



A Study of Palladium-Nickel Catalyst for Direct Synthesis of Hydrogen Peroxide: A DFT Approach

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Abstract

Hydrogen peroxide is an important material for bleaching agent in paper production related to the low price and environmentally friendly chemical. The current production of H₂O₂ is well-known as indirect synthesis, which uses danger anthraquinone. The synthesis was improved by using the direct reaction of H₂ and O₂ on Pd or PdAu alloy's catalyst surface and has been known as direct synthesis. The current catalyst used is Pd-Au, but it has limited availability in nature. Therefore we need the alternative of Pd-Au. We investigated Ni alloyed with Pd for the new H₂O₂ direct synthesis using density functional theory approach. The 7-slab model with 2x2 surface size was used for the calculation using ab initio simulation package. We selected the O adsorption to screen the catalysts and compared the species adsorption trend on the surfaces of PdNi and the proven catalysts such as Pd, PdAu, and PdHg. Since the trend of O adsorption on the PdAu and PdNi is similar, it can be concluded that the catalytic selectivity of PdNi equal with PdAu. Further, the stability of PdNi alloy was explored by calculating the binding and compared it with Pd, which leads to the conclusion that PdNi can be a good catalyst for H₂O₂ synthesis.

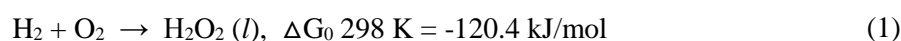
Keywords: Palladium-nickel, catalyst, H₂O₂ synthesis, density functional theory.

1. Introduction

Hydrogen peroxide (H₂O₂) is an important chemical used in many industries, such as detergent, medical/pharmaceutical, paper, and fine chemical manufactures. In the paper industry, H₂O₂ was used as a bleaching agent, which diluted the lignin to screen the cellulose and improve the color by removing the unwanted colored material from the pulp [1]. The production of H₂O₂ reached 2.2 million metric tons, of the 60% was used for paper production. The rest was used to clean agents and solvent cosmetics, medicine, and others [2]. The use of H₂O₂ in papermaking was driven by a green issue related to chlorine and halogen compound, which poisoned the environment [3]. The H₂O₂ was a green chemical compared with halogen-based compound since the side product of the H₂O₂ reaction was water [4].

The need for H₂O₂ always increases annually caused by the growth of fine chemical needs in the industry. For example, propylene epoxidation's commercialization was getting more important due to the hydrogen peroxide propylene oxide (HPPO) needed to synthesize other chemicals [5]. The growth trend was unstoppable in accordance with the need of a cleaning agent in electronic industry. Based on the importance of H₂O₂ in human life, producing it has become attractive for the researchers to explore.

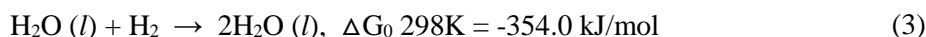
The production method of H₂O₂ has been known as an indirect synthesis of hydrogen peroxide (ISHP), which used anthraquinone as auto-oxidation agent. However, the anthraquinone was dangerous for humans and the environment [6]. To have more green production of H₂O₂, avoiding the use of anthraquinone was needed. The term of direct synthesis of hydrogen peroxide (DSHP) was proposed to substitute the ISHP [7]. The DSHP meant the forming of H₂O₂ occurred directly from H₂ and O₂ on the catalyst surface. Even though the DSHP seemed a simpler step than ISHP, there were some possible reactions on the catalyst as follow [8],



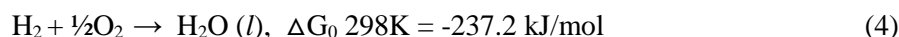
The symbol of ΔG_0 298 K means the free energy of a substance reaction measured under the conditions of 1 atm pressure or an effective concentration of 1 molar and a temperature of 298 K. In fact, the H_2O_2 could be easy to dissociate becoming water since the energy was closed to the H_2O_2 forming as follow



The H_2 gas in the presence of water also leads to form further water as follow



Besides, there was non-selective reaction which thermodynamically preferred as follow



The Gibbs free energy showed in (1) to (2) was calculated by the previous research [8]. From the reactions fore mentioned, (1) and (2) competed with each other, and (4) was preferable. Since the direct forming of H_2O on the catalyst was more likely than H_2O_2 , the researchers investigated the suitable catalyst that optimized the selective forming toward H_2O_2 product.

