because they exhibit distinctly different and often superior activities for many chemical transformations as compared to pure monometallic systems as determined in experimental and theoretical investigations (e.g., selectivity, activity, and stability).

The palladium–gold (Pd–Au) bimetallic catalyst has shown promising catalytic properties in aerobic oxidation of primary alcohols, direct synthesis of H₂O₂, hydrocarbon hydrogenation, CO oxidation, and oxidation of alcohols to aldehydes. For example, it was found that isolated single Pd atoms constitute the minimum ensemble needed for CO adsorption while a larger set is required for proton adsorption. For hydrogen peroxide formation, Au shows a promotional effect because it drives the formation of the preferred selective catalytic ensemble. Other Au-containing alloys like AuNi have been reported active in oxidized CO at very low temperatures (77 K) because of the participation of Au in the active sites adsorbing the reactants.

Received: November 12, 2019  
Accepted: December 25, 2019  
Published: January 7, 2020

https://dx.doi.org/10.1021/acsomega.9b03845
ACS Omega 2020, 5, 1270−1276
Furthermore, the combination of silver and palladium (Ag–Pd) has been widely applied in ethylene hydrogenation,\(^{17}\) hydrogenation of CO\(_2\) to produce formic acid,\(^{18}\) hydrogenation of acetylene to ethylene, and oxygen reduction.\(^{6,19,20}\) It was shown that for alloys of AgPd, the surface contained single Pd atoms surrounded by Ag atoms, which maximized the ability of a hetero atomic site to amplify the activity of each Pd atom.\(^{6}\)

Moreover, acetylene hydrogenation reactions have been studied theoretically on both pure Pd and bimetallic PdAg surfaces.\(^{17,21–24}\) It is found that on alloying with Ag and Au, the selectivity of Pd(111) surfaces for the hydrogenation of acetylene to ethylene is enhanced.\(^{21}\)

Much is understood about heterogeneous bimetallic catalysts for hydrogenations but some issues remain unresolved and a deeper understanding of this mechanism on the bimetallic catalysts is necessary for a rational design of selective hydrogenation catalysts. We herein first report and compare the reaction network for two different hydrogenation reactions on the bare and alloyed surfaces by density functional theory (DFT). For the first reaction we study the O\(_2\) hydrogenation in the direct synthesis of water peroxide mechanism on Pd and PdAu surfaces and for the second one the alkyne hydrogenation over Pd and AgPd surfaces is taken as another example.

All possible reactions in the direct synthesis of hydrogen peroxide (DHSP) mechanism are summarized in Figure 1a. The scheme shows not only the hydrogenation steps conducting to H\(_2\)O\(_2\) formation but also lateral decomposition paths readily including dissociation of reactants and intermediates, 2O, O + OH, 2OH, or over hydrogenation to O + H\(_2\)O and OH + H\(_2\)O. Combining several of these steps they provide all possible decomposition routes.

The DHSP mechanism essentially requires that oxygen is adsorbed molecularly on the catalyst surface, and the dissociated hydrogen atoms are added to it sequentially at both oxygen ends. However, several of the intermediates, O\(_2\), O\(_2\)H\(_2\), and H\(_2\)O\(_2\) are likely to undergo spurious reactions like O–O bond scission and over hydrogenation to an already formed OH fragment. Table 1 summarizes all possible reactions in this mechanism including reactant adsorption, hydrogenation, and product desorption with the respective reaction energies and activation barriers and Table 2 reports the adsorption energies for the all intermediate states. The full energy profiles for the DHSP mechanism on Pd and PdAu surfaces are illustrated in Figure 2a.

