**First-principles study of N and H atoms adsorption and NH formation on
Pd(111) and Pd₃Ag(111) surfaces**

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Abstract

The role of the presence of Ag atom in Pd₃Ag(111) surface on the adsorption of N and H atoms and NH species was studied by using first-principles calculations based on density functional theory (DFT). The adsorption energies of N and NH species are weakened by at least 0.50 eV when Ag atom is one of the nearest neighbors, in contrast to the case of H, in which the adsorption energies are weakened by at most 0.15 eV. Local density of states (LDOS) profiles show that for N and NH adsorption near the silver alloy atom, the derived anti-bonding states are shifted below the Fermi level and hence the adsorption energy is weakened on the alloyed surface. In the presence of adsorbed N, the adsorption energies of H on the nearby sites are also reduced. Nonetheless, this reductions in H adsorption energies on the most stable sites are lower in Pd₃Ag(111) surface. NH formations with H moving across the Pd atom on both surfaces show comparable activation barriers but the barrier is increased by 0.2-0.3 eV when the formation happens across Ag atom.

Keywords: NH formation, Pd(111) surface, Pd₃Ag(111) surface, N and H co-adsorption, Density functional theory (DFT)

1. Introduction

Hydrogen purification is increasingly important due to the promising role of hydrogen as a possible energy carrier. Hydrogen-based fuel cell provides high efficiency with zero emission of greenhouse gases and is therefore considered a promising alternative power generator. Realization of such technology requires sustainable hydrogen source in which, biomass is regarded as a favorable candidate. The produced gas from biomass, however, is a mixture of gases (CO , CO_2 , N_2 , H_2) [1] and H_2 needs to be separated. Usually, this process is done through the use of separation membrane due to the practical advantage of this method.

Dense metallic membranes are normally employed in purification process because of their capability of producing highly purified hydrogen gas [2]. Pure Pd membrane is commonly used due to its high permeation rate over a wide range of temperature; however, its low durability affects its performance [2]. Alloying Pd with other metals is proposed to solve this issue but this requires the evaluation of the performance of the alloy system toward various applications. In particular, Pd-Ag is known to have higher durability and better hydrogen permeation by a factor of around 1.7 [2,9] in comparison with pure Pd. Notably, Pd-Ag membrane with Ag composition of 23-26% by weight is identified to be the optimum composition to offer highest permeation of H [10].

From the point of view that H_2 is produced along with other gases, it can be expected that these gases can affect the performance of the surface toward H. Specifically, the poisoning effect of N_2 on H permeation was experimentally demonstrated by Wang et al. [3]. In their investigation, the membrane was exposed with equimolar N_2/H_2 at 673 K temperature with total flow rate of 200 ml/min and pressure difference of 1.6 bar ($1.6 \times 10^5 \text{ Pa}$). After 280 minutes of operation, the membrane became inactive as depicted from the reduced H_2 permeation. This observation suggests the possible formation of NH_x on the surface which affected the performance of the membrane. The formation of NH_x ($x = 0-3$) on Pd surfaces has also been addressed in other studies. It was found from NH_3 decomposition investigation that desorption of N from Pd surface is an endothermic process which suggests that the reverse process of NH_3 formation from

adsorbed N and H atoms is feasible [4]. In addition, NH_x formation was also observed even at low pressure at 5.00×10^{-7} Torr (6.67×10^{-2} Pa) but requires the bombardment of electron in order to realize the reaction [5]. It is implied from these previous works that the surface plays crucial role in facilitating the formation of NH_x which was proposed to occur from the interaction of adsorbed N and H atoms [3]. Although N species exist on the surface, the purity of the permeated H does not change [2,3] which indicates that NH_x has impact only with reactions occurring on the surface. It is also worth mentioning that NH formation on surfaces are equally important for investigations on ammonia production as had been recognized in previous literatures [7,8].

Theoretical investigations on H absorption and N_2 and H_2 dissociation on Pd_3Ag surfaces have been carried out [11-14]. Our previous study showed that H_2 dissociative adsorption on Pd(111) and $\text{Pd}_3\text{Ag}(111)$ proceeds with very small or negligible activation barrier [11]. On the contrary, N_2 dissociative adsorption on both surfaces is accompanied by high activation barrier [12]. These results are in good agreement with experimental findings that H_2 has high solubility over a wide range of temperature [2] and pressure [3,9,10] while N_2 dissociation requires not only high temperature and pressure [15] but also longer duration of operation [3].

