A DFT Study of Arsine Adsorption on Palladium Doped Graphene: Effects of Palladium Cluster Size

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Abstract

In this study, we have investigated the size effects of palladium (Pd) doped single-vacancy defective graphene (SDG) surface to the adsorption of AsH_3 and its dehydrogenated products on Pd using density functional theory calculations. Here, Pd cluster binding study revealed that Pd_6 nanocluster bound strongest to the SDG surface, while adsorption of AsH_x ($x = 0 - 3$) on the most stable Pd_n doped SDG showed that dehydrogenated arsine compounds adsorbed onto the surface stronger than the pristine AsH_3 molecule. Charge analysis revealed that considerable amount of charge migration from Pd to dehydrogenated arsine molecules after adsorption may constitute strong adsorption for dehydrogenated arsine. In addition, study of thermodynamic pathways of AsH_3 dehydrogenation on Pd_n doped SDG adsorbents indicated that Pd cluster doping on SDG adsorbent tends to be thermodynamically favorable for AsH_3 decomposition than the single-Pd atom doped SDG. Hence, our study has indicated that Pd_6 clusters doped SDG is more advantageous as adsorbent material for AsH_3 removal.

Keywords: Arsine removal; Pd cluster; defective graphene; adsorbent; cluster size; density functional theory

1. Introduction

Coal combustion in a coal power plant is a major source causing severe environmental implication. Coal power plant emitted various hazardous compounds, which are predominantly sulfur oxides (SO_x) and nitrogen oxides (NO_x). These major harmful components are generally removed from flue gas using selective catalytic reduction (SCR).[1] However, numerous toxic compounds are still presented and released into the atmosphere in trace amounts, such as mercury and arsine (AsH_3).[2-4] AsH_3 is of specific concern due to its extreme toxicity and volatility. AsH_3 is colorless, slightly soluble in water, and with mild garlic-like odor in gas form. It can trigger serious health problem even if small amount of AsH_3 was ingested into human body[5-13] causing acute fatal intoxication or long-term chronic disease such as arsenicosis. Without suitable exclusion of AsH_3 from flue gas, AsH_3 would be released into the atmosphere and subsequently contaminated the water resources and agricultural soils.[4, 14] Thus, finding an effective method to remove AsH_3 from flue gas stream is essential for reducing environment impact from coal power plants.

Generally, AsH_3 is eliminated non-specifically along with other trace elements in flue gas, since it is not economical and practical to use a specific adsorbent for its sole removal. For example, activated carbon injection (ACI) method in a coal-fired power plant,[15] where injected activated carbons were used to adsorb unwanted components from flue gas stream. Although carbon-based adsorbent such as activated carbon is known for its high surface area and its cost efficiency[16-18], it is not sufficiently effective for AsH_3 removal from flue gas.

To effectively remove AsH_3 , catalytic reaction is required to transform AsH_3 into AsH_2 , AsH and elementary arsenic (As^0) to improve adsorbability before elimination. Noble metal such as Pd adsorbents was reported for its high AsH_3 adsorption capability and its catalytic property converting AsH_3 into AsH . [19] To improve cost efficiency of noble metal adsorbents, noble metals were doped onto the carbon-based adsorbents such as activated

carbon and graphene nanosheets.[20-27] The defect-rich carbon materials (*e.g.* contains high carbon vacancies and edges) served well as adsorbents for metal nanocluster deposition, since bindings at the edge and carbon-vacancy site were more favorable[28-38] than inefficiently adding metal dopant directly onto pristine graphene.[39, 40] For example, Quinn *et al.* reported that CuO-doped carbon adsorbent was a good candidate for arsine removal from syngas.[41] There were numbers of studies focusing on removal of arsenic compounds from water [42-46], but a few were specifically addressed AsH₃ removal from gas stream [41]. In addition, Pd also gained attention to have decent adsorption capability for other toxic elements such as mercury.[19, 47, 48] However, it is not known whether the doped Pd cluster size will affect the adsorption and catalytic prosperities. Thus, study Pd cluster-size effect for AsH₃ removal will be profoundly beneficial.