**Table 1. Reaction Energy (\(\Delta E\)) and Corresponding Activation Barrier (\(E_a\)) for the Elementary Steps Involved in the H\(_2\)O\(_2\) Formation on Pd and PdAu Surfaces**

| elementary step                                      | Pd     | PdAu   |
|-----------------------------------------------------|--------|--------|
| O\(_2^*\) + 2H\(_*\) → O\(_2\)H\(_*\) + H\(_*\)   | −0.11  | −0.22  |
| O\(_2\)H\(_*\) + H\(_*\) → OH\(_*\) + H\(_*\) + O\(_*\) | −1.47  | −0.77  |
| O\(_2\)H\(_*\) + H\(_*\) → H\(_2\)O\(_2\)* + O\(_*\) | −2.34  | −2.33  |
| O\(_2\)H\(_*\) + H\(_*\) → H\(_2\)O\(_2\)* trans | −0.21  | −0.45  |
| H\(_2\)O\(_2\) → H\(_2\)O\(_2\)           | 0.26   | 0.17   |
| H\(_2\)O\(_2\) → OH\(_*\) − OH\(_*\)    | −1.63  | −1.48  |
| H\(_2\)O\(_2\)* + H\(_*\)                    | −0.34  | −0.21  |
| H\(_2\)O\(_2\)* + H\(_*\)                    | −2.43  | −2.3   |
| O\(_2\)* + 2H\(_*\) → 2O\(_*\) + 2H\(_*\)       | −1.16  | −0.81  |
| 2O\(_*\) + 2H\(_*\) → OH\(_*\) + H\(_*\) + O\(_*\) | −0.42  | −0.19  |
| OH\(_*\) + H\(_*\) + O\(_*\) → OH\(_*\) + OH   | −0.37  | −1.16  |
| OH\(_*\) + OH → H\(_2\)O\(_*\) + O\(_*\) | −0.50  | −0.40  |

**Table 2. Adsorption Energy (\(E_{ads}\)) of the Intermediate States on Pd and PdAu Surfaces with Respect to a Free O\(_2\) Molecule and a Reference Surface**

| intermediate                                      | Pd     | PdAu   |
|---------------------------------------------------|--------|--------|
| O\(_2^*\) + 2H\(_*\)                             | −1.22  | −0.78  |
| O\(_2\)H\(_*\) + H\(_*\)                        | −1.33  | −0.88  |
| H\(_2\)O\(_2\)*                                 | −1.54  | −1.46  |
| H\(_2\)O\(_2\)* − H\(_*\)                       | −1.89  | −1.66  |
| H\(_2\)O\(_2\)* − OH\(_*\)                      | −4.30  | −3.96  |
| 2O\(_*\) + 2H\(_*\)                             | −2.38  | −1.58  |
| OH\(_*\) + H\(_*\) + O\(_*\)                    | −2.80  | −1.77  |
| OH\(_*\) + OH\(_*\)                             | −3.17  | −2.93  |
| H\(_2\)O\(_2\)* + O\(_*\)                       | −3.67  | −3.33  |

**The asterisks denote adsorbed atoms.**

The first reaction step of the H\(_2\)O\(_2\) direct synthesis mechanism on Pd and PdAu surfaces is the adsorption of molecular O\(_2\). This process is exothermic (−1.22 eV for Pd and −0.78 eV for PdAu, 1 eV = 96 kJ mol\(^{-1}\)) on both the surfaces where the O\(_2\) molecule adsorbed on a fcc configuration on the Pd while it adsorbed on a tbt configuration on the PdAu surface. The O–O bond stretches from 1.23 Å in the gas phase to 1.36 Å

![Figure 1](https://example.com/image1.png)

**Figure 1.** Competitive paths involved in the direct hydrogen peroxide synthesis (a) and acetylene hydrogenation reactions (b). Reactions that drive to the formation of the desired products H\(_2\)O\(_2\) and C\(_2\)H\(_4\) formation are written in green color.
on the Pd and 1.31 Å on the PdAu surfaces. On the Pd surface, the charge transfer to the oxygen atom on the fcc site (−0.29 e) is slightly larger than to the atom on the top site (−0.23 e), thus causing the magnetic moment of the atom at the top site to be slightly smaller. On the PdAu surface, the charge transfer to both the oxygen atoms (−0.20 e) is similar and the partial magnetic moment for each atom is 0.27 μB. Table 3 compiles the charges and magnetic moments that characterize O2, OOH, and H2O2 in the gas phase, on Pd(111) and on PdAu(111) Surfaces.

