Article

Influences of Work Function Changes in NO₂ and H₂S Adsorption on Pd-Doped ZnGa₂O₄(111) Thin Films: First-Principles Studies

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Featured Application: This work provides a detailed analysis of the gas-sensing performance of Pd-doped ZnGa₂O₄-based gas sensors.

Abstract: The work function variations of NO₂ and H₂S molecules on Pd-adsorbed ZnGa₂O₄(111) were calculated using first-principle calculations. For the bonding of a nitrogen atom from a single NO₂ molecule to a Pd atom, the maximum work function change was +1.37 eV, and for the bonding of two NO₂ molecules to a Pd atom, the maximum work function change was +2.37 eV. For H₂S adsorption, the maximum work function change was reduced from −0.90 eV to −1.82 eV for bonding sulfur atoms from a single and two H₂S molecules to a Pd atom, respectively. Thus, for both NO₂ and H₂S, the work function change increased with an increase in gas concentration, showing that Pd-decorated ZnGa₂O₄(111) is a suitable material in NO₂/H₂S gas detectors.

Keywords: first-principles calculation; Pd-doped ZnGa₂O₄; gas sensor

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1. Introduction

Gas sensors for household and industrial usages have attracted much attention since 1970 [1]. Toxic gases, such as hydrogen sulfide (H₂S), sulfur dioxide (SO₂), nitrogen dioxide (NO₂), carbon monoxide (CO), and nitric oxide (NO), are harmful to plants, organisms, and people's health. Therefore, finding a suitable sensor for toxic gases is an emerging and interesting research field. Experimentally, several key problems and challenges persist in the development of sensing components. For example, the sensor's working or operating temperature may be too high or too low, which restricts its use. The size of the gas-sensing application is also a key factor for a wearable device. Moreover, distinguishing the component and concentration of a specified gas from mixing gases is difficult.

The realization of the sensor response to functional or target gases can significantly enhance applications of the biomimetic response and controlling, as well as autonomously release functional gases [2,3]. The conjugated bimetallopolymer with Pt(II)-acetylide and Ru(II)-porphyrin-pyridyl is polymerized with oligo (phenylene ethynylene) (OPE) backbones and insulated by permethylated α -cyclodextrins (PM α -CDs) [2]. The conjugated bimetallopolymer is depolymerized by Ru complexes, which behave as acceptors with carbon monoxide (CO) reactivity. The depolymerization of the non-radiative conjugated polymer to luminescent monomers of Pt-acetylide complexes is the first self-activation threshold for the activation of the system. The luminescent intensity increase with the increase in CO concentration is an autonomous response above the threshold. Approaching constant amounts of luminescent Pt-monomers is the second self-regulation threshold for the rate-determining step of the Ru complex. The dual self-controlling system of

artificial biomimetic materials can be used as sensors, catalytic systems, and machines transporting materials.

The charge-compensating anions HS^- and NO_2^- and hydrated water ($m\text{H}_2\text{O}$) in $\text{Mg}_y\text{Al}(\text{OH})_{2(y+1)}$ (y is in the range of 2~4) layered double hydroxides ($\text{Mg}/\text{Al}(y/1)$ LDHs) are used as the gas release system for medical applications [3]. Interlayer HS^- and NO_2^- in LDHs are protonated with aerial CO_2 and H_2O , releasing H_2S or HNO_2 under air. NO and NO_2 can be further generated through an automatic disproportionation reaction of HNO_2 . LDHs ($\text{Mg}/\text{Al} = 2/1$ or $3/1$) mixed with NaHS , Na_2S , and NaNO_2 , i.e., $\text{NaHS-Mg}/\text{Al}(2/1)$, $\text{NaHS-Mg}/\text{Al}(3/1)$, $\text{Na}_2\text{S-Mg}/\text{Al}(2/1)$, $\text{Na}_2\text{S-Mg}/\text{Al}(3/1)$, $\text{NaNO}_2\text{-Mg}/\text{Al}(2/1)$, and $\text{NaNO}_2\text{-Mg}/\text{Al}(3/1)$ LDHs, have been successfully synthesized to release p.p.m.-level H_2S and NO derived from aerial CO_2 -stimulated anion exchange, respectively. $\text{NaHS-Mg}/\text{Al}(2/1)$ and $\text{NaNO}_2\text{-Mg}/\text{Al}(3/1)$ LDHs showed the best release profile for H_2S and NO in a rather flat and elongated gas release, respectively. $\text{NaNO}_2\text{-Mg}/\text{Al}(3/1)$ LDHs have been demonstrated to produce a battery-free respirator for inhaled NO , which is a selective and quick-acting pulmonary vasodilator after inhalation.