In this study, suitable binding modes of various sizes of Pd_n nanoclusters (n = 1, 4, and 6) onto graphene surface were investigated using density functional theory (DFT) calculations. Then, we examined AsH₃ adsorption and its dehydrogenated products such as AsH₂, AsH, and As species on the most stable modes of Pd doped SDG surface. In such calculations, thermodynamic pathways of AsH₃ oxidation on those adsorbents were proposed according to the stable adsorptions of AsH_x (x = 0–3). The Pd cluster-size effect on the AsH₃ decomposition pathway was discussed. Electronic properties such as finite charge transfer, partial density of states (PDOS), d-band centers were intensively characterized in order to understand the AsH₃ decomposition process which is an efficient catalytic reaction for AsH₃ removal.

2. Computational Details

In this work, DFT calculations were performed using the DMol³ module from Material Studio software package version 5.5.[49, 50] Here, exchange and correlation

interactions were based on the generalized gradient approximation (GGA) using Perdew–Wang functional (PW91).[51] A double-numerical basis with polarization functions (DNP) was chosen within the effective core potential (ECP)[52, 53] with real-space cutoff radius of 4.1 Å and spin polarization was allowed. The partial occupancies were treated using smearing energy of 0.005 Ha. The $7 \times 7 \times 1$ k -point grids were used for 5×5 pristine graphene (PG) supercells in a periodic system (total of 50 carbon atoms). For all calculations, simulation box was fixed after the bulk parameters were optimized based on a hexagonal lattice system with a , b parameters of 12.3×12.3 Å, respectively, while the vacuum space was added in z direction so that c of lattice parameter became 30 Å to avoid interaction between periodic images (see **Fig. S1(a)**). An SDG was constructed by optimizing structure after removing one carbon atom from the pristine graphene, thus 49 carbon atoms were presented in the SDG system (see **Fig. S1(b)**).

The binding energy (E_b) of Pd_n ($n = 1, 4$, and 6) on SDG was calculated from:

$$E_b = E(\text{Pd}_n - \text{SDG}) - E(\text{SDG}) - E(\text{Pd}_n) \quad (1)$$

where $E(\text{Pd}_n - \text{SDG})$, $E(\text{SDG})$, and $E(\text{Pd}_n)$ are the total energies of Pd_n doped on SDG, clean SDG, and relaxed free Pd_n systems, respectively. Noted that negative binding energy represents stronger binding between Pd_n and SDG.

Next, adsorption energy (E_{ad}) of AsH_x molecule ($x = 0, 1, 2$, and 3) on Pd_n doped SDG was calculated from:

$$E_{ad} = E(\text{AsH}_x/\text{Pd}_n - \text{SDG}) - E(\text{Pd}_n - \text{SDG}) - E(\text{AsH}_x) \quad (2)$$

where $E(\text{AsH}_x/\text{Pd}_n - \text{SDG})$ refers to the total energy of AsH_x adsorbed on Pd_n doped SDG, while $E(\text{AsH}_x)$ is the total energy of isolated AsH_x molecule. Also, negative adsorption energy indicates stronger interaction between AsH_x and adsorbent.

3. Results and Discussion

3.1 Pd atom and Pd clusters deposition on single-vacancy defective graphene surface

In this section, Pd atom, Pd₄, and Pd₆ clusters deposition on SDG surface will be discussed. For simplicity, Pd_n doped on SDG is denoted as Pd_n-SDG hereinafter. In the first step, Pd₄ and Pd₆ clusters were optimized to find stable configuration and their corresponding energies. For Pd₄ cluster, the most stable structure was tetrahedral with average Pd-Pd bond length of 2.66 Å (see **Fig. 1(a)**). In the case of Pd₆ cluster, octahedral was the most stable configuration with the average distance between two Pd atoms of 2.71 Å (see **Fig. 1(b)**).

Next, Pd atom and the optimized Pd₄ and Pd₆ clusters were adsorbed onto the SDG surface to find an optimized structure of Pd_n deposition. Noted that vacancy site of SDG was chosen to be the binding site due to its high reactivity as suggested in the previous studies.[54, 55] The binding calculation result indicated that Pd atom adsorbed strongly at the vacancy site ($E_b = -5.47$ eV) with mean average distance from C near vacancy site to Pd atom of 1.951 Å (see **Fig. 2(a)**).

