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Comparison of CO Adsorption on Undoped and Ti Doped ZnO $(10\bar{1}0)$ Surface: A Density of Functional Study

Vo Thanh Cong[1], Van-Son Nguyen[2], Pham Thanh Tam[3], Nguyen Thi Ai Nhung[4], Jyh-Chiang Jiang[5]

[1,2,3]Faculty of Chemical Engineering, Industry University of Ho Chi Minh City, Viet Nam
[4] Department of Chemistry, University of Sciences, Hue University, Hue City, Viet Nam
[5]Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan
[1] vothanhcong@iuh.edu.vn,[2] nguyenvanson@iuh.edu.vn,[3]phamthanhtam@iuh.edu.vn,
[4]nguyenthiainhung.hueuni@gmail.com, [5] jcjiang@mail.ntust.edu.tw

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Abstract

In this works, we have employed the density functional theory (DFT) calculations with the generalized gradient approximation to investigate the carbon monoxide (CO) adsorption on undoped and Ti (Titanium) doped ZnO $(10\bar{1}0)$ surfaces. In performances, the positions of atomic zinc (Zn) on ZnO $(10\bar{1}0)$ surfaces were substituted by atomic Ti to find the model of Ti doped ZnO $(10\bar{1}0)$ surface, namely Ti-D-ZnO. Continuously, the CO adsorption on undopedZnO surface and Ti-D-ZnO model were examined to compare together, respectively. Further, the effect of Ti dopant on CO adsorption sites and bonding energies were studied also using density of states (DOS) and electron density difference (EDD) contour plots. The results of adsorption energy pointed out that CO adsorption on Ti-D-ZnOwas more stable than the undopedZnO surface. Interestingly, we found that the Ti doping can significantly modify the chemistry and improves the adsorption properties of ZnO surface..

Keywords; *undopedZnO surface; Ti-D-ZnO, DFT, CO adsorption, DOS*

I. INTRODUCTION

CO adsorption on metal oxide systems (M_mO_n) has been extensively performed for theoretical investigations [1-4], which this is the first step towards more complex processes in hetero-catalysis like methanol synthesis, reduction of CO, water gas shift, and other reactions in fuel cell fields. In addition, the adsorption of gas phase (adsorbate) on semiconducting metal oxide surface such as ZnO (adsorbent) has been known to be the best materials for making gas sensors because its advantages as low cost, small dimensions, and great compatibility with microelectromechanical processing [1]. Considering the adsorption mechanism of this gas sensor formation are that the charge transfer occurrence between the adsorbed gas species and the surface of semiconducting metal oxides, which this charge transfer will either increase or decrease the concentration (or mobility) of the major carriers in the metal oxides under operating conditions. Thus, one of this target working is performed to consider the adsorption ability of CO on metal oxides, included both ZnO and modified ZnO surfaces.

On the other hand, metal-oxide adsorbents are attracted considerable attention owing to their potential applications in industry and academic research. In the last years, several experimental and theoretical studies on metal oxides have been performed to increase their performance and reduce the energy required for their practical use [2,5,6].

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Among the oxide adsorbents, zinc oxide (ZnO) has become a frequently studied material in surface science because of its wide range of applications such as a basic material for varistors, as a chemical sensor in gas-detecting systems and as a adsorbent to catalyze for many important chemical processes on the industrial scale (e.g., de-/hydrogenation and methanol synthesis/conversion) [7-9]. Among of four main ZnO surfaces, the non-polar $(10\bar{1}0)$ surface has been the focus of several experimental and theoretical studies due to its most abundant and stable nature [8-10]. The surface is obtained by cutting the crystal perpendicular to the hexagonal Zn and O layers. Atomic planes perpendicular to the $(10\bar{1}0)$ direction consist of equal numbers of zinc and oxygen ions and can be formed as rows of zinc-oxygen dimmers. These dimmers are then bonded to dimmers in the next layer [10,11]. In many these potential reasons, one of present work, the ZnO $(10\bar{1}0)$ surface is used thus to adsorb the CO molecular in gas phase.

Moreover, recent theoretical studies [12-18] showed that the adsorbed properties of the oxides could be improved by replacing a small fraction of the cations at their surface with other cations[15, 17]. In general, one such treatment substitutes some of the cations, M, at the surface of an oxide, M_mO_n, with a different cation, D, to form a single-phase compound having the chemical formula $D_xM_{m-x}O_n$. In this frame work, disnormally called a dopant, $M_mO_n$is the host oxide, and $D_xM_{m-x}O_n$is doped oxide. With the large number of possible D-oxide pairs, it is hoped that some useful adsorbents may be found in this class of compounds.