Metal oxide semiconductors [4], such as SnO_2 , Ga_2O_3 , and WO_3 , have been widely studied and used as gas sensors [5–11]. The important features of metal oxide semiconductor sensors are reversible interactions between gas and the surface of metal oxide semiconductors [10]. The SnO_2 , Ga_2O_3 , WO_3 and other metal oxide semiconductor sensors can be worked stably at a high temperature from 200 °C to 900 °C and can be used for a long time. In recent years, SnO_2 , Ga_2O_3 , WO_3 , and other sensors have been determined as sensors for detecting CO , H_2 , CH_4 , O_3 , NO_2 , H_2S , SO_2 , and other gases [11]. The metal oxide semiconductor sensors with good thermal stability and long-term working stability have greatly aroused the interest of researchers and have been extensively studied [7–10] in the past decade. The gas adsorption reaction is converted into the sensitivity response of the sensor to detect gas by measuring the work function, capacitance, conductivity [10,12–15], optical characteristics, and other parameters of the sensing material surface. Kolmakov et al. reported that nanowire sensors made by SnO_2 can detect CO at temperatures between 200 °C and 280 °C [16]. The $\beta\text{-Ga}_2\text{O}_3$ films can be used to detect several gases, such as CO , hydrogen, methane (CH_4), NO , and ammonia (NH_3) [17].

The structure of ZnGa_2O_4 is spinel (space group: $F\bar{4}3m$). Both ZnGa_2O_4 and n -type semiconductor ZnGa_2O_4 thin films have been successfully developed as gas sensors. Satyanarayana et al. [13] reported that ZnGa_2O_4 films can be used to sense liquid petroleum gas (LPG). When the ZnGa_2O_4 sensor is further doped with palladium at approximately 320 °C, the sensitivity of detecting LPG increases, but the sensitivity to CH_4 and CO [13] gas becomes poor. Despite the introduction of new approaches for developing gas sensors, the fundamental interaction between gas molecules and metal oxide compounds remains unclear. In recent decades, the density functional theory (DFT) has been widely used in the fields of the gas-sensing mechanism, adsorption of atoms and molecules on surfaces, and surface reconstruction [6,7]. For example, the gas-sensing mechanism of ZnO applied to H_2 , NH_3 , CO , and ethanol ($\text{C}_2\text{H}_5\text{OH}$) was studied by first-principles DFT calculations [7]. Due to the adsorption of surface molecules, the ZnO surface is reconstructed. The charge is transferred from the gas to the ZnO surface and vice versa, which affects the conductivity of the ZnO in gas detection. Vorobyeva et al. reported that the resistance of ZnO increases (decreases) in the presence of NO_2 (H_2S) [8] adsorption. Recently, we demonstrated that the use of the metal organic chemical vapor deposition (MOCVD) technique to grow epitaxial ZnGa_2O_4 films on sapphire substrates can produce highly selective gas sensors [9].

Reactions of NO_2 and H_2S molecules on Ga-Zn-O terminated $\text{ZnGa}_2\text{O}_4(111)$ surfaces were modeled and carried out using a first-principles density functional theory method [18]. Based on our previous theoretical study, we report on the palladium adsorbed on the $\text{ZnGa}_2\text{O}_4(111)$ surfaces and the work function changes with and without NO_2 (H_2S)

molecules. In principle, the sensitivity response of the sensor to detect the target gas can be determined by the following work function changes $\Delta\Phi$ according to

$$\Delta\Phi = \Delta X + kT \ln(Rg/Ra)$$

where ΔX is the change in electron affinity, and kT is the product of the Boltzmann's constant k and the temperature T . Rg is the resistance in the presence of the target gas. Ra is the resistance in the reference gas, which is usually air. We hope that this work can help experimental researchers to effectively develop gas-sensing devices.