Table 3. Atomic (ΔqO) and Molecular (Δqtot) Bader Charges, Partial (μO) and Total (μtot) Magnetic Moment, and the O−O Bond Length (dO−O) for O2, OOH, and H2O2 in the Gas Phase, on Pd(111) and on PdAu(111) Surfaces

| species | ΔqO ε | Δqtot ε | μO, μB | μtot, μB | dO−O Å |
|---------|--------|----------|---------|----------|--------|
| O2      | −0.23 b(−0.29)c | −0.52 | 0.10b(0.09)c | 0.19 | 1.36 |
| Pd(111) | −0.20 | −0.40 | 0.27 | 0.54 | 1.31 |
| PdAu(111) | −0.20 | −0.40 | 0.27 | 0.54 | 1.31 |
| OOH     | −0.19(−0.20)d | −1.01 | 0.08(0.03)d | 0.11 | 1.50 |
| Pd(111) | −0.13(−0.15)d | −0.90 | 0.00(0.00)d | 0.00 | 1.44 |
| PdAu(111) | −0.13(−0.15)d | −0.90 | 0.00(0.00)d | 0.00 | 1.44 |
| H2O2    | −0.04 | −0.08 | 0.02 | 0.04 | 1.52 |
| Pd(111) | −0.02 | 0.00 | 0.00 | 0.00 | 1.48 |

The values in parenthesis refer to the oxygen atom: b on top site, c on fcc site, d bound to hydrogen.

for this reaction on the clean surface are −0.11 and 0.68 eV. The corresponding values on the top PdAu surface are −0.22 and 0.68 eV. The O−O bond length of the OOH intermediate on Pd and PdAu surfaces is 1.50 and 1.44 Å, respectively, which is compatible with a peroxo (O22−) bond length. The smaller bond length of O−O indicates that on the PdAu surface OOH dissociation on PdAu is more impeded than on the clean surface.

The addition of the second hydrogen atom to the OOH intermediate leads to the formation of H2O2; at the same time, this process also may yield water. In addition, the dissociation of OOH* to O* + OH* may happen as well. On the clean surface, the barrier energy of both side reactions is lower than the formation of H2O2, limiting the selectivity of the clean Pd surface as a catalyst. Dissociation of the OOH* intermediate to OH* + O* is hindered by 0.44 eV on the bare surface.

Figure 2. (a) Reaction pathway for the hydrogen peroxide formation from its elements, and for the competitive formation of water or hydroxyl groups on Pd and PdAu surfaces. (b) Energy profile of the full acetylene hydrogenation mechanism on Pd and AgPd surfaces.
However, as shown in Figure 2a, different positions for OOH hydrogenation are possible: the attack on the already hydroxylated O, or as *syn* or *trans* on the nonhydroxylated one. The first reaction on the bare surface is hindered by a barrier of 0.35 eV and leads to the formation of coadsorbed water and oxygen (H$_2$O$^*$ + O$^*$). As for the two attacks on the rest O both lead to the formation of H$_2$O$_2$, the barrier being 0.89 eV with a reaction energy of 0.01 eV, which indicates that this is an exothermic process. Hydrogenation of OOH on the PdAu surface is more exothermic than that on the clean surface with an activation barrier and reaction energy of 0.39 and 0.45 eV, respectively. As a result, the PdAu surface should be more selective than the clean Pd surface for H$_2$O$_2$ formation. This process on the PdAu surface has lower energetic requirements than side reactions (0.53 eV for O$_2$ + O$^*$ and 0.56 eV for H$_2$O$^*$ + O$^*$). This means that the two channels for selectivity reduction (OOH breaking and over hydrogenation to H$_2$O$^*$ + O$^*$) are no longer open. The bond length of O−O in H$_2$O$_2$ on the PdAu surface is 1.48 Å which is smaller than that of the clean surface (1.52 Å) (Table 3).