Fig. 1: Optimized structure of Pd_n clusters **(a)** $n = 4$ and **(b)** $n = 6$.

After that, we doped the Pd₄ cluster onto the SDG surface at vacancy site. Based on the tetrahedral geometry of Pd₄, two binding positions on SDG were considered: (1) top-down tetrahedral (Pd_{4A} position), where one of Pd atom is put on top of the vacancy site (see **Fig. S2(a)**); and (2) facet-down tetrahedral (Pd_{4B} position), in which one center of the tetrahedral facet was laid at the vacancy site of SDG (see **Fig. S2(b)**). Considering Pd_{4A} deposition on SDG, one atom at the corner of Pd_{4A} cluster bound strongly onto the SDG

surface with $E_b = -5.52$ eV (see **Fig. 2(b)**). The average bond length between the nearest C atoms to the closest Pd atom was 1.967 Å, which was slightly longer ($+0.015$ Å) than that of the single Pd atom deposition. For $\text{Pd}_{4\text{B}}$ deposition, the $\text{Pd}_{4\text{B}}$ cluster was tilted after the geometry was relaxed such that one Pd atom aligned on top of the vacancy site and another two Pd atoms also bound to SDG (see **Fig. 2(c)**). The E_b of $\text{Pd}_{4\text{B}}$ binding on SDG was -5.59 eV, which was comparable to that of the $\text{Pd}_{4\text{A}}$ system. The average bond length of C-Pd in this system is 1.960 Å; a $+0.009$ Å increases from the single Pd atom deposition case.

For Pd_6 cluster deposition on SDG, we found only one stable deposited configuration, which is one corner of Pd_6 situated at the top of vacancy site (see **Fig. S2(c)** for configuration before optimization). After optimization of deposited structure, the Pd_6 configuration tend to be similar to the $\text{Pd}_{4\text{B}}$ binding result, where one Pd atom was located at the vacancy site and the other two adjacent Pd atoms bound onto the SDG surface (see **Fig. 2(d)**). The binding energy of Pd_6 cluster doped on SDG was -5.99 eV, which was the strongest binding among all Pd_n depositions in our study. Table 1 shows all related binding parameters after Pd_n deposition on SDG.

Fig. 2 The optimized structures after Pd_n ($n = 1, 4$, and 6) deposition on SDG: (a) Pd atom (b) $\text{Pd}_{4\text{A}}$ cluster (c) $\text{Pd}_{4\text{B}}$ cluster and (d) Pd_6 cluster.

To provide an insight of the Pd interaction with SDG, we analyzed partial density of states (PDOS) of Pd_n binding onto SDG surface. **Figure 3(a)** shows PDOS of $2s$ and $2p$

orbitals of the C atoms near SDG vacancy versus 4d orbital of Pd atom. The figure shows that 2s orbital of C atoms slightly overlapped with 4d orbital of Pd atom within the range of -19.74 (not shown in the figure) to -3.14 eV below the Fermi level, where only their PDOS tails were intersected. On the other hand, 2p orbital of C atoms broadly overlapped with Pd's 4d orbital so that their highest density peaks were closer to each other (-6.41 eV and -4.24 eV for 2p-C and 4d-Pd orbitals, respectively). PDOS of Pd₁-SDG is in agreement with the previous studies.[54, 55] The d-band center of Pd atom is found at -4.51 eV. Next, **Fig. 3(b)-(d)** shows PDOS of 2s and 2p orbitals of three C atoms near vacancy site versus 4d orbital of Pd_{4A} (**Fig. 3(b)**), Pd_{4B} (**Fig. 3(c)**), and Pd₆ (**Fig. 3(d)**) clusters. Considering 4d orbital of Pd_n clusters, d-band centers of Pd_{4A}, Pd_{4B}, and Pd₆ clusters were found at -1.38, -1.57, and -1.51 eV, respectively. The d-band result shows that 4d orbital of Pd clusters shifted much closer toward the Fermi level, which is a significant difference compared to that of Pd atom. The highest 4d orbital density peaks of Pd_{4A}, Pd_{4B}, and Pd₆ clusters were found at -0.82, -0.49 and -0.76 eV, respectively. Noted that 4d orbitals of Pd clusters mostly overlap with 2p orbital rather than 2s orbital of C atoms.

