ENERGY AND BONDING STATE CALCULATIONS OF ADSORBED CH_3OH ON 2Pd/ZnO $(10\bar{1}0)$ ADSORBENT SURFACE USING DENSITY FUNCTIONAL THEORY STUDY

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Abstract. In this examination, density functional theory (DFT) was used to investigate the calculated energies and structures of two Palladium atoms (2Pd) adsorption on a ZnO $(10\bar{1}0)$ surface, forming a 2Pd deposition over the ZnO surface model, namely 2Pd/ZnO adsorbent surface. Subsequently, 2Pd/ZnO was employed to adsorb a CH_3OH (methanol) molecule in gas phase. In the detailed analysis, 2Pd was adsorbed at various positions on the ZnO surface, resulting in four structural sites and corresponding energies for the 2Pd/ZnO adsorbent surface, designated as site A, site B, site C, and site D. Herein, based on the resulted calculations of adsorption energies pointed out that the structural 2Pd/ZnO adsorbent surface of site A was the most stable one. Hereafter, site A was used to adsorb CH_3OH molecule in gas phase. There were six-adsorbed CH_3OH at positions on the adsorbent surface of site A with structure and energy was found namely as ADS-A, ADS-B, ADS-C, ADS-D, ADS-E, and ADS-F sites. In which, based on the calculations of adsorption energy, ADS-A and ADS-B were identified to be the initially- stable sites in considering details of this work.

Keywords: DFT, 2Pd/ZnO adsorbent surface, adsorbed CH_3OH, energy, bonding state

1. INTRODUCTION

The adsorption capacity of gases on metal oxide surfaces is important in industrial, environmental, and medical monitoring fields [1-3]. In particular, semiconducting metal oxides, such as ZnO [2, 4, 5] are known as material for applications in gas sensors, CO_2 capture, and catalysts. In Comparison with other semiconductors, ZnO possesses many advantageous properties for scientific and technological applications, including stability in hydrogen environments, photo-chemical capacity, and thermal stability.

Regarding properties and applications, methanol is a flammable liquid at low temperatures and is recognized as a promising fuel for converting hydrogen into renewable energy [6, 7]. Methanol offers several advantages, such as a high H/C ratio, low cost, and manageable storage and dispensing requirements compared with other liquid fuels. Consequently, it is used as a solvent in research on adsorption properties. Additionally, due to its lower evaporation rate and safer burning compared with gasoline, methanol's decomposition into hydrogen fuel for replacing gasoline is of great importance. This process requires careful consideration of the kinetic and thermodynamic properties of methanol adsorption on catalyst surfaces [8-13]. Thus, detailed adsorption data, such as the positions and energetics of methanol on adsorbent surfaces, are necessary.

Zinc oxide (ZnO), with a band gap of 3.37 eV, is a semiconductor widely applied in fields such as laser diodes, ultraviolet detection, gas sensing, and even as a biosensor [14-16]. Furthermore, ZnO was considered a promising photocatalyst out of its unique properties for example as high thermal, chemical stability, friendly and cheap materials. However, ZnO use is limited that the fast recombination of photochemical electrons into holes to make the decrease of photocatalytic efficiency. Therefore, ZnO is modified to change the photochemical electron properties in structure. The effective modification methods for making increased photocatalytic efficiency of ZnO is doped another atomic metal or deposited (supported) atomic metals cluster on the surface, in which the method of metals cluster deposition has been performed in present work. In addition, structural ZnO crystal is consisted as hexagonal symmetry with a chain combination of Zn (zine) and O (oxygen) atoms plane. It is dominated including four Miller index with polar (0001) and $(000\bar{1})$, non-polar $(10\bar{1}0)$ and $(11\bar{2}0)$ surfaces direction, respectively. Herein, the

surface direction of non-polar $(10\bar{1}0)$ in ZnO crystal has been detemined in previous report [15, 21, 22] that it is most stable one with the total surface area of 80 percentage. Alternatively, it demonstrated also in our previous investigation [15] that CH_3OH decomposition on non-polar surface ZnO $\mathbf{(10\bar{1}0)}$ was able unfavorable pathway in mechanism to dissociate final CO and H_2 products. Thus, a required modification though depositing metals cluster on ZnO $\mathbf{(10\bar{1}0)}$ surface was needed.