Still two routes are possible for dissociation of this moiety on the surface, namely, direct decomposition to 2OH or over hydrogenation to coadsorbed water and a hydroxyl group. The activation barriers for decomposition and over hydrogenation on the bare Pd surface are smaller than H$_2$O$_2$ desorption. By comparing the H$_2$O$_2$ steps, it can be judged that on the clean Pd surface no H$_2$O$_2$ will be obtained. In contrast, the barrier for H$_2$O$_2$ desorption on the PdAu surface is lower than the barriers for H$_2$O$_2$ decomposition and over hydrogenation. As a result, other intermediates cannot compete with H$_2$O$_2$ desorption and H$_2$O$_2$ will be desorbed from the PdAu surface.

On the other hand, oxygen can dissociate to 2O* on the surface and the process is detrimental to selectivity. However, the activation energy for this reaction on both surfaces is smaller than that of the desired hydrogenation to OOH* barrier energy is increased by 0.23 eV on the PdAu surface with respect to the Pd one. This process on both Pd and PdAu surfaces is exothermic in a reaction energy of −1.16 and −0.81 eV. The next side reaction is hydrogenation of oxygen atoms: the first hydrogenation on both surfaces has a higher barrier than the second one. The last side reaction (OH$^*$ + OH$^*$ → H$_2$O$^*$ + O$^*$) has the same barrier energy (0.42 eV) on both surfaces with a reaction energy of −0.5 and −0.4 eV for Pd and PdAu surfaces, respectively.

PdAu alloys have been found to be active and selective in different reactions showing complex mechanisms. In the present case the first main difference with the clean Pd(111) surface is the increase in the barrier for O$_2$ dissociation for the PdAu case with respect to the Pd one (from 0.76 to 0.99 eV). This is due to two main aspects, first due to the presence of Au blocks, active sites enforce a different path for O$_2$ dissociation, see Figure 3. In addition, hydrogen transfer is eased because of the presence of Au on the surface; the result being a better branching reaction than in the previous case. In addition, the resting hydrogenation reactions are more competitive than in the previous case, thus reducing side reactions.

### 2.2. Acetylene Hydrogenation on Pd and AgPd Surfaces

The reaction scheme for acetylene hydrogenation is also described in Figure 1b. The complete reaction pathways of acetylene hydrogenation with all respective reaction energies and activation barriers are reported in Table 4. In addition, the adsorption energies for all intermediate states are reported in Table 5. The full energy profiles for the acetylene hydrogenation mechanism on Pd and AgPd surfaces are illustrated in Figure 2b. The reaction network starts by the adsorption of the alkyne on the surface, which is considerably exothermic on Pd(111) by −2.51 while it is slightly exothermic on AgPd by −0.05 eV (with respect to gas-phase acetylene and H$_2$). Afterward, the sequential addition of the H atom follows a Horiiuti–Polanyi mechanism. The first hydrogenation of the adsorbed acetylene moiety is exothermic and leads to a single product vinyl (HCCH$_2^*$) on both surfaces. The reaction energies for this step are −0.17 and −1.26 eV with activation barriers of 0.67 and 0.77 eV on Pd and AgPd, respectively. The second hydrogen addition can result in two competitive products, ethene (H$_2$CCH$_2^*$) or ethylene (HCCH$_3^*$). The formation of the former features a reaction energy of 0.66 and 1.36 eV for Pd and AgPd, respectively, and shows an exothermic behavior by −0.31 and −1.52 eV. Because of kinetic reason, ethene formation on the clean Pd surface is more favored.