2. Computational Details

The work functions of NO₂ and H₂S adsorbed on Pd-decorated ZnGa₂O₄(111) (Pd-ZGO) surfaces were systematically studied. All calculations were performed by using the density functional theory as implemented in the Vienna ab initio simulation package (VASP) [19,20] with the exchange correlation function described by generalized gradient approximation (GGA) and the Perdew–Wang (PW91) correction [21,22]. The crystal structure of ZnGa₂O₄ is displayed in Figure 1a. We used a conventional crystal structure containing 56 atoms, i.e., 8 Zn, 16 Ga, and 32 O atoms. The cutoff energy was set to 500 eV, and the self-consistent total energy criterion was 10^{−5} eV/unit cell.

Figure 1. Left and right panels illustrate bulk ZnGa₂O₄ crystal structure and top view of the adsorption sites O_{3C}, Zn_{3C}, O_{4C}, and Ga_{3C} on ZnGa₂O₄(111) surface, respectively. These sites are labeled for the adsorption sites of the Pd atom.

To understand the work function changes when NO₂ (H₂S) is adsorbed on Pd-ZGO surfaces, we built a supercell containing 112 atoms to simulate ZnGa₂O₄(111) surfaces with a vacuum of 20 Å, which should be wide enough to decouple the nearest surface interaction. This preferred Ga-Zn-O-terminated surface was selected from the previous study on ZnGa₂O₄, and its surface energy was 0.01 eV/Å² [23]. In order to describe the effect of changes in the work function of the NO₂ and H₂S on the surface of Pd-ZGO, we firstly calculated the work function Φ_S using the following formula [24]:

$$\Phi_S = E_{VAC} - E_F$$

where Φ_S is the work function of ZnGa₂O₄(111) surface. E_{VAC} and E_F are the energy of the vacuum and the Fermi energy, respectively.

Second, we constructed four adsorption models of Pd atoms, denoted as Pd-ZGO_{*i*} (*i* = 1,2,3,4). Here, the superscripts 1, 2, 3, and 4 in Pd-ZGO, respectively, indicate the positions of the initial adsorbed sites Ga_{3C}, Zn_{3C}, O_{3C}, and O_{4C} on the ZnGa₂O₄(111) surface, as shown in Figure 1b. The initial distance from the Pd atom to the ZnGa₂O₄(111) surface was set as the sum of the van der Waals radii of the Pd atom and Ga (Zn or O)

surface atoms, as shown in Figure 2. Third, we considered one NO₂ (H₂S) molecule and two NO₂ (H₂S) molecules adsorbed on the surface Pd atoms and compared the corresponding results of the calculated work functions in the second step, denoted as $n\text{NO}_2\text{-Pd-ZGO}_i$ and $n\text{H}_2\text{S-Pd-ZGO}_i$ ($n = 1, 2$; $i = 1, 2, 3, 4$). Here, n represents the number of molecules. All supercells were fully relaxed until the force attraction on each atom was less than 0.001 eV/Å, and a $3 \times 3 \times 1$ Monkhorst–Pack grid was used. The initial distance from NO₂ (H₂S) molecules to Pd surface atoms was also set to the sum of the van der Waals radii of N (S) from the NO₂ (H₂S) molecules and the Pd surface atoms. The van der Waals distances of H, N, O, S, Zn, Ga, and Pd atom were 1.20 Å, 1.55 Å, 1.52 Å, 1.80 Å, 1.39 Å, 1.87 Å, and 1.63 Å, respectively.

Figure 2. Side view of the Pd atom on ZnGa₂O₄(111) surface. Pd-ZGO_{*i*}, showing Pd atoms located on the top of Ga_{3C}, Zn_{3C}, O_{3C}, and O_{4C} sites for $i = 1, 2, 3$, and 4, respectively. The bond lengths of Pd-ZGO_{*i*} are listed in Table 1.

Table 1. Calculated equilibrium bond length (Å) for the Pd-ZGO_{*i*}, $n\text{NO}_2\text{-Pd-ZGO}_i$, and $n\text{H}_2\text{S-Pd-ZGO}_i$ structures.