Experimental studies [12, 17] have demonstrated that catalysts composed of atomic metals, such as Pd clusters supported on oxide-based materials, are widely utilized for methanol adsorption and decomposition reactions. These findings highlight that Pd/ZnO exhibits enhanced catalytic efficiency for methanol-related processes. Furthermore, previous reports [12, 18, 19] indicate that the presence of metallic Pd phases on catalyst surfaces reduces CO_2 selectivity. This suggests that Pd/ZnO catalysts are particularly suitable for environmental applications, including reactions such as dehydrogenation, oxidation, and reduction.

Additionally, studies [17, 20, 21] on the physicochemical properties of Pd clusters supported on ZnO have provided valuable insights into designing new catalytic systems. Previous investigations [12, 17, 19, 21] have further demonstrated that Pd-based catalysts are highly effective for methanol (CH_3OH) adsorption and decomposition, given their potential for hydrogen energy applications. While experimental research has explored CH_3OH decomposition on Pd/ZnO(0001) and Pt/ZnO(0001) surfaces[22, 12], there is a lack of data on CH_3OH adsorption on Pd clusters supported on the ZnO $(10\bar{1}0)$ surface. This gap underscores the need for theoretical studies to examine CH_3OH adsorption on the Pd/ZnO $(10\bar{1}0)$ surface using density functional theory (DFT).

This research aims to assess the stability and diffusion of Pd clusters on the ZnO $(10\bar{1}0)$ surface and improve the structural and adsorption properties of Pd clusters. It also seeks to compare CH_3OH adsorption between Pd/ZnO and pure ZnO $(10\bar{1}0)$ surfaces. As a result, a new surface model with two dispersed Pd atoms, termed 2Pd/ZnO $(10\bar{1}0)$, has been developed as the primary target for adsorption analysis in this study.

DFT has been established as a powerful quantum-based theoretical tool for investigating the physicochemical properties of elementary reactions in atomic, molecular, and material chemistry [9, 17, 23] Leveraging this method, this study investigates CH_3OH adsorption on the 2Pd/ZnO $(10\bar{1}0)$ surface. The most stable configuration for the deposition of 2Pd on ZnO $(10\bar{1}0)$, forming the 2Pd/ZnO $(10\bar{1}0)$ surface model, is determined in detail. Various adsorption sites for CH_3OH are analyzed, with two primary stable adsorption modes (ADS-A and ADS-B) being identified and examined on the 2Pd/ZnO $(10\bar{1}0)$ surface.

2. Computational details

All computational analyses in this study were conducted using density functional theory (DFT), implemented via the Vienna Ab initio Simulation Package (VASP) [24-26]. The exchange-correlation energy was computed within the framework of the generalized gradient approximation (GGA) using the Perdew-Wang 91 (PW91) functional [27, 28]. The Kohn–Sham one-electron wave function was expanded in plane-wave basis set finite with the cutoff energy of 380 eV. Projector augmented wave (PAW) method [29] was used to be pseudopotential for the description of electron-ion interactions. The Brillouin zone was sampled with Monkhorst-Pack grid [30] to calculate being (4 × 4 × 4) and (4 × 4 × 1) Monkhorst-Pack mesh k-points for ZnO bulk and ZnO $(10\bar{1}0)$ surface, respectively. A hexagonal supercell with a dimension of (6.50 × 10.41 × 21.57) $Å^3$, included a p(2 × 2) unit cell with periodic boundary conditions was modeled for ZnO $(10\bar{1}0)$ surface in a vacuum slab of 15 Å for interactions. All calculations were performed with spin polarization, and supercell model in this work has been reported in our previous work [31].