![Figure 3. Initial, final, and transition state for the decomposition of molecular oxygen on the Pd surface, and on a gold-containing alloy, PdAu.](https://dx.doi.org/10.1021/acsomega.9b03845)
than the formation of ethylidene, where $E_a$ is 0.72 eV and $\Delta E$ is +0.05 eV. While ethylene formation on AgPd is impeded because the barrier of vinyl hydrogenation to ethylidene (HCCH$_2$) is lower ($E_a = 0.92$ and $\Delta E = -0.41$). At this stage, the H$_2$CCH$_2$ desorption could eventually undergo over hydrogenation to ethyl (H$_2$CCH$_3$). The desorption of H$_2$CCH$_2$ is impeded on Pd(111) surface since its energy (0.85 eV) is higher than the third hydrogenation barrier (0.45 eV) whereas on AgPd surface ($E_a = 0.68$ eV) it is energetically advantageous over its further hydrogenation (1.21 eV). The ethyl formation on both surfaces is exothermic by a reaction energy of $-0.20$ and $-0.24$ eV for clean Pd and AgPd surfaces, respectively. On the other hand, HCCH$_2$ hydrogenation can also lead to H$_2$CCH$_2$ formation which is exothermic on both surfaces by $-0.54$ and $-1.35$ eV and a barrier of 1.07 and 0.52 eV for Pd and AgPd. The fourth hydrogenation leads to ethane which is exothermic on both surfaces with a reaction energy (activation barrier) of $-0.67$ (0.44) eV on Pd and $-1.10$ (1.46) eV on AgPd. The last step is ethane desorption which is easy on the Pd (0.05 eV) surface while it has a reaction energy of 0.38 eV on the AgPd surface.

### 2.3. Dynamic Properties of Intermediates

An important aspect concerns the dynamic properties of hydroperoxide on the surface. Figure S1 depicts the top views of the DFT-optimized adsorption configuration of the OOH and HCCH$_2$ intermediates on different surfaces that we used for MD calculations. The OOH intermediate fluctuates between the 6 Pd atoms neighboring the Pd–O bond; rotation of this moiety requires an energy of 0.10 eV on the Pd surface. The fluctuation of this system on the PdAu surface occurs between the two pairs of Pd atoms separated by Au atoms (Figure 4a). The barrier for OOH rotation on the PdAu surface is 0.16 eV which is greater than that on the Pd surface. The Born-Oppenheimer MD (BOMD) results unveiled that the OOH fluctuation is limited in a small area on both the Pd and PdAu surfaces while no rotation has been seen for this moiety on the PdAu surface. Figure 4c,d...
and Movies 1 and 2 illustrate the BOMD results for OOH on clean Pd and PdAu surfaces. In addition, the OH group rotates also almost freely along the O–O atom. The potential energy surface for the dynamics OH group at 300 and 400 K is shown in Figure S3. Both movements effectively lead to the unselective hydrogenation of OOH or its dissociation over the bare Pd surface because the contact time with the active Pd site is smaller than any other process, and thus only the already hydrogenated O in the hydroxyl group can be attacked by H. In contrast, the nonhydrogenated oxygen of the hydroxyl group can be attacked by hydrogen atoms over the PdAu surface resulting in the H2O2 product.

On the other hand, rotation of the HCCH2 intermediate requires an energy of 0.26 eV on the Pd surface which is much greater than the barrier on the AgPd surface (0.025 eV) which means rotation on the AgPd surface is easier. The energy barrier for HCCH2 fluctuation on Pd and AgPd surfaces is depicted in Figure 4b. The BOMD results revealed that the HCCH2 fluctuation is limited in a small area between 3 Pd atoms on the clean Pd surface at 473 K while a complete rotation occurred for this moiety on the AgPd surface (Figure 4e,f and Movies 3 and 4). This movement over the PdAg surface effectively blocks the selective semi-hydrogenation to H2CCH2 formation. While on the bare Pd surface, limited HCCH2 fluctuation leads to the HC head of the HCCH2 molecule to be attacked by H which forms H2CCH2.