The well-known catalyst for this area was the alloy of palladium-gold (PdAu), which reached the selectivity to 95% [8]. This alloy has replaced the use of monometallic Pd which had lower selectivity toward H_2O_2 compared with the use of PdAu alloy catalyst.

The reaction of H_2O_2 forming on the catalyst surface followed the steps such as (a) the adsorption of molecular oxygen (O_2) and hydrogen (H_2) occurred on the catalyst surface, (b) the adsorbed O_2 was maintained on the catalyst surface and noted as surface molecular oxygen (O_2^*) while H_2 was dissociated becoming 2H^* (the * symbolized a surface species), (c) O_2^* was hydrogenated becoming OOH^* , and further hydrogenation as HOOH^* ; (d) HOOH^* was released from the catalyst surface to form $\text{H}_2\text{O}_2 (l)$ [9], [10].

The presence of Au in the surface of PdAu alloy catalyst weakened the bonding of Pd- O_2 compared with the binding on the monometallic Pd catalyst. The stronger the O_2 surface bonding, the easier for O_2 to dissociate, becoming 2O^* , which leads to the more difficult to form OOH^* . The weaker the O_2 surface bonding, the easier O_2 released from the surface, and OOH^* could not be formed [4]. Therefore, in the H_2O_2 forming, the bonding of the O_2 surface did not need too strong or weak.

The drawback of PdAu alloy catalyst was the use of expensive metal, as seen in Table 1 [16]. PdAu also needed acid condition to optimize the selectivity, which needs to be improved, such as avoiding the use of acid to have cleaner production. Therefore, finding the alternative catalyst might help to get friendly environment production compared with a current catalyst such as PdAu alloy. Using the more abundant material of catalyst, which had the same selectivity as the current, could also improve the production cost, which meant it supported the green synthesis of H_2O_2 . Some researchers have proposed alternative catalysts to replace the use of PdAu alloy catalysts. For example, palladium-platinum alloy (PdPt) was the more stable catalyst compared with PdAu, however, PdPt did not offer better catalytic performance compared with PdAu. PdPt did not also indicate low-cost material, which lead not to be a favorite choice for replacing PdAu alloy catalyst [11]. Palladium-mercuri alloy (PdHg) showed a better alternative catalyst compared to PdAu related to the selectivity toward H_2O_2 forming by ab initio study [4]. Since Hg might offer serious poisoning for humans and the environment, the choice of PdHg could not be a good alternative for replacing PdAu alloy catalyst. Paladium-silver alloy (PdAg) has also been proposed to replace the use of PdAu, but the study showed PdAg alloy had no better catalytic performance than PdAu alloy [12], [13].

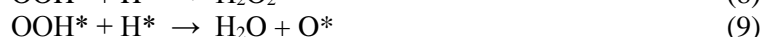
Palladium nickel alloy (PdNi) indicated a catalytic capacity for H_2O_2 direct synthesis based on previous work [14]. However, the mechanism of Ni role in the PdNi was still unclear. The availability of Ni in nature was more abundant than Au, which offered more benefits based on the price. For example, Indonesia had a stock of Ni reached 137 thousand wet metric tons (wmt) [15]. In this study, we want to confirm the catalytic capacity of PdNi for DSHP compared with Pd monometallic and PdAu alloy catalysts.

Table 1. The world price metal per OZT (Troy ONZ).

Metal	Price (USD/ OZT)
Palladium (Pd)	1,567
Gold (Au)	1,515
Platinum (Pt)	841
Silver (Ag)	15.4
Nickel (Ni)	6.0

Considering the drawback of PdAu alloy catalyst, this work offered the finding technique of the alternative catalyst which is abundant in Indonesia and globally environmentally friendly. The presence of O_2^* and H^* on the catalyst surface is the key, which leads to the two-step mechanism of O_2^* hydrogenation to form H_2O_2 [7]. The overall reactions of H_2O_2 forming directly on the surface are written in the reaction (5) to (14). In the direct synthesis of hydrogen peroxide, starting from stable adsorbed O_2 and dissociative adsorption of H_2 .

The O_2^* was hydrogenated to form OOH^* (reaction (5)) as the first step hydrogenation. The intermediate OOH^* was further hydrogenated to $HOOH^*$, which was released from the surface results H_2O_2 (reaction (8)). However, at the same time of OOH hydrogenation reaction (reaction (8)), H_2O can also be formed as reaction (9), as well as OH species forming for reaction (10) and (11). However, if the interaction of OOH^* and surface is weak, the OOH^* may be released as a reaction (12) [9].