To obtain the deposition of 2Pd cluster over ZnO $(10\bar{1}0)$ surface, 2Pd positions were adsorbed on ZnO $(10\bar{1}0)$ surface to form the configuarions of 2Pd/ZnO surface model. The adsorption energies were

calculated respectively in equations as following (1) dispersion energy (E_{dispPd}) and (2) surface energy (E_{Pd-ZnO}) , which this equations agreed with previous study [32].

$$E_{dispPd} = \frac{E_{nPd/slab} - (E_{slab} - nE_{Pd})}{n} \quad (1)$$

$$E_{Pd-ZnO} = \frac{E_{nPd/slab} - (E_{slab} - E_{nPd})}{n} \quad (2)$$

In which, $E_{nPd/slab}$ as total energy is of 2 Pd/ZnO surface, E_{slab} of ZnO surface, E_{Pd} of Pd bulk (in gas phase), and E_{nPd} of 2Pd bulk, respectively. Valuable n ($n = 2$) is the number of adsorbed Pd. It noted that the values of (E_{dispPd}) and surface energy (E_{Pd-ZnO}) is minus energy indicated that adsorption systems to be the exothermic.

Continuously, to consider the possible methanol adsorptions on 2Pd/ZnO $(10\bar{1}0)$ surface, the adsorbed CH_3OH was placed at diferencet sites on surface to find the adsorption structures. The methanol adsorption energies (E_{ads}) were calculated in equation (3) as following, which given an agreement with our previous work [33].

$$E_{ads} = E_{adsorbate-surface} - E_{surface} - E_{adsorbate} \quad (3)$$

In which, $E_{adsorbate-surface}$ as total energies are of adsorbed CH_3OH on 2Pd/ZnO surface, $E_{surface}$ of 2Pd/ZnO surface, and $E_{adsorbate}$ of CH_3OH bulk (in gas phase), respectively. E_{ads} values is also a minus energy.

3. Results and Discussion

3.1. Surface 2Pd/ZnO $(10\bar{1}0)$ model

The deposition of 2Pd on the ZnO $(10\bar{1}0)$ surface obtained four energies of adsorbed 2Pd are listed in Table 1,

Table 1. The calculated dispersion energy (E_{dispPd}) and surface energy (E_{Pd-ZnO}) of two adsorbed Pd on ZnO $(10\bar{1}0)$ surface. In which, d(Pd-Pd) was noted as bond distances of two Pd atoms on ZnO surface.

Energy	Site A	Site B	Site C	Site D
$E_{disp,\ Pd}$ (eV)	-2.01	-1.87	-1.74	-1.03
$E_{Pd\text{-}ZnO}$ (eV)	-1.48	-1.24	-1.16	-1.08
d(Pd-Pd) (Å)	2.79	2.72	2.48	2.43

It is observed in Table 1 that adsorption energy valuas of site A resulted as the dispersion energy of -2.01 eV and surface energy of -1.48 eV, which these values are higher than that of site B, site C, and site D, respectively. This indicated that site A is the most stable one. After deposition of 2Pd on ZnO, 2Pd/ZnO surface model formation on site A with Pd-Pd bond distance of 2.79 Å is measured. Herein, structural surfaces of adsorbents from site B to site D are more unstable that of site A shown in Fig. 1, which they are not particularly to comment in this study.

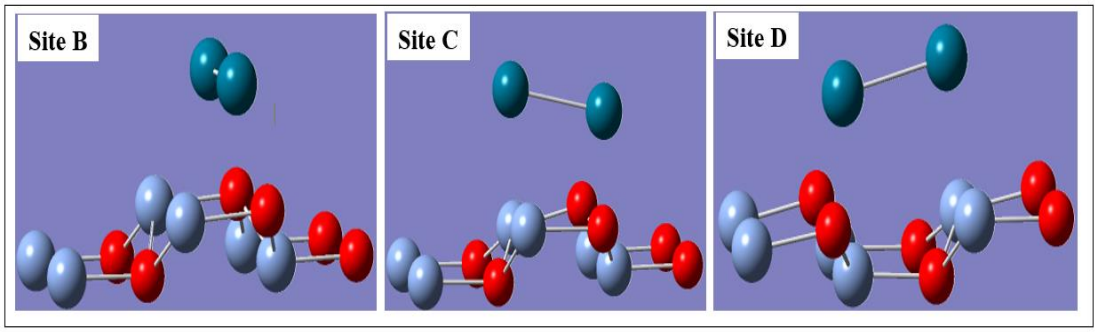

Fig. 1. The adsorption structures from site B to site D of adsorbed Pd on ZnO surface