3. CONCLUSIONS

We have analyzed the O2 hydrogenation in the direct synthesis of the water peroxide mechanism on Pd and PdAu surfaces and the alkene hydrogenation to alkene over Pd and AgPd surfaces by means of DFT. Particularly, the energy profiles of hydroperoxide (OOH) and vinyl (HCCH2) hydrogenation over both bare and alloyed surfaces were compared to each other. Moreover, BOMD were performed to study the dynamic aspects of OOH and HCCH2 intermediates in the selectivity of hydrogenation by heterogeneous catalysts. Our results show that OOH hydrogenation on the PdAu surface is more exothermic than that on the clean Pd surface, thereby the PdAu surface should be more selective than the clean Pd surface for H2O2 formation. On the clean Pd surface, the barrier energy of side reactions (OOH* dissociation and water formation) is lower than the formation of H2O2, limiting the selectivity of the clean Pd surface as a catalyst. The BOMD results confirm that the OOH intermediate has a complete rotation on the bare Pd surface while no rotation has been seen for this moiety on the PdAu surface. Therefore, only the already hydrogenated O in the hydroxyl group can be attacked by H over the bare Pd surface resulting in water formation. In contrast, on the PdAu surface the nonhydrogenated oxygen of OOH can be attacked by hydrogen atoms which lead to the H2O2 product. Likewise, the complete rotation of the HCCH2 intermediate on the AgPd surface effectively blocks the selective semi-hydrogenation to H2CCH2 formation. This moiety has limited fluctuation on the bare Pd surface resulting in higher selectivity toward formation of H2CCH2 in comparison with the AgPd surface. Our results show that intermediate dynamics control selectivity in hydrogenation by heterogeneous catalysis.

4. COMPUTATIONAL METHODS

DFT calculations in this study were performed using the Vienna Ab initio Simulation Package,76 with the generalized gradient approximation, and the revised Perdew–Burke–Ernzerhof functional as exchange–correlation functional to obtain the energy. Spin-polarized effects were taken into account for intermediates including oxygen atoms. Monoenergetic valence states were expanded in plane waves with kinetic cutoff energy of 450 eV, while core electrons were described with the projected augmented wave method.28 In all calculations, van der Waals contributions were described using the semiempirical DFT-D2 approach,29,30 and the parameters were reoptimized for this metal.31 All calculations were performed on the (111) surfaces as it is the most stable for fcc metals. The clean Pd and Ag slabs were modeled by a slab consisting of a 3 × 3 surface unit cell whereas a 4 × 2 surface unit cell was used to study the hydrogenation reactions on the alloyed slabs (PdAu and AgPd). In all calculations, each slab contained five atomic layers (the three at the bottom were fixed and the two on the top were fully relaxed) and an empty space of 15 Å was introduced in the direction perpendicular to the surfaces (z-direction), which ensured that the interaction between the adsorbed molecules and the periodic images of the slabs is negligible. Sampling of the Brillouin zones was performed by using the Monkhorst–Pack methodology with gamma-centered k-point 4 × 4 × 1 and 3 × 6 × 1 grids for the clean and alloyed surfaces, respectively. The Climbing Image-modified Nudged Elastic Band method32,33 was used to assess the activation energies of the different reaction paths. The nature of all reaction minima and transition states was confirmed by means of numerical frequency analyses obtained from the numerical Hessian calculated with displacements of 0.015 Å. The PdAu slabs were represented by a substitutional model where only a 0.25 ML of Pd atoms on the surface was replaced by Au atoms. Under these conditions Au atoms tend to stay on the surface because of the lower surface energy of Au that provokes segregation of the surface.34 In the AgPd slabs only a 0.125 ML of Ag atoms on the surface was replaced by Pd atoms.

Standard BOMD were performed on the same slabs under the NVT ensemble. BOMD calculations for the OOH intermediate were performed at 300 and 400 K while the temperature for the CH3OH intermediate was set to 473 K controlled.35,36 All BOMD runs were performed over 11 ps for OOH and over 20 ps for CH3OH using a time step of 1 fs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03845.

Movie of the fluctuation of the hydroperoxide (O2H) intermediate on the Pd surface by BOMD calculations (MP4)

Movie of the fluctuation of the hydroperoxide (O2H) intermediate on the PdAu surface by BOMD calculations (MP4)

Movie of the fluctuation of the HCCH2 intermediate on the Pd surface (MP4)

Movie of the fluctuation of the HCCH2 intermediate on the AgPd surface (MP4)

The DFT-optimized adsorption configuration of the OOH and HCCH2 intermediates on different surfaces; trajectory of two oxygen atoms in the O2H intermediate on Pd and PdAu at 300 K from the BOMD simulation; and dynamics properties of hydroperoxide (O2H) on the
Pd and PdAu surfaces at 300 and 400 K from the BOMD simulation (PDF)

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Notes
The author declares no competing financial interest.

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