Pd-ZGO _{<i>i</i>}	Bond Length (Å)		
	Pd-Ga	Pd-Zn	Pd-O
Pd-ZGO1	2.32	-	-
Pd-ZGO2	-	2.57	-
Pd-ZGO3	-	-	2.04
Pd-ZGO4	2.37	2.66	-

Table 1. Cont.

$n\text{NO}_2\text{-Pd-ZGO}i$	Bond Length (Å)			
	N-Pd	Pd-Ga	Pd-Zn	Pd-O
1NO ₂ -Pd-ZGO1	2.01	2.53	-	-
1NO ₂ -Pd-ZGO2	1.94	2.34	-	2.17
1NO ₂ -Pd-ZGO3	1.96	-	-	2.10
1NO ₂ -Pd-ZGO4	1.96	2.31	2.86	2.48
2NO ₂ -Pd-ZGO1	2.04	2.04	2.51	-
2NO ₂ -Pd-ZGO2	2.03	2.21	2.44	2.82
2NO ₂ -Pd-ZGO3	2.11	2.05	-	2.15
2NO ₂ -Pd-ZGO4	2.04	2.12	2.46	-

$n\text{H}_2\text{S-Pd-ZGO}i$	Bond Length (Å)			
	S-Pd	Pd-Ga	Pd-Zn	Pd-O
1H ₂ S-Pd-ZGO1	2.37	2.38	-	-
1H ₂ S-Pd-ZGO2	2.26	2.82	2.89	2.18
1H ₂ S-Pd-ZGO3	2.25	2.62	-	2.11
1H ₂ S-Pd-ZGO4	2.38	2.38	-	-
2H ₂ S-Pd-ZGO1	2.52	2.54	2.34	-
2H ₂ S-Pd-ZGO2	2.41	2.60	2.81	2.88
2H ₂ S-Pd-ZGO3	2.31	2.99	-	2.13
2H ₂ S-Pd-ZGO4	2.54	2.56	2.46	-

When the NO₂ (H₂S) molecules were adsorbed on the ZnGa₂O₄(111) and Pd-ZGO(111) surface, we calculated the work function $\Phi_{S, \text{gas}}$, which in turn determined the work function differences $\Delta\Phi$ (eV) between $\Phi_{S, \text{gas}}$ and Φ_S . The difference in these obtained work functions is the key factor of gas sensor performance [25]. Finally, the adsorption response of the sensor is closely related to the energy lost or gained by the corresponding gas adsorption. The lost or gained energy of the adsorbed gas can be determined by the adsorption energy. The adsorption energy is the energy released when NO₂ (H₂S) molecules are adsorbed on the surface of Pd-ZGO_{*i*}. The adsorption energy ΔE was calculated as follows:

$$\Delta E = E_{\text{gas+Pd-ZGO}} - (E_{\text{gas}} + E_{\text{Pd-ZGO}})$$

where $E_{\text{gas+Pd-ZGO}}$ represents the energy of the Pd-ZGO_{*i*} surface with the adsorbed NO₂ (H₂S) molecules. E_{gas} represents the energy of free NO₂ (H₂S) molecules, and $E_{\text{Pd-ZGO}}$ represents the energy of the Pd-ZGO_{*i*} surface. Whether the adsorption energy is related to the work function is also a question to be discussed in this study.

3. Results and Discussion

3.1. Structures

The calculated equilibrium bond lengths of Pd-ZGO_{*i*}, 1NO₂-Pd-ZGO_{*i*}, 2NO₂-Pd-ZGO_{*i*}, 1H₂S-Pd-ZGO_{*i*}, and 2H₂S-Pd-ZGO_{*i*} ($i = 1, 2, 3, 4$) are listed in Table 1. The calculated Pd-Ga equilibrium bond lengths are 2.32 Å and 2.37 Å, respectively, for Pd-ZGO1 and Pd-ZGO4 structures; the calculated Pd-Zn equilibrium bond lengths are 2.57 Å and 2.66 Å, respectively, for Pd-ZGO2 and Pd-ZGO4 structures; the calculated Pd-O equilibrium bond length is 2.04 Å for the Pd-ZGO3 structure. The equilibrium bond length of Pd-Ga or Pd-Zn is significantly larger than that of Pd-O (see Figure 1 and Table 1). This is because the valence electron for the O atom is negative, while it is positive for Pd, Ga, and Zn atoms. The Wigner–Seitz radii of Pd, Zn, Ga, and O atoms are 1.434 Å, 1.217 Å, 1.402 Å, and 0.820 Å, respectively.