The target H_2O_2 can be dissociated to $2OH^*$ (reaction (13)) or attached on the surface as reaction (14).



If the presence of H^* is excessive on the surface, further hydrogenation of $H_2O_2^*$ may occur to form H_2O as a reaction (15) [17].



Research on finding the new catalyst is always attractive since environmental challenges such as global warming and limited energy resource become a big issue for human life. By the role of H_2O_2 , which used in a wide range of human life such as the production of detergent, medicine, paper, and textile, the catalyst used for direct synthesis of H_2O_2 is often reported. The catalyst needs to have good performance in durability, reactivity, selectivity, and environmentally friendly to fulfill the human need of H_2O_2 . The alternative catalyst was studied in single metal [18] or bimetallic as the surface alloy or core-shell system. The alloy catalyst was reported as PdHg [4], AuCu [19], PdAu [20], and PdAg [21].

Another strategy to get selective catalyst is alloying the metal to modify the surface electronic or local geometric structure [22], which improve reaction rate, change product selectivity and avoid catalyst deactivation [23]. The well-known Pd-based catalyst for H_2O_2 direct synthesis is PdAu alloy, which showed 80% selectivity without halide promotor and acid condition [3], [13], [24]. By halide promotor, acid condition, and support TiO_2 , the selectivity of PdAu alloy can be improved to 95% [25], although the ratio of Pd or Au and experimental condition need to be strongly considered [26].

The role Au alloyed to Pd is suppressing molecular oxygen dissociation to atomic oxygen on Pd site [27]. From this view, minimizing the atomic oxygen formation on the surface may avoid water formation and support H₂O₂ formation as the main target [25]. Therefore, the new catalyst should maintain the adsorbed O₂ first on the surface and then facilitate the OOH formation through hydrogenation reaction. The next step that took place on the catalyst surface is further hydrogenation of OOH to get HOOH. Therefore, determining the adsorption of O₂ on the catalyst surface may be a catalyst screening for several suspected candidate catalysts towards the better catalyst finding.

In this work, we explore PdNi alloy, whether it is possible to be a catalyst and Pd or PdAu alloy based on the theoretical approach. PdNi alloy as a catalyst of H₂O₂ direct synthesis has rarely been explored before. The exploration of PdNi as a catalyst candidate was done by observing its adsorption energy and comparing it to the well-known catalyst such as PdAu alloy. The comparison of adsorption energy between Pd and PdAu has been done [4], [9], which indicated the role of Au in the PdAu alloy surface is to decrease the adsorption energy of O₂ on the surface compared to the monometallic Pd catalyst surface. By comparing the adsorption energy of O₂ on PdNi to that on Pd, the potency of PdNi as a new catalyst of H₂O₂ direct synthesis can be defined.

2. Method

2.1. Design

In this work, the adsorption energy data were calculated using ab initio computational program that common for density functional theory (DFT) approach. Some requirements of the calculation were defined as follow, (a) the electron wave function was assumed as a plane wave with 400 eV of the kinetic energy cut off; (b) the interaction of electron valence and nucleus was defined using plane augmented wave (PAW) approach with Purdue and Engelhof (PE) basis set and general gradient approximation (GGA); (c) the Brillouin Zone was sampled in Monkhorst-Pack, with k mesh point $3 \times 3 \times 1$ grid sampling; and (d) Gaussian smearing (width 0,1 eV) was used for electronic occupancy. Convergence criteria for self-consistency were set up at 1×10^{-5} eV with 0.05 eV/Å of force energy. During optimization, the volume and shape of the model were not allowed.

2.2. Procedure and Data Collection

The slab model was used to conduct the calculation. The optimum slab number was observed by comparing the model's atomic energy for 4 to 12 slabs. The slab model then was determined by the principal, i.e., the lower the energy per atom, the more stable the model. However, to choose the slab number, stability of the model and time consumption of the calculation were also considered. The model of 2×2 Pd(111) with 4 to 12 of the slab number was built, as seen in Figure 1. Based on Figure 1, the energy of Pd atom was calculated using equation 16

$$E/n = \frac{1}{n} E_{tot} \quad (16)$$

where n is the number of an atom and is energy per atom, in one slab of a model, there are four atoms. Therefore we can calculate energy per atom in specific slab model as seen in Table 2.