Given these backgrounds, this present study is motivated with the goal of clarifying the role of Ag atom in Pd_3Ag surface toward NH formation by employing first-principles calculations based on density functional theory (DFT). The adsorption of N, H and NH species on Pd(111) and $\text{Pd}_3\text{Ag}(111)$ are initially discussed before analyzing the formation of NH from initially adsorbed N and H atoms on the surfaces. Co-adsorption of H atom with N atom is also investigated to basically determine the influence of N atom on H atom adsorption. The results show that the presence of Ag atom significantly reduces the adsorption energies of N and NH molecule but barely affects the adsorption energy of H. It also lowers the chance of NH formation due to the obtained higher activation barrier on $\text{Pd}_3\text{Ag}(111)$ than on Pd(111). Electronic structures are analyzed in order to elucidate the underlying mechanisms of the obtained results. We

believe that the conclusions of this work will aid in understanding the interaction of N and H atoms on Pd and Pd₃Ag surfaces.

2. Computational Details

In this study, spin-polarized DFT calculations were performed by using Vienna Ab-initio Simulation Package (VASP) [16-19]. Generalized gradient approximation (GGA) was used to treat exchange-correlation effects with Perdew-Burke-Ernzerhof (PBE) as exchange-correlation functional [20,21]. The ionic cores are formulated by using projector augmented wave (PAW) method [22]. The (111) surface facet is considered since it is the most stable among the low-index surfaces. Although this present study had focused only on the ordered structure of Pd₃Ag(111), the effect of the presence of Ag for the desired reactions has been successfully demonstrated.

The equilibrium lattice constants of bulk Pd and Pd₃Ag systems were initially calculated by using GGA functionals of PBE and PW91 (Perdew-Wang 91), in which, GGA-PBE gives better agreement with experiment. The lattice constants of Pd and Pd₃Ag are 3.938 and 3.996 Å, respectively, in good agreement with the experimental values of 3.89 and 3.92 Å [23]. The surfaces were modeled using the supercell approach and are consisted of 5 atomic layers with 4 atoms in each layer. A vacuum layer of 15 Å is introduced in the supercell to avoid the interaction of the slabs when repeated periodically. Brillouin zone sampling of $8 \times 8 \times 1$ k-points and cutoff energy of 400 eV in plane-wave basis sets were verified to be sufficient to obtain good numerical accuracy with reasonable computational costs. Before introducing the adsorbates on the surface, atoms in the upper layers are allowed to relax for them to respond to the change in the electronic structure due to the introduction of vacuum while keeping the interatomic distances of the atoms in the two lowest layers fixed in their bulk parameters.

Figure 1: High symmetry adsorption sites of (a) Pd(111) and (b) Pd₃Ag(111) surfaces.

Adsorption is investigated by initially placing the adsorbates in the high symmetry sites of the surfaces as shown in figure 1. The system (adsorbate and three topmost layers of the surface) is then allowed to relax in order for the adsorbate to optimize to its local stable adsorption sites. Climbing image-nudged elastic band (CI-NEB) [24,25] is used to find the minimum energy paths and to search the transition states of NH formation. In this method, the three topmost layers and the adsorbates are allowed to move until the forces on these unconstrained atoms are less than 0.03 eV/Å. The accuracy of the identified transition state is further verified by performing vibrational frequency calculation; i.e., existence of single imaginary vibrational frequency.

3. Results and Discussion

3.1 Single atomic adsorption: N and H atoms on Pd(111) and Pd₃Ag(111) surfaces

Adsorption energies on different adsorption sites are calculated by using the following equation:

$$E_{\text{adsorption}} = E_{(\text{surface} + \text{adsorbate})} - (E_{\text{surface}} + E_{\text{adsorbate}}) \quad (1)$$

Here, $E_{\text{adsorption}}$ is the adsorption energy of the adsorbate, $E_{(\text{surface} + \text{adsorbate})}$ is the total energy of the surface – adsorbate system, E_{surface} is the total energy of the clean surface, and $E_{\text{adsorbate}}$ is the total energy of the isolated adsorbate. Take note that this equation defines the adsorption energy for the case

where the adsorbate is far from the surface as the reference. A more negative value that can be obtained from it implies stronger adsorption energy.