The bond length of Pd-Zn is larger than that of Pd-Ga because it is dominated by the Coulomb interaction. In other words, the electronic configurations of Zn and Ga are [Ar] 3d¹⁰4p² and [Ar] 3d¹⁰4s²4p¹, respectively. When the NO₂ molecule is adsorbed on the Pd-ZGO structure, the Pd atom is a bridge connecting the NO₂ molecule and the ZGO(111) surface. The calculated equilibrium bond length is completely different from

Pd-ZGOi. In the 1NO₂-Pd-ZGO1 structure, the bond length of Pd-Ga is 2.53 Å, where it is 2.32 Å in the absence of the NO₂ molecule without Pd atoms. Note that in the initial structure of 1NO₂-Pd-ZGO1, the distance between the NO₂ molecule and the surface Pd atom is 3.18 Å. The electronic configuration of the Pd atom is [Kr]4d⁹5s¹. This implies the attraction between Pd and N atoms. As a result, the bond length of N-Pd is reduced to 2.01 Å, while the bond length for Pd-Ga is increased. Generally, the N-Pd bond lengths in nNO₂-Pd-ZGOi are about 2 Å.

In the 1NO₂-Pd-ZGO2 and 1NO₂-Pd-ZGO4 structures, Pd atoms do not remain on the top of the Zn_{3C} and O_{4C} sites. Therefore, the calculated bond lengths change significantly, especially for the O_{4C} site (see Figure 3). It seems that Pd atoms are attracted by Ga atoms on the ZGO(111) surface. In one and two NO₂ molecules attracted to Pd atoms, the results of 1NO₂-Pd-ZGO1 (1NO₂-Pd-ZGO3) and 2NO₂-Pd-ZGO1 (2NO₂-Pd-ZGO3) are similar, while Pd atoms are retained on the top of the Ga_{3C} and O_{3C} sites. When two NO₂ molecules are adsorbed into the Pd atom, the calculated bond length of N-Pd is larger. In the 2NO₂-Pd-ZGO4 structure, the interaction between the Pd and surface Zn (O) atom disappears. Generally, when NO₂ molecules are adsorbed on Pd atoms, the bond length of Pd-Ga, Pd-Zn, and Pd-O will increase.

Figure 3. Side view of the n NO₂ molecules on Pd-ZnGaOi surface. The equilibrium bond lengths of n NO₂-Pd-ZGOi are listed in Table 1.

When H₂S molecules were adsorbed on the surface of Pd-ZGO, as shown in Figure 4, we first noticed an increase in the bond lengths of Pd-Ga, Pd-Zn, and Pd-O. We also found that in the 1H₂S-Pd-ZGO1 and 1H₂S-Pd-ZGO4 structures, the Pd atom is approximately at the top of Ga_{3C} site, and the distances for the S-Pd and Pd-Ga are equal. The bond length of S-Pd in nH₂S-Pd-ZGOi ($i = 1,2,3,4$) is larger than that of N-Pd in nNO₂-Pd-ZGOi. This difference is mainly due to the van der Waals radii.

Figure 4. Side view of the $n\text{H}_2\text{S}$ molecules on Pd-ZnGaO i surface. The equilibrium bond lengths of $n\text{H}_2\text{S}$ -Pd-ZGO i are listed in Table 1.

3.2. Work Functions

Table 2 shows that the work function decreases when Pd atoms are adsorbed on the ZGO surface. The reduction in work function ranges from -0.44 eV to -0.15 eV. The larger magnitude of $\Delta\Phi$ is better. Therefore, the Pd-ZGO1 structure, i.e., Pd on the top of the Ga_{3C} site, is the most sensitive.

Table 2. Calculated work functions Φ_S and $\Phi_{S,\text{gas}}$, work function differences $\Delta\Phi$, and adsorption energies ΔE for the ZGO surfaces, NO₂ and H₂S molecules on ZGO surfaces, Pd-adsorbed ZGO surfaces, and NO₂/H₂S on Pd-adsorbed ZGO surfaces.

