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 the anthraquinone. The synthesis was improved by using the direct reaction of H2 and O2 on Pd or PdAu alloy catalyst's 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 compounds, which poisoned the environment [3]. The H2O2 was a green chemical compared with halogen-based compounds 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 an 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],

\[ \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 (l), \quad \Delta G^0 = 298 \text{ K} = -120.4 \text{ kJ/mol} \] (1)
The symbol of \( \Delta G_0 \) 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 \( \text{H}_2\text{O}_2 \) could be easy to dissociate becoming water since the energy was closed to the \( \text{H}_2\text{O}_2 \) forming as follow

\[
\text{H}_2\text{O}_2 (l) \rightarrow \text{H}_2\text{O}(l) + \frac{1}{2}\text{O}_2, \quad \Delta G_0 \text{ 298K} = -116.8 \text{ kJ/mol} \tag{2}
\]

The \( \text{H}_2 \) gas in the presence of water also leads to form further water as follow

\[
\text{H}_2\text{O}(l) + \text{H}_2 \rightarrow 2\text{H}_2\text{O}(l), \quad \Delta G_0 \text{ 298K} = -354.0 \text{ kJ/mol} \tag{3}
\]

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

\[
\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}(l), \quad \Delta G_0 \text{ 298K} = -237.2 \text{ kJ/mol} \tag{4}
\]

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 each other, and (4) was preferable. Since the direct forming of \( \text{H}_2\text{O}_2 \) on the catalyst was more likely than \( \text{H}_2\text{O}_2 \), the researchers investigated the suitable catalyst that optimized the selective forming toward \( \text{H}_2\text{O}_2 \) product.

The well-known catalyst for this area was the alloy of palladium-gold \((\text{PdAu})\), which reached the selectivity to 95% [8]. This alloy has replaced the use of monometallic Pd which had lower selectivity toward \( \text{H}_2\text{O}_2 \) compared with the use of PdAu alloy catalyst.

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

The presence of \( \text{Au} \) in the surface of \( \text{PdAu} \) alloy catalyst weakened the bonding of \( \text{Pd-O}_2 \) compared with the binding on the monometallic \( \text{Pd} \) catalyst. The stronger the \( \text{O}_2 \) surface bonding, the easier \( \text{O}_2 \) to dissociate, becoming \( 2\text{O}^* \), which leads to the more difficult to form \( \text{OOH}^* \). The weaker the \( \text{O}_2 \) surface bonding, the easier \( \text{O}_2 \) released from the surface, and \( \text{OOH}^* \) could not be formed [4]. Therefore, in the \( \text{H}_2\text{O}_2 \) forming, the bonding of the \( \text{O}_2 \) surface did not need too strong or weak.

The drawback of \( \text{PdAu} \) alloy catalyst was the use of expensive metal, as seen in Table 1 [16]. \( \text{PdAu} \) 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 \( \text{PdAu} \) 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 \( \text{H}_2\text{O}_2 \). Some researchers have proposed alternative catalysts to replace the use of \( \text{PdAu} \) alloy catalysts. For example, palladium-platinum alloy \((\text{PdPt})\) was the more stable catalyst compared with \( \text{PdAu} \), however, \( \text{PdPt} \) did not offer better catalytic performance compared with \( \text{PdAu} \). \( \text{PdPt} \) did not also indicate low-cost material, which lead not to be a favorite choice for replacing \( \text{PdAu} \) alloy catalyst [11]. Palladium-mercuri alloy \((\text{PdHg})\) showed a better alternative catalyst compared to \( \text{PdAu} \) related to the selectivity toward \( \text{H}_2\text{O}_2 \) forming by \textit{ab initio} study [4]. Since \( \text{Hg} \) might offer serious poisoning for humans and the environment, the choice of \( \text{PdHg} \) could not be a good alternative for replacing \( \text{PdAu} \) alloy catalyst. Palladium-silver alloy \((\text{PdAg})\) has also been proposed to replace the use of \( \text{PdAu} \), but the study showed \( \text{PdAg} \) alloy had no better catalytic performance than \( \text{PdAu} \) alloy [12], [13].