Previous studies [12,17-19] reported that the doped oxides are difficult to characterize experimentally due to several reasons. For instance, in the methods prepared to form doped oxides, unfortunately, they may be formed one of several alternatives i.e., a fine physical mixture of two oxides, forming an oxide clusters of D supported on the oxide M_mO_n, or very small neutral clusters of the metal D supported on the oxide M_mO_n, or a doped oxide in which all dopant atoms are hidden in the bulk of the material. To overcome the experimental difficulties, we use theoretical methods to qualitatively explore various possibilities and predict the best adsorbent candidates. In the present work, we have investigated the effect of Ti atom doping on ZnO surface layer to determine the Ti-D-ZnO surface model. Here, Ti atom was chosen because it allows to study the dopants which have a larger oxidation state than the Zn ions. To be specific, Ti can switch from the oxidation state of +4 to +3 and are able to compensate the disruption caused by doping, whereas Zn only has a +2 oxidation state and thus lacks this flexibility [15]. Hence, the Ti doped ZnO surface may improve some adsorption reactions compared to that of undoped surfaces. In detailed examinations, we concentrate on the calculated CO adsorption energies to find the most stable sites of CO adsorption on both undopedZnO and Ti doped ZnO $(10\bar{1}0)$ surface. A comparison adsorption enrgies in CO adsorption reaction between undopedZnO surface and Ti doped ZnO surface are also performed. In additions, we also investigated the nature of the surface –CO bonding through scrutiny of density of states (DOS) and electron density difference (EDD) contour plot.

II. COMPUTATIONAL DETAILS

All DFT calculations were performed with the Vienna ab initio Simulation Package (VASP) [20-22]. The electron-ion interactions are treated with the projector augmented wave method [23] in which all the electrons except the valence ones are kept frozen. Exchange-correlation energy was calculated using the GGA-PW91 function [24]. All reported results for a given species on the surface were obtained for its lowest-energy conformer. Normal-mode analysis was performed to verify the nature of several stationary points.

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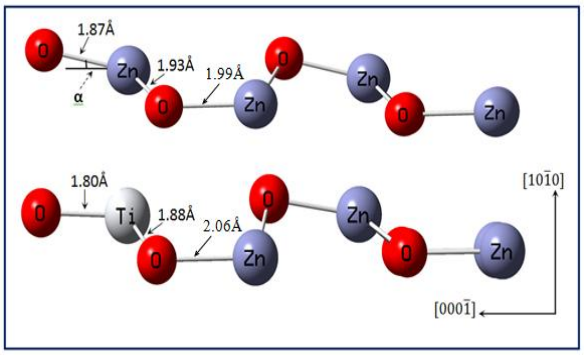

Fig. 1.The side-view of the (2x2)-ZnOsupercell of the optimized undoped (top) and Ti-doped (bottom) systems. Only first two outermostlayersin the direction are shown.

A (2×2)-ZnO $(10\bar{1}0)$ surface super-cell with six layers was used for all calculations, where the top three layers were relaxed and the bottom three layers were fixed. The Ti dopant is in the substitution position as depicted in Fig. 1, replacing one Zn atom for every 4 Zn atoms in the first two surface layers of ZnO in the $(10\bar{1}0)$ direction. A plane-wave cutoff energy of 380 eV and a (4×2×1)k-point grid set by Monkhorst-Pack [25] were used for all periodic calculations, except for ZnO bulk calculations where a (4×4×4) k-point grid was used. A vacuum space of 15 Å was introduced in the $(10\bar{1}0)$ direction to avoid the interactions of adjacent slabs.

We have calculated the chemisorption energy, E_{ads}, as the energy difference between the total energy of the chemisorbed molecular system and the sum of the total energies of the free elaxed molecule and the surface. In the case of CO adsorption on either undoped or Ti doped surface, the chemisorption energy is then given by

$$E_{ads} = E_{CO/surface} - (E_{CO} + E_{surface})$$

Where, E_{ads} is the adsorption energy of the adsorbate on the considered surface (either clean ZnO or Ti-D-ZnO); $E_{CO/surface}$ is the total energy of the optimized CO on the surface; E_{CO} is the total energy of the isolated CO molecule; and $E_{surface}$ is the total energy of the surface.