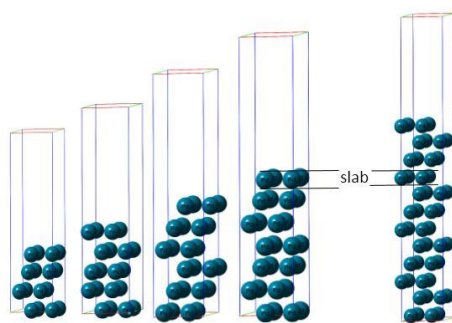


Figure 1. The 2×2 slab model structure of Pd(111) with 4 to 12 of the slab number.

Table 2. Total energy and energy per atom of the model.

Slab	Total Energy (eV)	Energy per Atom (eV)
4	-78.60	-4.91
5	-99.31	-4.97
6	-119.99	-5.00
7	-140.78	-5.03
8	-161.44	-5.04
9	-182.26	-5.06
10	-202.95	-5.07
12	-244.47	-5.09

Total energy (E) was computed based on formula, $E = \sum_i^n \varepsilon_i + \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} drdr' + E_{xc}[\rho] - \int V_{xc}(r)\rho(r)dr$,

where n = electrons, ε_i = the energy of the Kohn-Sham orbital, r = electron coordinate, $\rho(r)$ = ground-state electron density, E_{xc} = exchange correlation energy, and V_{xc} = exchange correlation potential [28].

The more the model, the more negative the total energy, which means the model is more stable. However, the simpler model, the better. Therefore, based on Figure 2, we choose 7th slab model for the model of 2 x 2 Pd (111) because at the 7th slab the slope starts to be less sharp compared to 4 to 6 slab models. Defining Ni's role to the catalytic performance of PdNi alloy, we significantly alloyed the Ni to Pd by 1: 1 of ratio. However, we modeled the surface as monometallic Pd to adapt the synthesis's acid condition where the interaction of Pd and H was strong and condensed slower than Ni, as seen in Figure 3. Therefore, we noted the model as PdNi≅Pd (111). We also considered the surface (111) rather than (110) or (111) because Pd(111) surface shows the highest catalytic selectivity for H₂O₂ among the three surfaces [29].

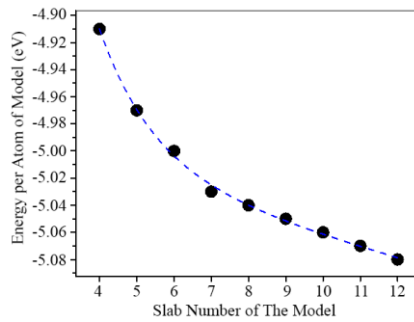


Figure 2. Energy per atom of the model.

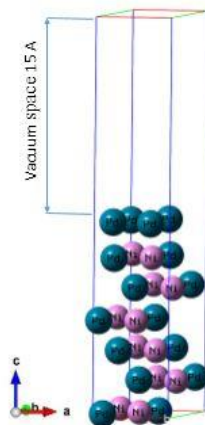


Figure 3. The 7 slabs alloy model of PdNi 2 x 2. Dark cyan and violet balls represent Pd and Ni atoms, respectively.

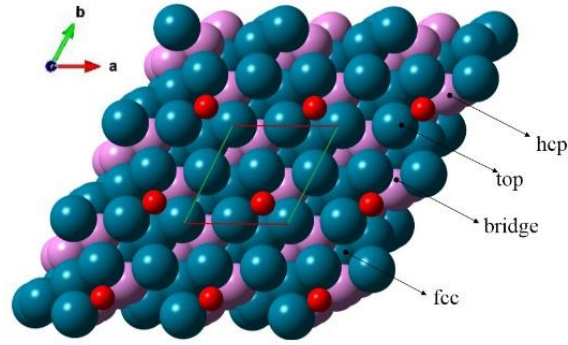


Figure 4. The 2 x 2 surface size of the PdNi(111) adsorption site in top view (c axis) widened toward a and b axes. Dark cyan, violet, and smaller red balls represent Pd, Ni, and O atoms, respectively.

Calculating the adsorption energy of species such as atomic oxygen, the species-surface distance was 2.6 Å before optimization. The most substantial adsorption is located at FCC (face-centered cubic) site, followed successively by HCP (hexagonal closest pack) and bridge sites, and the weakest is on the top site, see Figure 4.