Table 1 Pd_n (n = 1, 4, and 6) deposition on SDG showing binding energy (E_b) and the interatomic distance between closest Pd atom to the SDG surface and its nearest C atoms.

Surface	E _b (eV)	Bond length (Å)			
		C1-Pd	C2-Pd	C3-Pd	Average
Pd ₁ -SDG	-5.47	1.951	1.951	1.952	1.951
Pd _{4A} -SDG	-5.52	1.966	1.967	1.967	1.967
Pd _{4B} -SDG	-5.59	1.950	1.955	1.974	1.960
Pd ₆ -SDG	-5.99	1.963	1.970	1.956	1.963

Fig. 3: Partial density of states (PDOS) after Pd deposition showing 2s and 2p orbitals of C atoms near adsorption site versus the 4d orbitals of (a) Pd atom (b) Pd_{4A} cluster (c) Pd_{4B} cluster and (d) Pd₆ cluster.

3.2 Adsorption of AsH_x on Pd_n doped single-vacancy defective graphene surface

In this section, we studied adsorption of AsH_x ($x = 0-3$) molecule on PG and Pd_n doped SDG adsorbents obtained from section 3.1. We first begin with AsH₃ adsorption on PG surface. In this calculation, AsH₃ was adsorbed on three adsorption sites of PG: atop, bridge, and hollow sites (see **Fig. S3**). The adsorption result showed that AsH₃ adsorbed weakly on all adsorption site of PG surface with $|E_{ad}| < 0.1$ eV. The most stable adsorption of AsH₃ was on the bridge site with E_{ad} of -0.08 eV and distance between As-PG surfaces was 3.452 Å (see **Fig. 4**).

Fig. 4: The optimized structure of AsH₃ adsorption on PG surface

(a) top view and (b) side view.

Next, AsH₃, AsH₂, AsH, and As atom were adsorbed on Pd₁-SDG substrate. **Figures 5(a)-(d)** show the optimized structures after AsH_x adsorption. E_{ad} of AsH_x adsorption on Pd₁-SDG were -0.53, -1.73, -1.77, -1.64 eV for AsH₃, AsH₂, AsH, and As species, respectively. Noted that the adsorption strengths were significantly increased for AsH₂, AsH, and As systems comparing to that of AsH₃.

Next, we considered AsH_x adsorption on Pd_{4A}-SDG. **Figures 5(e)-(h)** show optimized structures of AsH₃, AsH₂, AsH and As atom after adsorption on the Pd_{4A}-SDG substrate. The result showed that AsH₃ adsorbed at the bridge site of Pd_{4A} cluster with As atom close to the cluster. In contrast, AsH₂, AsH, and As systems preferred to adsorb on the three-fold sites of Pd_{4A} cluster. In terms of adsorption strength, adsorption energy of AsH_x (x = 0, 1, 2, 3) on Pd_{4A}-SDG were -0.72, -2.42, -3.45 and -3.96 eV, respectively. This is considerably increased comparing to the E_{ad} of AsH_x on Pd₁-SDG. In case of AsH_x adsorption on Pd_{4B}-SDG, adsorption energies were found similar to that of Pd_{4A}-SDG systems with E_{ad} of -1.00, -2.50, -3.32 and -3.81 eV, for x = 0-3 of AsH_x adsorbate, respectively. For this adsorbent, AsH₃ and AsH₂ were adsorbed at the bridge sites of Pd_{4B} cluster, while AsH and As were adsorbed at the three-fold sites of Pd_{4B} cluster (see **Figs. 5(i)-(l)**).

Finally, we consider the adsorption of AsH₃, AsH₂, AsH and As on the Pd₆-SDG systems. **Figures. 5(m)-(p)** show the optimized configuration after adsorption of AsH_x on the Pd₆-SDG sorbent. The stable sites of AsH₂, AsH and As adsorption were found at the three-fold sites of Pd₆ cluster, while AsH₃ molecule adsorbed on top of one Pd atom in Pd₆ cluster. Adsorption energies of AsH₃, AsH₂, AsH and As on Pd₆-SDG were -0.88, -2.28, -3.46 and -4.06 eV, respectively.