III. RESULTS AND DISCUSSION

III.1. Undoped and Ti doped ZnO Surfaces

It is well known that the stoichiometric undopedZnO $(10\bar{1}0)$ surface is auto-compensated since it contains an equal number of zinc and oxygen atoms per unit area, and only one bond per atom is broken when the surface is created [7,10,26]. The step-edge Zn and O atoms have one dangling bond per atom [9,11]. The atomic planes, which are perpendicular to the $(10\bar{1}0)$ direction, consist of equal numbers of Zn and O ions and can be considered as rows of Zn-O dimmers. Fig. 1 (top) presents the optimized undopedZnO $(10\bar{1}0)$ surface where the Zn-O bond length in the first and the second outermost layers are 1.87 and 1.99 Å, respectively, and the inter-layer Zn-O distance between the two layers is 1.93Å. After structural reconstruction, the surface geometry distortion from the bulk structure is reflected in the tilt angle (α), which is found to be changed by about 10^o. It has been noticed that the calculated structural parameters for undopedZnO $(10\bar{1}0)$ surface is in agreement with the previous results [10,11]. Previously, it has been reported that, the dopant must replace a Zn atom at the surface of the oxide or in the first layer below the surface [12,13,15]. Also, the dopant may occupy either in an in-terstitial position or form a single neutral atom on the surface during synthesis. In this study, the position of doped Ti, replaces Zn atom on the surface which is shown in Fig. 1(bottom). In Fig. 1, it has been observed that the oxygen atom bonded with Ti moves outwards, resulting in a shortening of Ti–O bond length (1.80Å) compared to the corresponding Ti-O bond length (1.98 Å) of TiO_2 in the bulk. This indicates that, the oxygen atoms which are neighboring to the dopant in the ZnO $(10\bar{1}0)$ surface become less active after doped with Ti.

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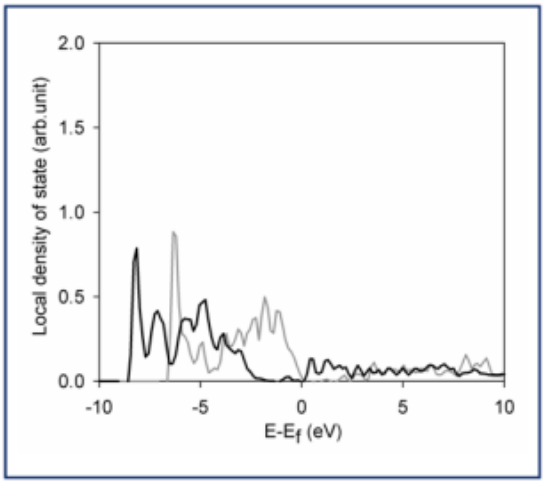

Fig. 2. Local density of states (LDOS) for neighboring O atoms bonded to Zn of undopedZnO surface (grey line) and to Ti of doped ZnO surface (black line).

To understand in more detail about doping, we analyzed the local density of states (LDOS) of O atoms of undoped and doped surfaces and the plotted LDOS is shown in Fig. 2. It can be seen that, the peaks which are corresponds to the interaction between neighboring O atoms and Ti doped surface has been shifted negatively *i.e.* moves away from the Femi level region, in comparison with the interaction between neighboring O atoms and undoped surface. This indicates that the neighboring O atoms of ZnO $(10\bar{1}0)$ surface become less active after doped with Ti, which agrees with the earlier results of Pala*et.al.*[12, 15, 17].

III.2. CO adsorption on undopedZnO surface

The CO adsorbed on the undoped surface either by C atom (C down) or O atom (O down) [2,3,18,27]. It is well known that, the surface area in the vicinity of the topmost O ion is purely repulsive for both the "C down" and "O down". Previous study [27] indicates that the "C down" orientation was found to be the most stable one. We also performed different orientation of CO adsorbed on undoped surface and found that the C down is the most stable conformer. Therefore, we considered "C down" orientation for all the other calculations in this study. The most stable configuration for the CO adsorbed on undoped surface is shown in Fig. 3 (top), and the calculated parameters are listed in Table 1. The other less stable configurations of CO adsorbed on the undopedZnO surface and their corresponding adsorption energies are presented in the Fig. S1 (supplemental material). The calculated adsorption energy of CO adsorbed on the undoped surface is 0.33 eV. The C-Zn distance and tilt angles (β and γ) are found to be 2.13 Å and 33º, respectively, which agree with the previous results [27]. The C-O bond length is slightly elongated (0.02Å) after adsorption on the surface, which may be due to the electron donation to the surface. It is interesting to note that, the tilt angle (α) changes from 10 to 0°when CO absorbed on the undoped surface. This is due to the formation of the bond between CO and Zn atom, which counter-balances the force pulling Zn atom towards the $(10\bar{1}0)$ direction, this causes the elongation of Zn-O bond length (from 1.93 Å to 1.99 Å) between topmost layer and sub-layer after CO adsorption.