Adsorption energy of atomic oxygen was calculated as follow [18],

$$E_{b,O} = E_{b,O/surface} - E_{clean} - \frac{1}{2}E_{O_2} \quad (17)$$

where $E_{b,O}$ is oxygen adsorption energy, $E_{b,O/surface}$ is the total energy of adsorbed O on the surface, E_{clean} is the total energy of bare Pd(111), and E_{O_2} is total energy of molecular oxygen as the gas state. Considering the stability of the catalyst as an important aspect, we calculated the binding energies, which is to define the energy needed for one atom on the surface to disassemble into single atom, using the formula adopted from previous research,[30] as follow,

$$E_b = \frac{E_{surface} + E_{core} + E_{slab}}{N_{surface}} \quad (18)$$

where E_b is binding energy, $E_{surface}$ is total energy of shell, E_{core} is total energy of core, E_{slab} is total energy of bare Pd(111), and $N_{surface}$ is atom number of surface.

3. Results and Discussion

Based on Table 3, the presence of Ni in the PdNi@Pd(111) weakened 0.22 eV O adsorption energy compared to the monometallic Pd(111) surface. Based on our previous work,[9] the weakening of O adsorption energy on the PdAu(111) surface is also 0.20 eV compared to the monometallic Pd(111) surface. Because O adsorption energy on PdNi@Pd(111) and PdAu(111) has the same trend, which is 0.2 eV lower value compared to that on the monometallic Pd(111), the catalytic selectivity of Pd(111), PdAu(111), PdHg(111) and PdNi@Pd(111) is discussed later based on O_2 and O adsorption energy trends. The comparison of O adsorption energy on Pd(111) and PdNi@Pd(111) can be seen in Table 3, while O's adsorption configuration is in Figure 4.

3.1. Trend of O_2 and O Adsorption on The Pd-Based Catalyst Surface

Considering the H_2O_2 synthesis, we explored the interaction of O_2 to the surface since the adsorption energy of O_2 determined the presence of O_2^* , which lead to the final product H_2O_2 . We did not consider the presence of H_2 in this working since H_2 adsorbed dissociated to H^* on the Pd(111). Based on the direct synthesis mechanism of H_2O_2 , the presence of O_2^* is the key. The adsorption energy of O_2 should be 'enough' to facilitate the O_2^* hydrogenation for HO_2H formation. If the interaction of O_2 and surface is too strong, the adsorbed O_2 can be dissociated to $2O^*$. However, if the O_2 surface interaction is too weak, O_2 may be released to the gas state. There is no exact number of interaction strength for the reference for finding a good catalyst.

Table 3. The comparison of O adsorption energy on 2 x 2 slabs of Pd(111) and PdNi(111) models.

Catalyst	Adsorption Energy of O (eV)
Pd(111)	-1.23
PdNi@Pd(111)	-1.01

Table 4. Adsorption energy of O₂ and O on the various surfaces.

Catalyst	Adsorption Energy of O ₂ (eV)	Adsorption Energy of O (eV)
Pd(111)	-1.07	-1.65
PdAu(111)	-0.88	-1.46
PdHg(111)	-0.87	-1.40

Identifying the interaction between O₂ and candidate catalysts, we compared the adsorption energy among the well-known catalysts. For example, PdAu(111) alloy is the better catalyst proven in experimental compared to monometallic Pd. Based on Table 4, the adsorption energy of O₂ on the better catalyst PdAu(111) alloy is lower compared to Pd(111). The Adsorption energy of O₂ on PdHg(111) alloy is closed to that on PdAu(111) alloy, which leads to the conclusion that PdHg(111) alloy also the better catalyst compared to Pd(111). The lower adsorption energy can be a better catalyst that was explored in previous research.

Edwards *et al.* [10] showed that the PdAu(111) alloy has better catalytic performance than monometallic Pd, see Table 5. The acid condition improves catalyst selectivity and productivity significantly. The role of acid is to suppress the O₂* dissociation caused by the change of surface characteristic, which weakens the interaction of O₂-Pd. A forementioned in Table 4, the strong interaction of O₂-Pd may lead to the dissociation of O₂* to 2O*. The presence of Au or Hg in the alloy of PdAu(111) or PdHg(111) decreases 0.2 eV of O₂ the adsorption energy on alloy surfaces compared to the monometallic Pd surface.

The spontaneous reaction of H₂O₂ formation and the kinetic and thermodynamic information was usually named as Bronsted-Evan Polanyi (BEP) relation. BEP relation has used to prove the higher composition of Au or Hg alloyed to Pd, the higher barrier energy to dissociate O₂* to 2O*, the more O₂* presence [9]. Even, the energy barrier for O₂* formation was higher than OOH formation, which meant that the main key of H₂O₂ formation was related to the adsorbed O₂ on the surface.