Fig. 5: The optimized structure of AsH_x ($x = 0-3$) adsorption on **(a)-(d)** Pd_1 -SDG **(e)-(h)** Pd_{4A} -SDG **(i)-(l)** Pd_{4B} -SDG and **(m)-(p)** Pd_6 -SDG.

In summary, AsH_x adsorptions on Pd clusters doped SDG were significantly stronger than the AsH_x adsorption on Pd atom doped SDG. Furthermore, AsH_3 adsorption was considerably weaker compared to the adsorption strength of AsH_2 , AsH , and As adsorbates on all Pd_n -SDG adsorbents.

To analyze charge interaction characteristics of AsH_x adsorption on Pd_n doped SDG, we compared charge difference (q) before and after AsH_x adsorption for each system. Here, Mulliken charge analysis[56] was used to calculate atomic charges for AsH_x and Pd_n -SDG substrate. Charge difference is calculated from:

$$\Delta q(s) = q_a(s) - q_b(s) \quad (3)$$

where $q_b(s)$ and $q_a(s)$ denoted net Mulliken charge of component “s” before and after adsorption, respectively. Table 2 shows q of AsH_x adsorbate, Pd_n cluster, and SDG surface

after adsorption. First, we considered AsH_x adsorption on $\text{Pd}_1\text{-SDG}$. In this case, AsH_x molecule received charge from $\text{Pd}_1\text{-SDG}$ substrate such that the molecular charges of adsorbates decreased by -0.02, -0.48, -0.57, and -0.62 e, for AsH_3 , AsH_2 , AsH , and As adsorbates, respectively. In the case of AsH_2 , AsH , and As , charges transferred to those molecules were mainly originated from the SDG surface, since the charge of SDG become more positive ($q(\text{SDG}) = +0.28, +0.35, +0.37$ e for AsH_2 , AsH , and As , respectively). In contrast, the charge received by AsH_3 was mostly come from Pd_1 atom ($q(\text{Pd}_1) = +0.100$ e) rather than the SDG.

Table 2 The adsorption of AsH_x ($x = 0\text{--}3$) on $\text{Pd}_n\text{-SDG}$; the adsorption energy (E_{ad}), the average distance between As atom and nearest Pd atoms ($d_{\text{As-Pd}}$), the Mulliken charges differences (q) of AsH_x , SDG, and Pd_n after AsH_x adsorption.

Surface	E_{ad} (eV)	$d_{\text{As-Pd}}$ (Å)	$\Delta q(\text{AsH}_x)$ (e)	$\Delta q(\text{SDG})$ (e)	$\Delta q(\text{Pd}_n)$ (e)
<i>$\text{Pd}_1\text{-SDG}$</i>					
AsH_3	-0.53	2.696	-0.02	-0.08	0.10
AsH_2	-1.73	2.564	-0.48	0.28	0.20
AsH	-1.77	2.403	-0.57	0.35	0.22
As	-1.64	2.337	-0.62	0.37	0.25
<i>$\text{Pd}_{4A}\text{-SDG}$</i>					
AsH_3	-0.72	2.515	-0.07	0.00	0.07
AsH_2	-2.42	2.511	-0.25	0.03	0.22
AsH	-3.45	2.549	-0.45	0.12	0.33
As	-3.96	2.467	-0.51	0.11	0.40
<i>$\text{Pd}_{4B}\text{-SDG}$</i>					
AsH_3	-1.00	2.598	0.00	-0.11	0.11
AsH_2	-2.50	2.555	-0.14	-0.01	0.15
AsH	-3.32	2.562	-0.35	-0.08	0.43
As	-3.81	2.458	-0.54	-0.01	0.55
<i>$\text{Pd}_6\text{-SDG}$</i>					
AsH_3	-0.88	2.443	0.08	0.00	-0.08
AsH_2	-2.28	2.532	-0.01	0.00	0.01
AsH	-3.46	2.484	-0.33	0.10	0.23
As	-4.06	2.421	-0.43	0.08	0.35