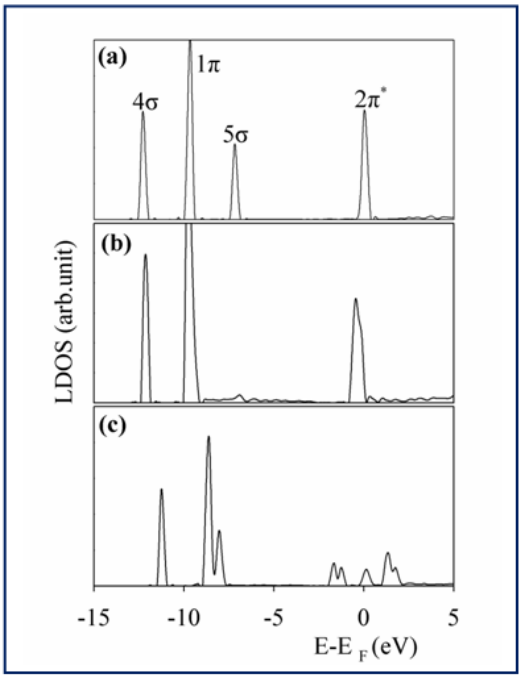

Fig. 4. Local density of states (LDOS) of (a) free CO molecule in a gas phase; (b) and (c) CO adsorption on undopedand Ti doped ZnO surface.

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The plotted local density of states (LDOS) for CO molecule in gas phase and CO adsorbed on the undoped surface are illustrated in Fig. 4(a) and 4(b), respectively. By analyzing the Fig. 4 (a) and (b), it has been found that, the 5σ states are vanished after the adsorption of CO on the undoped surface. Further, we noticed the broadening of the $2\pi^*$ states after adsorption, which indicates the interaction between CO and surface. To study this in detail, we plotted the partial density of states (PDOS) for s, p, and d orbitals of Zn atom before and after CO adsorption on the ZnO surface and shown in Fig. S3 and S4 (supplemental material), respectively. From the PDOS of 4s and 4p orbitals of Zn atom, we found that, there is a partial electron occupation through increased electron density and also shifting of peaks after CO adsorption, which indicates that CO has a broad electron distribution on the surface and it forms strong dative bond. It can be seen from Fig. S4, the d orbitals of Zn atom located away from the Fermi level (about 8 eV), which implies that the back donation of electrons from the surface to CO will be less. In addition, after CO adsorption, an increase in electron density has been noticed in the $3d_{z2}$, 3dyz, and 3dxz orbitals (Fig. S4), which is due to formation of the dative bond. These results indicate that, the CO molecule interacted with ZnO surface via formation of dative bond (i.e., the electron donation from C atom to Zn atom). To gain more information about the charge distributions of CO adsorbed on ZnO $(10\bar{1}0)$ surface, we plotted the electron density difference (EDD) contour plots and shown in Fig. 5(a). It has been observed that the electron density near C and Zn atoms are increased, which confirms the formation of dative bond between these two atoms. The decrease in electron density near C-O bond clearly demonstrates the electron donation from CO to the surface.

III.3. CO adsorption on Ti doped ZnO surface

As like, undoped surface, we considered only C down orientation to interact with the Ti doped ZnO surface. The most stable configuration of CO adsorption on the Ti doped ZnO surface and the calculated adsorption energy are shown also in the Fig. 3 (bottom) and Table 1, respectively. The other less stable configurations and corresponding adsorption energies are summarized in the supporting information as Fig. S2. It has been noticed that, the dopant bond lengths (O-Ti) are elongated after CO adsorption, which is likely due to the formation of the bond between CO and Ti atom, which counter-balances the force pulling Ti atom towards the bulk. However, this force is ignored because the tilt angle (α) of reconstruction surface doped with Ti atom does not change much. The adsorption energy for CO absorbed on the Ti doped ZnO surface is found to be -0.86 eV, which is much larger than that of the undopedZnO surface. The calculated C-Ti distance and the tilt angles ($\beta$and γ) are found to be 2.10 Å and 24°, respectively. Also, C-O bond length is found to be 1.16 Å, which is longer than the gas phase CO molecule (1.13Å). These results indicate the interaction of CO with the doped surface is stronger than the undoped surface.