Site	Number of Sites per Unit Cell	Adsorption Energy (eV)	
		N Atom	H Atom
Top	4	-2.28	-2.29
HCP Hollow	4	-4.66	-2.76
FCC Hollow	4	-4.74	-2.80
Bridge	4	FCC Hollow	-2.66

Table 1: Adsorption energies and number of adsorption sites of N and H atoms on Pd(111) surface.

Site	Number of Sites per Unit Cell	Adsorption Energy (eV)	
		N Atom	H Atom
Top _{Pd}	3	-2.27	-2.26
Top _{Ag}	1	-0.82	-1.49
HCP Hollow _{3Pd}	1	-4.76	-2.78
HCP Hollow _{2PdAg}	3	-3.73*	FCC Hollow _{3Pd}
FCC Hollow _{3Pd}	1	-4.55	-2.87
FCC Hollow _{2PdAg}	3	-3.87*	-2.66*

Table 2: Adsorption energies and number of adsorption sites of N and H atoms on Pd₃Ag(111) surface.

Table 1 summarizes the adsorption energies of N and H atoms on Pd(111) surface after performing relaxation. It is observed that the N atom that is initially placed on bridge site moves to nearby FCC hollow site after relaxation. Table 2 lists the adsorption energies of N and H atoms on Pd₃Ag(111) surface. On this surface, all of the adsorbates that were initially placed on the bridge sites of Pd₃Ag(111) surface had moved to the nearby hollow sites after relaxations. The asterisks indicate that the adsorbates were displaced from their initially defined position (high symmetry site) after relaxation and are illustrated in figure 2. Notably, the movement of the adsorbates signifies their preference to interact with Pd atoms over the Ag atom. This can be understood from the basis that the *d* orbital of Ag is fully filled while it is only partially filled for Pd. Ag atom, therefore, cannot efficiently establish chemical bonding with the adsorbates.

Figure 2: Adsorbates that are displaced from their initial position (high symmetry sites) after relaxation.

Red broken circles show the initial positions of the adsorbates: (a) HCP Hollow_{2PdAg} site for N atom

(b) FCC Hollow_{2PdAg} site for N atom (c) FCC Hollow_{2PdAg} for H atom.

The data from tables 1 and 2 suggest that the presence of Ag atom weakens the adsorption energies of both N and H, especially on top of Ag (Top_{Ag} site). With the adsorption energies on Pd(111) as reference, adsorption energies of N near Ag atom are reduced by at least 0.87 eV while the adsorption energies of H are reduced by at most 0.15 eV (except on Top_{Ag} site). Therefore, this indicates that the presence of Ag atom reduces the adsorption energies of N on the majority of adsorption sites while nearly retaining the adsorption energies of H which is the desired result. Pd₃Ag(111) surface also reduces the number of preferable adsorption sites for N. For example, there is only one HCP Hollow_{3Pd} (from the second column of table 2) site which is the preferable adsorption site for N, but there are three HCP Hollow_{2PdAg} sites that are less preferred.

Figure 3: Local density of states (LDOS) of p orbitals of N and d orbitals of the surface atoms for adsorbed N on (a) FCC Hollow site of Pd(111) (b) FCC Hollow_{2PdAg} site of Pd₃Ag(111). Partial charge density distributions are plotted in order to show the antibonding states characteristics of the highlighted energy range.

Figure 3 shows the LDOS profile of adsorbed N on FCC Hollow site of Pd(111) and FCC Hollow_{2PdAg} site of Pd₃Ag(111). The LDOS of N is projected on p orbitals while the LDOS of Pd and Ag atoms are projected on their d orbitals. The bottom right insets of figure 3 (a) and (b) show the partial charge densities that are projected in the highlighted energy range in order to verify that the states in the region have antibonding characteristics. The derived antibonding state, arising from the interaction of adsorbate and substrate, can reveal the reason behind the difference in adsorption energies especially in case of adsorption with and without the Ag as the nearest neighbor. Filling the antibonding state with electron will result to the repulsion between the adsorbate and substrate, which reduces the adsorption energy [26,27]. Figure 3 (a) shows that the antibonding states are above the Fermi level, while figure 3 (b) shows that the antibonding states are partially occupied. The partially occupied antibonding states when N is near the Ag atom results in the weakening of the N adsorption energy.