Continuously, structural 2Pd/ZnO surface of site A is prsented in Fig. 2 as follows,

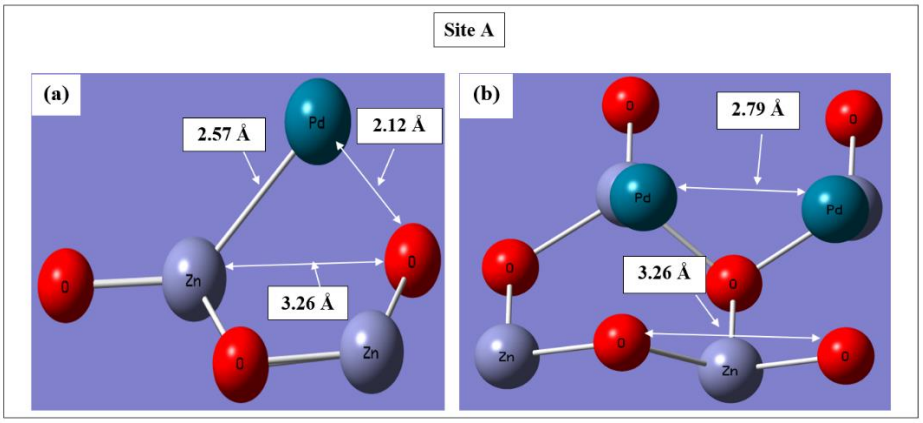

Fig. 2. Adsorbed 2Pd on ZnO$(10\bar{1}0)$ surface. In which, Fig. 1(a) and Fig. 1(b) are side view and top view structures of site A, respectively.

On site A, we observed side view configuration in Fig. 2(a) that each of 2Pd is bounded respectively on Zn and O atoms of surface ZnO to form Zn-Pd-O dimmer. Pd-Zn bond distance of 2.57 Å and a Pd-O length of 2.12 Å are measured. Continuously, keeping an observation at top view configuration in Fig. 1(a) showing that bonded Pd to top site of correspondent Zn on ZnO surface with the Pd-Pd bond length of 2.79 Å is measured for 2Pd/ZnO surface formation. By this way, Pd is oxidized on Zn of ZnO to become Pd^+ ion as active sites formation of 2Pd/ZnO surface to be more active than that of ZnO surface. Thus, 2Pd/ZnO surface configuration of site A is used for methanol adsorption in this investigation.

3.2. CH_3OH adsorption on 2Pd/ZnO adsorbent surface

In this work, it has six positions of adsorbed CH_3OH modes, namely ADS-A, ADS-B, ADS-C, ADS-D, ADS-E, ADS-F sites on 2Pd/ZnO$(10\bar{1}0)$ adsorbent surface are found, in which two stable ADS-A and ADS-B sites are considered particularly with site view structures in Fig. 3,

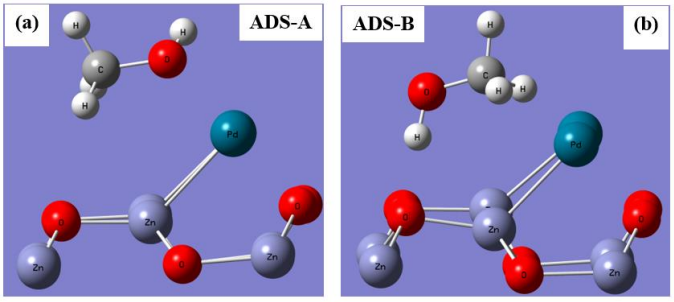

Fig. 3. Two stable structures of adsorbed CH_3OH on 2Pd/ZnO surface are considered as ADS-A site (Fig. 3(a)) and ADS-B site (Fig.3(b)).