Model	Φ_S (eV)	$\Phi_{S,\text{gas}}$ (eV)	$\Delta\Phi$ (eV)	ΔE (eV)
ZGO	4.09	-	-	-
NO ₂ -ZGO	-	5.01	+0.92	+0.64
H ₂ S-ZGO	-	2.40	-1.69	+2.32
Pd-ZGO1	3.65	-	-0.44	-
Pd-ZGO2	3.84	-	-0.25	-
Pd-ZGO3	3.94	-	-0.15	-
Pd-ZGO4	3.75	-	-0.34	-
1NO ₂ -Pd-ZGO1	-	5.02	+1.37	-1.30
1NO ₂ -Pd-ZGO2	-	5.06	+1.22	-2.94
1NO ₂ -Pd-ZGO3	-	5.23	+1.29	-2.25
1NO ₂ -Pd-ZGO4	-	5.08	+1.33	-2.14
2NO ₂ -Pd-ZGO1	-	6.02	+2.37	-2.64
2NO ₂ -Pd-ZGO2	-	5.61	+1.77	-3.72
2NO ₂ -Pd-ZGO3	-	5.38	+1.44	-3.06
2NO ₂ -Pd-ZGO4	-	5.62	+1.87	-2.53
1H ₂ S-Pd-ZGO1	-	2.93	-0.72	-0.73

Table 2. Cont.

Model	Φ_S (eV)	$\Phi_{S, \text{gas}}$ (eV)	$\Delta\Phi$ (eV)	ΔE (eV)
1H ₂ S-Pd-ZGO2	-	3.16	−0.68	−2.89
1H ₂ S-Pd-ZGO3	-	3.04	−0.90	−1.85
1H ₂ S-Pd-ZGO4	-	3.26	−0.49	−0.95
2H ₂ S-Pd-ZGO1	-	1.88	−1.77	−0.45
2H ₂ S-Pd-ZGO2	-	2.58	−1.26	−2.44
2H ₂ S-Pd-ZGO3	-	2.62	−1.32	−1.80
2H ₂ S-Pd-ZGO4	-	1.93	−1.82	−1.03

When a NO₂ molecule was adsorbed on the surface of Pd-ZGO_i, we found that 1NO₂-Pd-ZGO1 had the largest $\Delta\Phi$ (+1.37 eV). In the 1NO₂-Pd-ZGO1 structure, N-Pd and Pd-Ga have the largest bond lengths. The magnitude of $\Delta\Phi$ ranges from +1.22 eV to +1.37 eV in 1NO₂-Pd-ZGO_i. This increase in $\Delta\Phi$ is further increased as the number of NO₂ molecules becomes two. Note that when H₂S is adsorbed on the ZGO surface, the work function difference $\Delta\Phi$ changes significantly to −1.69 eV. When H₂S molecules are adsorbed on the surface of Pd-ZGO_i, the magnitude of $\Delta\Phi$ is about half that of H₂S-ZGO, ranging from −0.49 eV to −0.90 eV in 1H₂S-Pd-ZGO_i. The 1H₂S-Pd-ZGO3 structure has the largest $\Delta\Phi$ (−0.90 eV). When two H₂S molecules are adsorbed on the surface of Pd-ZGO_i, the magnitudes of $\Delta\Phi$ of 2H₂S-Pd-ZGO1 (−1.77 eV) and 2H₂S-Pd-ZGO4 (−1.82 eV) are larger than that of H₂S-ZGO without the Pd atom (−1.69 eV), showing that the sensitivity of the ZGO surface doped with palladium becomes higher.