Figure 4: LDOS of s orbital of H and d orbitals of the surface atoms for H adsorbed on (a) FCC Hollow site of Pd(111) surface (b) FCC Hollow_{2PdAg} site of Pd₃Ag(111) surface. Partial charge density distributions are plotted in order to show the antibonding states characteristics of the highlighted energy range.

Figure 4 shows the LDOS profile of H and its nearest neighbor metal atoms, which are projected on the s and d orbitals, respectively. In the figure, H is adsorbed on FCC Hollow site of Pd(111) and FCC Hollow_{2PdAg} site of Pd₃Ag(111). For both cases, the positions of the derived antibonding states of H are comparable and are located above the Fermi level. This finding provides the explanation for the small difference in the adsorption energies of H on Pd(111) and Pd₃Ag(111).

3.2 NH adsorption on Pd(111) and Pd₃Ag(111) surfaces

Pd(111) Surface		Pd ₃ Ag(111) Surface	
Site	Adsorption Energy (eV)	Site	Adsorption Energy (eV)
Top	-1.47	Top _{Pd}	-1.49
		Top _{Ag}	-0.53
HCP Hollow	-3.74	HCP Hollow _{3Pd}	-3.86
FCC Hollow	-3.88	HCP Hollow _{2PdAg}	-3.15
		FCC Hollow _{3Pd}	-3.81
		FCC Hollow _{2PdAg}	-3.27

Table 3: Adsorption energies of NH molecules on Pd(111) and Pd₃Ag(111) surfaces.

NH always prefers to adsorb vertically where N is on the bottom and H is on top (N-end configuration). Even when it is intentionally placed parallel to the surface, it will adsorb perpendicularly. Because of this adsorption geometry, the adsorption energies on high symmetry sites of the surfaces have the same trend with that of N adsorption. Table 3 summarizes the adsorption energies of NH on Pd(111) and Pd₃Ag(111) surfaces. The adsorption energies of NH on both surfaces are weaker than that of N atom adsorption; nevertheless, the obtained values suggest that NH molecules are energetically stable on the surfaces. The weaker adsorption energy for NH adsorption is attributed to the smaller amount of charge that is transferred from the surface to NH. Bader charge analysis [28] depicts that N adsorbed on FCC₃Pd site has gained 0.74 amount of charge while NH adsorbed on the same site has only gained 0.59 amount of charge.

Figure 5: LDOS of *s* and *p* orbitals of NH molecule and *d* orbitals of the surface atoms for NH adsorbed on (a) Pd(111) surface (b) Pd₃Ag(111) surface. Partial charge density distributions are plotted in order to show the antibonding states characteristics of the highlighted energy range.

Figure 5 shows the LDOS profiles of NH molecule and of the Pd and Ag atoms, in which, the LDOS of NH is projected on both *s* and *p* orbitals while the LDOS of Pd and Ag are projected on their *d* orbitals. NH molecule is adsorbed on FCC Hollow site of Pd(111) and on FCC Hollow_{2PdAg} site of Pd₃Ag(111). Similar to the case of N adsorption, the adsorption of NH on Pd(111) shows that the derived antibonding

states are unoccupied while it is partially occupied when NH is adsorbed near Ag atom. Therefore, Ag weakens the adsorption of NH on Pd₃Ag(111) surface.

3.3 Adsorption of H in the Vicinity of adsorbed N

This section demonstrates the poisoning effect of the adsorbed N atom toward H. The adsorption energies from tables 1 and 2 indicate that both N and H have the same preferable adsorption sites. In the trivial case, it can be seen that once N is adsorbed on these sites, it can block the active adsorption site of the H. The more interesting question is how the adsorbed N influences the adsorption energy of nearby H.

Energy	Pd(111) Surface		Pd ₃ Ag(111) Surface

E_1 (H with N)	-2.44	-2.42	-2.51	-2.57
E_2 (H w/o N)	-2.80	-2.76	-2.87	-2.78

Figure 6: Most stable configurations for H atom with the presence of initially adsorbed N atom on Pd(111) and Pd₃Ag(111) surfaces.