Palladium nickel alloy \((\text{PdNi})\) indicated a catalytic capacity for \( \text{H}_2\text{O}_2 \) direct synthesis based on previous work [14]. However, the mechanism of \( \text{Ni} \) role in the \( \text{PdNi} \) was still unclear. The availability of \( \text{Ni} \) in nature was more abundant than \( \text{Au} \), which offered more benefits based on the price. For example, Indonesia had a stock of \( \text{Ni} \) reached 137 thousand wet metric tons \((\text{wmt})\) [15]. In this study, we want to confirm the catalytic capacity of \( \text{PdNi} \) for \( \text{DSHP} \) compared with \( \text{Pd} \) monometallic and \( \text{PdAu} \) alloy catalysts.
Table 1. The world price metal per OZT (Troy ONZ).

| Metal       | Price (USD/OZT) |
|-------------|-----------------|
| Palladium (Pd) | 1567           |
| Gold (Au)   | 1515           |
| 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$_2$O$_2$ [7]. The overall reactions of H$_2$O$_2$ 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$_2$O$_2$ (reaction (8)). However, at the same time of OOH hydrogenation reaction (reaction (8)), H$_2$O 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].

\[
\begin{align*}
O_2^* + H^* & \rightarrow OOH^* \\
O_2^* & \rightarrow O^* + O^* \\
O_2^* & \rightarrow O_2 \\
OOH^* + H^* & \rightarrow H_2O_2 \\
OOH^* + H^* & \rightarrow H_2O + O^* \\
OOH^* + H^* & \rightarrow OH^* + OH^* \\
OOH^* & \rightarrow O^* + OH^* \\
OOH^* & \rightarrow OOH
\end{align*}
\]

The target H$_2$O$_2$ can be dissociated to 2OH* (reaction (13)) or attached on the surface as reaction (14).

\[
\begin{align*}
H_2O_2^* & \rightarrow OH^* + OH^* \\
H_2O_2^* & \rightarrow H_2O_2
\end{align*}
\]

If the presence of H* is excessive on the surface, further hydrogenation of H$_2$O$_2^*$ may occur to form H$_2$O as a reaction (15) [17].

\[
H_2O_2^* + H^* \rightarrow 2H_2O + OH^*
\]

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$_2$O$_2$, 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$_2$O$_2$ is often reported. The catalyst needs to have good performance in durability, reactivity, selectivity, and environmentally friendly to fulfill the human need of H$_2$O$_2$. 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$_2$O$_2$ direct synthesis is PdAu alloy, which showed 80% selectivity without halide promoter and acid condition [3], [13], [24]. By halide promoter, 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 \( \text{H}_2\text{O}_2 \) formation as the main target [25]. Therefore, the new catalyst should maintain the adsorbed \( \text{O}_2 \) first on the surface and then facilitate the \( \text{OOH} \) formation through hydrogenation reaction. The next step that took place on the catalyst surface is further hydrogenation of \( \text{OOH} \) to get \( \text{HOOH} \). Therefore, determining the adsorption of \( \text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \) 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 \( \text{O}_2 \) on the surface compared to the monometallic Pd catalyst surface. By comparing the adsorption energy of \( \text{O}_2 \) on PdNi to that on Pd, the potency of PdNi as a new catalyst of \( \text{H}_2\text{O}_2 \) 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 Engelholf (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 \( 1 \times 10^{-5} \) 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 \( 2 \times 2 \text{Pd}(111) \) 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

\[
E / n = \frac{1}{n} E_{\text{tot}}
\]

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 x 2 slab model structure of Pd(111) with 4 to 12 of the slab number.](image-url)
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, $E = \sum_n \varepsilon_i + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r-r'|} drdr' + E_{xc}[\rho] - \int V_{xc}(r)\rho(r)dr$, where $n = \text{electrons}$, $\varepsilon_i = \text{energy of the Kohn-Sham orbital}$, $r = \text{electron coordinate}$, $\rho(r) = \text{ground-state electron density}$, $E_{xc} = \text{exchange correlation energy}$, and $V_{xc} = \text{exchange correlation potential}$ [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](image1.png)

**Figure 2.** Energy per atom of the model.

![Figure 3](image2.png)