Next, we considered AsH_x adsorption on $\text{Pd}_{4\text{A}}\text{-SDG}$ and $\text{Pd}_{4\text{B}}\text{-SDG}$. Here, AsH_x molecules received charges from the adsorbent, where the net charges of AsH_x molecule after adsorption on $\text{Pd}_{4\text{A}}\text{-SDG}$ decreased by -0.07, -0.25, -0.45, and -0.51 e, for x in AsH_x ranging from 3 to 0, respectively. Similarly to $\text{Pd}_{4\text{A}}\text{-SDG}$ case, E_{ad} on $\text{Pd}_{4\text{B}}\text{-SDG}$ substrate were decreased by 0.00, -0.14, -0.35, and -0.54 e for AsH_3 , AsH_2 , AsH , and As , respectively. For AsH_x adsorption on both $\text{Pd}_{4\text{A}}\text{-SDG}$ and $\text{Pd}_{4\text{B}}\text{-SDG}$ substrate, charge received by AsH_2 , AsH , and As adsorbates mainly come from the SDG surface, while that was originated from Pd_4 cluster in case of AsH_3 .

Finally for AsH_x adsorption on $\text{Pd}_6\text{-SDG}$, the charge characteristics after adsorption were similar to the previous results. The result showed that $q(\text{AsH}_3) = 0.08$ e while $q(\text{AsH}_2)$, $q(\text{AsH})$ and $q(\text{As})$ were -0.01, -0.33, and -0.43 e, respectively.

In addition, we also found a relation between adsorption strength and amount of charges received by AsH_x adsorbate. **Figure 6** shows E_{ad} of AsH_x molecule on $\text{Pd}_n\text{-SDG}$ substrate versus $q(\text{AsH}_x)$. The figure indicated that the AsH_x adsorption is stronger when molecular charge of AsH_x molecule became more negative. This circumstance is even stronger in case of AsH_2 , AsH , and As adsorbates. Furthermore, the slope of linear regression for each $\text{Pd}_n\text{-SDG}$ result indicated that charge migration from $\text{Pd}_n\text{-SDG}$ to AsH_x significantly enhanced adsorption strength in the cases of Pd clusters doped SDG more than the single Pd atom doped SDG. The relationship between charge difference and adsorption strength emphasizes the role of charge migration promoting AsH_x adsorption on $\text{Pd}_n\text{-SDG}$.

Fig. 6: The diagram shows adsorption energy of AsH_x molecule on $\text{Pd}_n\text{-SDG}$ substrate versus the amount of charges received by AsH_x after adsorption. Dashed line illustrates the linear regression for each result on $\text{Pd}_n\text{-SDG}$.

3.3 Thermodynamic stability of AsH_x adsorption

In this section, we investigated thermodynamic stability of AsH_x ($x = 0-3$) molecule adsorption on Pd_n doped SDG adsorbents to find the most preferable reaction pathways of AsH_3 decomposition and the effect of Pd cluster size on the decomposition reaction. Considering the elementary-step reactions of AsH_3 decomposition during adsorption on Pd cluster where dissociated hydrogen atoms were formed and released as hydrogen gas:

Here, reaction energy (E) of Reactions (I)-(III) are calculated from

$$\Delta E = E(\text{AsH}_{x-1}/\text{Pd}_n\text{-SDG}) + \frac{1}{2}E(\text{H}_{2(g)}) - E(\text{AsH}_x/\text{Pd}_n\text{-SDG}) \quad (4)$$

where $E(\text{AsH}_x/\text{Pd}_n\text{-SDG})$ denoted the energy of the system with AsH_x adsorption on $\text{Pd}_n\text{-SDG}$, $E(\text{H}_{2(g)})$ is the energy of free H_2 molecule, Thus, reaction energy of total reaction for each AsH_3 decomposition products (E_{total}) are calculated from:

$$\Delta E_{\text{total}} = E(\text{AsH}_{3-m}/\text{Pd}_n\text{-SDG}) + \frac{1}{2}mE(\text{H}_{2(g)}) - E(\text{AsH}_3/\text{Pd}_n\text{-SDG}) \quad (5)$$