Figure 6 illustrates the most stable configurations where H is adsorbed near the initially adsorbed N atom on Pd(111) and Pd₃Ag(111) surfaces. In the table, E_1 represents the adsorption energies of H in the presence of N, and E_2 represents the adsorption energies of single H (results presented in tables 1 and 2). It is shown here that the presence of N reduces the adsorption energy of H. However, the binding energy of H in the most stable sites is energetically more preferred on Pd₃Ag(111) than on Pd(111). Thus, in this co-adsorption of N and H atoms, Pd₃Ag surface lowers the reduction in the adsorption energy of H which is an advantage in comparison to pure Pd surface. The dissociation of H₂ in the presence of adsorbed N atom on the surface is likewise investigated in order to fully describe the effect of N atom toward H. The activation barrier for H₂ dissociative adsorption on top of N atom is ~1.5 eV. This barrier is much higher than the results presented in previous literature [11], which shows that the most efficient H₂ dissociative

adsorption on both Pd(111) and Pd₃Ag(111) surfaces is only accompanied by small or negligible activation barriers (~0.1 eV). It is also verified from this that the presence of N atom can possibly prohibit the dissociation of H₂ on the surface.

3.4 NH formation on Pd(111) and Pd₃Ag(111) surfaces

Figure 7: Reaction path of NH formation with H atom moving across the Pd atom of (a) Pd(111) and (b) Pd₃Ag(111). Below the graphs are the geometric structures in the initial, transition, and final states.

N-H interatomic distances are also indicated.

As mentioned in the introduction, NH formation is suggested to be crucial factor in H permeation. In this section, the formation of NH from the initially adsorbed N and H atoms on the surfaces are discussed. Figures 7 (a) and (b) show the minimum energy path for NH formation with H atom moving across the Pd atom of Pd(111) and Pd₃Ag(111) surface, respectively. The results show that the activation barriers of the reaction in these two cases differ only by 0.07 eV. Although the barrier is higher on Pd₃Ag(111) surface, it is difficult to conclude that such phenomenon is due to the presence of Ag atom.

Figure 8: Reaction path of NH formation along the minimum energy path that occurs across the Ag atom of Pd₃Ag(111) surface. On the right hand side of the graph are the corresponding geometries in the initial, transition, and final states. N-H interatomic distances are also indicated.

From the adsorption energies of adsorbates near the Ag atom, it is expected that the NH formation across Ag atom should be more difficult. In order to verify this assumption and to obtain quantitative value of the activation barrier, reaction path of NH formation across the Ag atom is determined. Figure 8 shows the case of NH formation with H moving across Ag atom. NH formation across Ag atom is not the minimum energy path, and therefore, the reaction will not go along this intended path. To overcome this problem, H is first optimized on top of the Ag atom, and then two NEB calculations are performed in order to connect the initial and final states. The result shows that the activation barrier is higher by 0.2-0.3 eV than the case when H is moving across Pd atom. It is important to note that there are two imaginary vibrational frequencies from this case since the reaction is forced to occur. However, it was verified that Ag atom does not only reduce the adsorption energies of N and NH, but it also prevent NH formation.

Wang et al. [3] reported the disadvantageous effect of N₂ towards H₂ permeation on Pd membrane due to the formation of NH molecules. On the other hand, our study shows better property of Pd₃Ag(111) over Pd(111) in prohibiting NH formation. Also, the poisoning effect is found to be lower in Pd₃Ag(111) based on the adsorption energies of H, N, NH and from the findings on N and H co-adsorption. Thus, our results

will contribute in understanding the important role of Ag in PdAg membrane for hydrogen-related applications.

4. Conclusion

The presence of Ag in Pd₃Ag(111) surface offers better prohibition of NH formation compared to Pd(111) surface and reduces the adsorption energies of N and NH while barely affecting the adsorption energies of H. In addition, the Pd₃Ag(111) substantially decreases the preferable adsorption sites for N and NH. Local density of states profiles reveal that the derived antibonding states are shifted below the Fermi level when either N or NH molecule is adsorbed near the Ag atom, and is the reason for the weakening of the adsorption energies. It is also found that H adsorption energies are reduced when N is present on the surface but this effect is more obvious in Pd(111) surface than in Pd₃Ag(111) surface. This result also justifies the poisoning effect of the N towards H. The activation barrier for NH formation strongly depends on the surface atom where the reaction proceeds. Comparable activation barriers are obtained when H moves across the Pd atom of both surfaces to form NH. However, a higher activation barrier by ~0.2-0.3 eV is observed when H moves across the Ag atom. The presence of Ag, therefore, does not only prevent N adsorption but also reduces the chance of NH formation.

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