Simultaneously, the calculations of adsorbed CH_3OH on 2Pd/ZnO surface of site A with adsorption structures and energies from ADS-C to ADS-F sites are obtained and represented in Fig. 4, which they are not commented also in the detailts of this study.

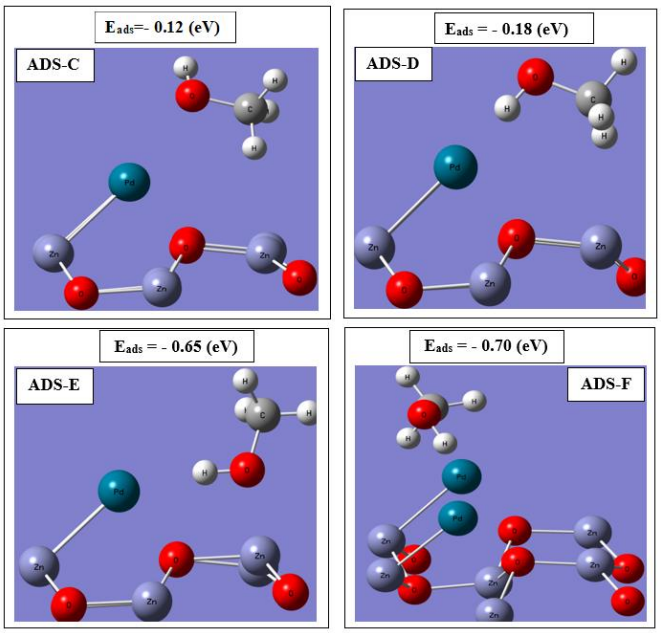

Fig. 4. The CH_3OH adsorption structures and energies of unstable sites from ADS-C to ADS-F on 2Pd/ZnO surface.

In further, the parameters and energies of adsorbed CH_3OH configuration on 2Pd/ZnO surface of ADS-A and ADS-B sites are calculated and listed in Table 2, respectively.

Table 2. Parameters and energies of adsorbed CH_3OH configuration on 2Pd/ZnO surface. It noted that adsorption energy values are E_{ads} (eV), parameters included as bond length (L, in Å), bond distance (D, Å), and M-Surf (Å) as bond distane between CH_3OH and 2Pd/ZnO surface. The surface oxygen atom (O_s), methanol oxygen atom (O_a), and bonded Pd to the surface (Pd_B) are also denoted.

Species	Sites	E_{ads}	L			D	
			C-H	C-O	O-H	M-Suf	D(M-Suf)
CH_3OH	ADS-A	-0.95	1.10, 1.09, 1.09	1.45	0.98	O_a-Pd_B/H-O_s	2.14/2.59
	ADS-B	-0.93	1.11, 1.10, 1.21	1.38	1.01	H-Pd_B/H-O_s	1.76/1.75
CH_3OH gas phase [31]			1.09	1.43	0.96	-	-

In this case, we observed the configuration of ADS-A site in Fig. 3(a) that CH_3OH is adsorbed by O_a of methanol, interacting to Pd on 2Pd/ZnO surface. E_{ads} calculated as-0.95 eV, which this value is lower than that of ZnO surface (-1.14 eV) in our previous works [31], indicating bonded O_a in methanol to Zn of ZnO surface is more favourable than that to Pd of 2Pd/ZnO surface. Continuously observing on ADS-A site finds that, CH_3OH is oriented to sit horizontally on 2Pd/ZnO surface via two chemical bonds with the O_a-Pd_B bond distance of 2.14 Å, and H-O_s bond distance of 2.59 Å are calculated. Simultaneously, C-O of 1.45 Å and O-H of 0.98 Å bond lengths are elongated to compare with CH_3OH gas phase (see in Table 2), implying that CH_3OH has been donated electrons while bonding to 2Pd/ZnO surface. Continously, the configuration of ADS-B site is observed in Fig. 3(b), H in CH_3 group of CH_3OH is bound horizontally to