3.3. Adsorption Energies

Table 2 also shows adsorption energies of the NO₂ and H₂S molecules on the surface of ZGO with and without Pd atoms. It can be clearly seen that a NO₂ (H₂S) molecule is adsorbed to the ZGO surface, which is endothermic by 0.64 eV (2.32 eV). In contrast with Pd atoms adsorbed on the surface of ZGO, i.e., Pd-ZGO_i, the NO₂ and H₂S molecules on the surface of Pd-ZGO_i have exothermic or negative adsorption energy. It should be noted that the spontaneous reaction occurs in the direction where the Gibbs free energy change, ΔG , decreases. The Gibbs free energy change consists of enthalpy change ΔH and entropy change ΔS by the following equation:

$$\Delta G = \Delta H - T\Delta S$$

The enthalpy change is defined as the sum of the internal energy change ΔE and the product of the pressure P and volume change ΔV , as follows:

$$\Delta H = \Delta E + P\Delta V$$

Therefore, the Gibbs free energy change can be expressed by the following equation:

$$\Delta G = \Delta E + P\Delta V - T\Delta S$$

In our study, we ignored the contribution of entropy change, and the volume change in the Pd-ZGO_i structures was negligible. The Gibbs free energy change can be further simplified as the internal energy change caused by the kinetic energy, potential energy, and chemical energy of the target system. The negative Gibbs free energy change, its negative internal energy change, or its negative adsorption energies, ΔE , provides a means of spontaneous physical and chemical changes to take place without any external help. On the contrary, the positive adsorption energy indicates that the corresponding endothermic process can be supported by the increase in temperature. A higher positive adsorption energy means that more energy is required from the outside world, which also indicates that the endothermic reaction does not occur easily. Our results on the surface of ZGO

show that the adsorption of NO₂ molecules on the surface is energetically more favorable than the adsorption of H₂S molecules on the surface by 1.68 eV.

Our results on NO₂ (H₂S) molecules adsorbed on the surface of Pd-ZGO_i show that the adsorption reaction is spontaneous and exothermic. Most importantly, the structures of Pd atoms remaining at the top of the Zn_{3C} site, namely, 1NO₂-Pd-ZGO₂, 2NO₂-Pd-ZGO₂, 1H₂S-Pd-ZGO₂, and 2H₂S-Pd-ZGO₂, have the overall lowest adsorption energy for NO₂ and H₂S molecules, regardless of the number of NO₂ and H₂S molecules. It is interesting to note that the magnitudes of adsorption energy of 1NO₂-Pd-ZGO₂ (−2.94 eV) and 2NO₂-Pd-ZGO₂ (−3.72 eV) are larger than that of 1H₂S-Pd-ZGO₂ (−2.89 eV) and 2H₂S-Pd-ZGO₄ (−2.44 eV), showing that the surface of ZGO doped with palladium benefits the adsorption reaction to increase the amount of NO₂. However, the adsorption reaction on the surface of Pd-ZGO_i is unfavorable for the increase in the amount of H₂S. The largest adsorption energy occurs in the structures of the Pd atoms remaining on the top of the Zn_{3C} site, but the largest work function difference occurs in the structures of Pd atoms remaining on the top of the Ga_{3C} site. Overall, the difference in work functions is not closely related to their respective adsorption energies.

4. Conclusions

Using the framework of density functional theory, we studied the adsorption reactions and work functions of NO₂ and H₂S on Pd-ZnGa₂O₄(111) surfaces. Our previous studies showed that the bonding of the nitrogen (sulfur) atom from a single NO₂ (H₂S) molecule to the Ga atom of Ga-Zn-O-terminated ZnGa₂O₄(111) surfaces exhibits the highest work function change of +0.92 eV (−1.69 eV). In this study, we found that the work function change of one NO₂ (H₂S) molecule on the Pd-ZGO(111) surface is enhanced (reduced) to +1.37 eV (−0.90 eV). This difference is mainly due to the decrease in work function when the palladium is adsorbed on the ZGO(111) surface. The work function difference for two NO₂ (H₂S) molecules adsorbed on the surface of Pd-ZGO_i is about twice as large as that for one NO₂ (H₂S) molecule, showing a higher work function difference, i.e., a higher sensitivity. The resistance response experiment of ZnO(Ga) samples to NO₂ (H₂S) molecules shows that the sensitivity response of ZnGa₂O₄-based thin-film sensors to NO₂ (H₂S) molecules presents the same trend as the positive (negative) work function differences [8]. Adsorption energies of NO₂ (H₂S) molecules on the surface of ZGO with and without Pd atoms were analyzed to explain the exothermic and endothermic adsorption reactions, but no fully satisfactory explanation related to their respective work function differences can be provided at this time.

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