The existence of O₂* was the main focus in this work since it can lead to the comparison of catalytic performance among the catalysts. As seen in Table 4, the adsorption energy of O₂ on the surfaces of the catalyst has the same trend as adsorption of atomic O [4]. Therefore, calculating the adsorption energy of O can be used to predict the trend of O₂ adsorption energy on the same catalyst surfaces. Since the atomic O adsorption can predict the trend of O₂ adsorption among different surfaces, while the O₂ adsorption can predict the relative selectivity, we considered the O adsorption as a “selector” to find the new catalyst.

The calculation of O's adsorption energy is easier and faster compared to the calculation of O₂ adsorption. Therefore, we chose the adsorbed atomic oxygen to be used to predict the relative catalytic selectivity of the candidate catalyst, such as PdNi≡Pd(111). Based on the same trend of O₂ and O adsorption energy on surfaces of PdAu(111), PdHg(111), and PdNi≡Pd(111) compared to monometallic catalyst Pd(111), PdNi≡Pd(111) shows the possibility of a new catalyst for H₂O₂ direct synthesis.

Table 5. Comparison of catalyst composition and selectivity.

Catalyst	Treatment	Selectivity (%)
5% Pd/C	-	42
5% Pd/C	2% HNO ₃	42
2.5% Au – 2.5% Pd/C	-	80
2.5% Au – 2.5% Pd/C	2% CH ₃ COOH	98

Table 6. Comparison of binding energy (E_b) on Pd(111) and PdNi(111).

Catalyst	$E_{b,Pd}$, eV/atom
Pd(111)	1.23
PdNi@Pd(111)	1.12

The catalytic performance of PdAu(111) or PdHg(111) compared to the monometallic Pd(111) catalyst was explored using “in silico” approach. The catalytic kinetic was studied by calculating reaction steps to get energy barrier information to indicate the reaction rate. The catalytic thermodynamic was observed by calculating the reaction energy to identify.

3.2. PdNi≡Pd(111) Stability

The stability of the catalyst is also an important factor in getting the optimum catalytic process. Therefore we investigated the stability of PdNi@Pd(111) by calculating the binding energy defined as the energy needed to release one atom from its bulk structure, as seen in Table 6. The binding energies of monometallic Pd(111) and PdNi≡Pd(111) were 1.23 eV and 1.12 eV, respectively, which means that one atom requires 1.23 eV and 1.12 eV, respectively, to be removed from their structure.

Based on binding, the bimetallic PdNi≡Pd(111) alloy has less stable than the monometallic Pd(111). However, the difference of binding energy between monometallic and bimetallic PdNi≡Pd(111) alloys is relatively small so that by referring to the stability of monometallic Pd, the structure of PdNi≡Pd(111) has adequate stability as a catalyst for direct synthesis of H₂O₂.

4. Conclusion

The bimetallic gold-palladium alloy or PdAu(111) is the well-known catalyst for H₂O₂ synthesis. However, the gold has limited availability in the nature and we propose Ni as the alternative alloyed to Pd(111). To investigate PdNi@Pd (111) alloy as the catalyst, we compare PdNi@Pd(111) alloy with catalysts that have been proven based on the literatures, such as Pd(111), PdAu(111), and PdHg(111) by using atomic O adsorption energy as the basis of observation. Based on our calculations, the metal Ni alloyed to metal Pd causes the atomic oxygen adsorption energy on the surface of the PdNi≡Pd (111) to be the same trend as the surface of PdAu(111) and PdHg(111) compared to monometallic catalyst Pd, which indicates the equivalent catalyst selectivity among catalysts of PdNi≡Pd (111), PdAu(111), and PdHg(111) alloys. Considering this fact, we also calculate the PdNi≡Pd (111) alloy's stability compared with the monometallic Pd to prove that PdNi≡Pd (111) alloy stability is acceptable. Thus, this paper proposes PdNi≡Pd (111) alloy as a cheaper catalyst choice compared to PdAu(111). However, this work has some limitations that need further exploration, such as Pd surface electronic change caused by Ni presence. The ratio of Ni and Pd in the core catalyst structure model can be further investigated to determine the composition's effect on the catalytic selectivity. The surface alloy between Pd and Ni also needs to be studied to determine surface composition's effect on the catalytic selectivity.

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