Noted that $m = 3-x$ is the number of released hydrogen atoms from the reactions. Previous study of AsH_3 decomposition on Pd (111) surface by Hu and colleagues suggested the low activation energy (E_a) of Reactions (I) – (III) ($E_a < 0.27$ eV) [19]. **Figure 7** shows the ΔE_{total} in different pathways of $\text{AsH}_3 \Rightarrow \text{AsH}_2 \Rightarrow \text{AsH} \Rightarrow \text{As}$ reactions on $\text{Pd}_1\text{-SDG}$, $\text{Pd}_{4A}\text{-SDG}$, $\text{Pd}_{4B}\text{-SDG}$ and $\text{Pd}_6\text{-SDG}$ based on **Equation 5**. Considering the reactions on $\text{Pd}_1\text{-SDG}$ system, Reaction (I) is slightly exothermic with ΔE of -0.20 eV, while Reactions (II) and (III) are highly endothermic with ΔE of 0.58 and 1.37 eV, respectively. AsH_2 is the most stable adsorption form of AsH_x adsorbed on $\text{Pd}_1\text{-SDG}$ with ΔE_{total} of -0.20 eV. This is in opposite to our findings in $\text{Pd}_{4A,B}\text{-SDG}$ and $\text{Pd}_6\text{-SDG}$ systems, where ΔE of Reactions (I) and (II) are all exothermic while Reaction (III) is slightly endothermic. The most thermodynamically stable products for $\text{Pd}_{4A}\text{-SDG}$, $\text{Pd}_{4B}\text{-SDG}$ and $\text{Pd}_6\text{-SDG}$ adsorbents are AsH with ΔE_{total} of -0.91, -0.50 and -0.76 eV, respectively, while AsH on $\text{Pd}_{4A}\text{-SDG}$ adsorbent is the most stable product overall. In these results, ΔE_{total} of the most thermodynamically stable products on Pd clusters doped SDG are significantly lower compared to that of Pd atom on SDG, signifying that Pd cluster doping on SDG adsorbent tends to be thermodynamically favorable for AsH_3 decomposition than the single-Pd atom doped SDG.

Fig. 7: The potential energy diagram of AsH_x ($x = 0-3$) adsorption on Pd_n -SDG surface along the AsH_3 decomposition reaction pathways.

4. Conclusions

In this work, the study of Pd_n binding on SDG showed that Pd_6 cluster binds on the surface slightly stronger than the Pd_4 and the single Pd atom. Our calculated binding energy of Pd atom deposited on SDG is -5.47 eV, which is in agreement with the result reported by Jia *et al.* (-5.63 eV).[55] In addition, PDOS analysis signifies the major difference between Pd atom and Pd clusters in terms of their PDOS interaction with SDG, where the d-band centers of Pd clusters are close to the Fermi level, suggesting the higher reactivity of Pd_6 , Pd_{4A} , Pd_{4B} clusters doped SDG surface over single Pd atom doped SDG. In terms of AsH_3 removal, our studies suggested that Pd cluster doped on SDG has superior adsorbability compared to the single Pd atom doped SDG. Adsorption strength of AsH_3 molecule on Pd_n -SDG substrates are as the following orders: $\text{Pd}_6 > \text{Pd}_{4A} \sim \text{Pd}_{4B} \gg \text{Pd}_1$. Dehydrogenated compounds (AsH_2 , AsH , As) adsorb Pd_n -SDG significantly stronger than its pristine AsH_3 .

form. In most cases, the more hydrogen atoms dissociated from the AsH_3 , the stronger the adsorption of AsH_x adsorbate on the $\text{Pd}_n\text{-SDG}$ surface. In-depth charge analysis further revealed substantial charge migration from $\text{Pd}_n\text{-SDG}$ surface (mostly from Pd_n) to the AsH_x adsorbate after adsorption, which is proportional to the amount of dissociated hydrogen atoms and adsorption strength of the adsorbate. Relationship between amount of charge transferred to AsH_x adsorbate and its adsorption strength may indicate that charge migration from $\text{Pd}_n\text{-SDG}$ to AsH_x constitute strong adsorption for dehydrogenated arsine. This may suggested that the dominating interaction between $\text{Pd}_n\text{-SDG}$ and AsH_x might be the electrostatic interaction. In addition, thermodynamic evaluation of AsH_3 decomposition suggested that Pd_6 , Pd_{4A} , Pd_{4B} clusters doped SDG are more favorable than Pd atom doped SDG adsorbent. These results have contended that larger size of Pd nanoclusters doped on SDG is recommended as a superior adsorbent material for AsH_3 removal.

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