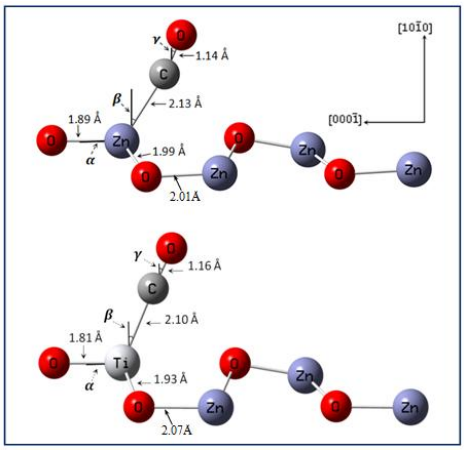

Fig. 3. The most stable structures of CO adsorption on the undoped(top) and the Ti-doped (bottom) ZnO surface.

Table 1. The calculated bond distances (d in Å), bond angles (in degrees) and binding/adsorption energies (E_{ads} in eV) for CO adsorption on undoped and Ti doped ZnO $(10\bar{1}0)$ surfaces. The bond angles (α, βandγ) are defined in Figure 3.

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Parameters	Undoped	Ti-doped
d_{C-O}	1.14	1.16
d_{Zn-C}	2.13 (2.17)[a]	/
d_{Ti-C}	/	2.10
α	0	0
β	33 (30)[a]	24
γ	33 (30)[a]	24
E_{ads}	-0.33 (-0.36)[a]	-0.86

[a] Taken from Ref. [27]

In order to study the bonding nature of the CO on Ti doped ZnO $(10\bar{1}0)$ surface, we plotted LDOS of CO before and after adsorption and shown in Fig. 4(c). By examining the individual quantum states at 5σ and $2\pi^*$ of CO molecule, the shifting of 5σ states reveal the electron donation of C atom in CO molecule to the surface, whereas the splitting of $2\pi^*$ states indicate the electron back donation from the surface to CO molecule. These interactions cause the bond formation between CO and Ti doped ZnO surface. To explain these interactions in detail, we plotted PDOS for s, p, and d orbitals of Ti atom before and after CO adsorption on Ti doped ZnO surface and shown also in Fig. S3 and S4 (supplemental material), respectively.From the PDOS of 4s and 4p orbitals of Ti atom, Fig. S3 (b-b_1), it has been noticed that, there is a partial electron occupation through increased electron density and shifting of peaks at energy region from -5 to -10 eV after CO adsorption, resulting that CO has a broad electron distribution to make surface becoming good hybridization with adjacent O atoms. From Fig. S4 (b-b_2), it has been observed that, the d orbitals of Ti atom are located very near to the Fermi level, hence the back donation of electrons from the surface to the CO becomes more compared to the undopedZnO surface.

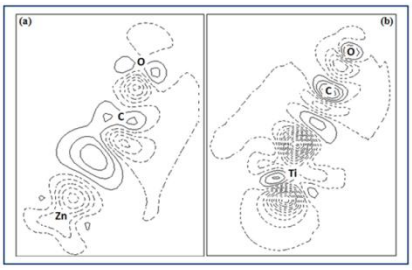

Fig.1. Electron density difference (EDD) contour plots of CO molecule adsorbed on (a) undoped and (b) Ti-doped ZnO $(10\bar{1}0)$ surface. The solid and dashed lines represent increasing and decreasing electron densities

Further, EDD analyses have been performed for the bonding of CO on Ti doped ZnO $(10\bar{1}0)$ surface and shown in Fig. 5(b). From this figure, we can find an increase in electron density between C and Ti atoms and decrease in electron density between the C and O atoms, which indicates the strengthening and weakening of C-Ti and C-O bonds, respectively. In addition, the back donation of electrons from Ti increases the electron density at anti bonding π orbital of CO molecule. As a result, it makes decrease in the bond order of CO molecule, which causes the elongation of CO bond length compared to the undoped surface (see Table 1).

IV. CONCLUSIONS

We have carried out a systematic periodic plane ware DFT calculations on CO adsorption on undoped and Ti doped ZnO surface. All of important structural parameters of both undoped and doped surfaces were obtained by optimization. The adsorption of CO causes significant structural changes in CO, undoped and doped surfaces. We found that, the presence of dopant increases the absorption ability of CO on the ZnO surface. The interaction of CO with undoped and Ti doped ZnO surface has been studied in detail and explained using LDOS, PDOS and EDD plots. The calculated results show that interaction of CO with the doped surface is stronger than the undoped surface.

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Appendix A. Supplementary material the Fig. S1 and S2 show the less stable configurations of CO adsorbed on the undoped and Ti doped ZnO surfaces, respectively. Fig. S3 and S4 present partial density of state (PDOS) analysis of orbitals (s, p, and d) bonded on undoped and Ti doped ZnO surface. This material is available free of charge via the Internet at http://www.sciencedirect.com/.

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