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

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

\[ E_{b,O} = E_{b,O\text{surface}} - E_{\text{clean}} - \frac{1}{2}E_{O_2} \]  

where \( E_{b,O} \) is oxygen adsorption energy, \( E_{b,O\text{surface}} \) is the total energy of adsorbed O on the surface, \( E_{\text{clean}} \) 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,

\[ E_b = \frac{E_{\text{surface}} + E_{\text{core}} + E_{\text{slab}}}{N_{\text{surface}}} \]

where \( E_b \) is binding energy, \( E_{\text{surface}} \) is total energy of shell, \( E_{\text{core}} \) is total energy of core, \( E_{\text{slab}} \) is total energy of bare Pd(111), and \( N_{\text{surface}} \) 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 O₂ 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 O₂ and O Adsorption on The Pd-Based Catalyst Surface

Considering the \( \text{H}_2\text{O}_2 \) synthesis, we explored the interaction of \( \text{O}_2 \) to the surface since the adsorption energy of \( \text{O}_2 \) determined the presence of \( \text{O}_2^* \), which lead to the final product \( \text{H}_2\text{O}_2 \). We did not consider the presence of \( \text{H}_2 \) in this working since \( \text{H}_2 \) adsorbed dissociated to \( \text{H}^* \) on the Pd(111). Based on the direct synthesis mechanism of \( \text{H}_2\text{O}_2 \), the presence of \( \text{O}_2^* \) is the key. The adsorption energy of \( \text{O}_2 \) should be ‘enough’ to facilitate the \( \text{O}_2^* \) hydrogenation for \( \text{HOOH} \) formation. If the interaction of \( \text{O}_2 \) and surface is too strong, the adsorbed \( \text{O}_2 \) can be dissociated to \( 2\text{O}^* \). However, if the \( \text{O}_2 \) surface interaction is too weak, \( \text{O}_2 \) may be released to the gas state. There is no exact number of interaction strength for the reference for finding a good catalyst.
Identifying the interaction between O$_2$ 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 O$_2$ on the better catalyst PdAu(111) alloy is lower compared to Pd(111). The Adsorption energy of O$_2$ on PdHg(111) alloy is close 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 O$_2^*$ dissociation caused by the change of surface characteristic, which weakens the interaction of O$_2$-Pd. A forementioned in Table 4, the strong interaction of O$_2$-Pd may lead to the dissociation of O$_2^*$ to 2O*. The presence of Au or Hg in the alloy of PdAu(111) or PdHg(111) decreases 0.2 eV of O$_2$ the adsorption energy on alloy surfaces compared to the monometallic Pd surface.

The spontaneous reaction of H$_2$O$_2$ 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 O$_2^*$ to 2O*, the more O$_2^*$ presence [9]. Even, the energy barrier for O$_2^*$ formation was higher than OOH formation, which meant that the main key of H$_2$O$_2$ formation was related to the adsorbed O$_2$ on the surface.

The existence of O$_2^*$ 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 O$_2$ 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 O$_2$ adsorption energy on the same catalyst surfaces. Since the atomic O adsorption can predict the trend of O$_2$ adsorption among different surfaces, while the O$_2$ 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 O$_2$ adsorption. Therefore, we chose the adsorbed atomic oxygen to be used to predict the relative catalytic selectivity of the candidate catalyst, such as PdNi$\approx$Pd(111). Based on the same trend of O$_2$ and O adsorption energy on surfaces of PdAu(111), PdHg(111), and PdNi$\approx$Pd(111) compared to monometallic catalyst Pd(111), PdNi$\approx$Pd(111) shows the possibility of a new catalyst for H$_2$O$_2$ direct synthesis.

| Catalyst     | Adsorption Energy of O (eV) | Adsorption Energy of O$_2$ (eV) |
|--------------|-----------------------------|---------------------------------|
| Pd(111)      | -1.23                       | -1.65                           |
| PdNi@Pd(111) | -1.01                       |                                  |

Table 4. Adsorption energy of O$_2$ 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                       |

Table 5. Comparison of catalyst composition and selectivity.
Further investigated to determine the work has some limitations to be studied to determine the composition’s effect of monometallic and bimetallic Ni and Pd in the core catalyst structure model can be further explored. However, the monometallic Pd(111) alloy stability is acceptable. Thus, this paper proposes PdNi alloyed to metal catalysts that have been proven based on the literatures, such as Pd(111), PdAu(111), and PdHg(111). Pd(111) . However, the gold has limited availability in the nature and we propose Ni as the alternative alloyed to Pd 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.

### 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 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 H$_2$O$_2$.

### 4. Conclusion

The bimetallic gold-palladium alloy or PdAu(111) is the well-known catalyst for H$_2$O$_2$ 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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