2Pd on the surface 2Pd/ZnO. And, H in OH group of CH_3OH is oriented bonding to O_s. E_{ads} value of ADS-B site calculated as -0.93 eV, which this value is a bit lower than that ADS-A. Herein, the reason may be due to adsorbing configuration of ADS-B site is existed the physical bond as hydrogen bond. To demonstrate this reason, observing previous Table 1 is that resulted bond lengths of C-H and O-H elongated as 1.21 Å and 1.01 Å, whereas, bond distances shortened being H-O_s of 1.75 Å, H-Pd_B of 1.76 Å, respectively. By this rusult, the interaction between CH_3OH and 2Pd/ZnO has happened. Additionally, resulting C-O bond length in CH_3OH after adsorption on ADS-B site is 1.38 Å shortened to compare that with CH_3OH gas phase, implying 2Pd/ZnO is an acceptor surface, which back-donated electrons to CH_3OH while bonding. As the result, the shortening of C–O bond length is measured.

4. Conclusions

The results of CH_3OH adsorption on 2Pd/ZnO $(10\bar{1}0)$ surface was investigated using DFT calculation method in this work. From detailed calculations, we have done followable conclusions as,

(1) Many positions of 2Pd deposited over ZnO $(10\bar{1}0)$ surface to form 2Pd/ZnO surface model were found and obtained with four energies and structures, in which most stable structure of 2Pd/ZnO surface is determined namely as site A.

(2) In study of methanol adsorption, six positions of CH_3OH adsorbed on 2Pd/ZnO $(10\bar{1}0)$ surface were found. Based on adsorption energy, two stable structures of ADS-A and ADS-B sites are considered, which the structure of ADS-A site is the most stable one.

Our calculation results in this study are an exploring step in applications of 2Pd/ZnO surface as an adsorbent. Other applications of 2Pd/ZnO are for example as a catalyst will be studied in next time.

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TÍNH TOÁN NĂNG LƯỢNG VÀ TRẠNG THÁI LIÊN KẾT CỦA CH_3OH HẤP PHỤ TRÊN BỀ MẶT 2Pd/ZnO SỬ DỤNG NGHIÊN CỨU LÝ THUYẾT HÀM MẬT ĐỘ

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Tóm tắt. Trong nghiên cứu, lý thuyết hàm mật độ (DFT) được sử dụng để tính toán năng lượng và cấu trúc hấp phụ của hai nguyên tử Palladium (2Pd) trên bề mặt ZnO$(10\bar{1}0)$, hình thành bề mặt chất hấp phụ kiểu 2Pd lắng đọng trên ZnO, tên là bề mặt chất hấp phụ 2Pd/ZnO. Sau đó, 2Pd/ZnO được sử dụng để hấp phụ phân tử CH_3OH (metanol) trong pha khí. Cụ thể trong nghiên cứu, 2Pd được hấp phụ tại nhiều vị trí trên bề mặt ZnO, thu được bốn kiểu cấu hình và năng lượng bề mặt chất hấp phụ 2Pd/ZnO, được gọi là site A, site B, site C và site D. Ở đây, dựa trên tính toán kết quả năng lượng hấp phụ chỉ ra rằng, bề mặt chất hấp phụ cấu hình 2Pd/ZnO của site A là bề mặt bền nhất. Ở đây sau đó, bề mặt chất hấp phụ site A được dùng để hấp phụ CH_3OH trong pha khí. Có 6 kiểu phân tử CH_3OH bị hấp phụ tại các vị trí trên bề mặt chất hấp phụ của site A với cấu trúc và năng lượng được tìm thấy, ký hiệu các sites là ADS-A, ADS-B, ADS-C, ADS-E, và ADS-F. Trong đó, dựa trên tính toán năng lượng hấp phụ, kiểu site của ADS-A và ADS-B được xác định là các cấu trúc bền và được xem xét chi tiết hơn trong nghiên cứu.

Từ khóa: DFT, bề mắt chất hấp phụ 2Pd/ZnO, chất bị hấp phụ CH_3OH, năng lượng, trạng thái liên kết

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