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A Density Functional Theory Study of Methoxy and Atomic Hydrogen Chemisorption on Au(100) Surface

M. N'dollo[1], P. S. Moussounda[1*], T. Dintzer[2], F. Garin[2]
[1]Groupe de Simulations Numériques en Magnétisme et Catalyse, Département de Physique,
Faculté des Sciences, Université Marien Ngouabi, Brazzaville, Congo
[2]Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse (LMSPC),
Université de Strasbourg, Strasbourg, France
Email: *ps_moussounda@yahoo.fr

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ABSTRACT

The adsorption of CH_3O and H on the (100) facet of gold was studied using self-consistent periodic density functional theory (DFT-GGA) calculations. The best binding site, energy, and structural parameter, as well as the local density of states, of each species were determined. CH_3O is predicted to strongly adsorb on the bridge and hollow sites, with the bridge site as preferred one, with one of the hydrogen atoms pointing toward a fourfold vacancy (bridge-H hollow). The top site was found to be unstable, the CH_3O radical moving to the bridge –H top site during geometry optimization. Adsorption of H is unstable on the hollow site, the atom moving to the bridge site during geometry optimization. The 4-layer slab is predicted to be endothermic with respect to gaseous H_2 and a clean Au surface.

Keywords: Chemisorption; Density Functional Calculations; Gold; Methoxy; Hydrogen

1. Introduction

The methoxy group CH_3O and hydrogen H species have been identified as two intermediates in the decomposition of methanol through an initial O-H bond scission on several transition metal surfaces. For methoxy group CH_3O, it appears as an intermediate also in formaldehyde production and in the synthesis of hydrogenated products of CO or its inverse reaction. For catalytic reactions, knowledge of the adsorption geometry of reactants is crucial since it decides on the energy changes during the reaction as well as on the capability of adsorbed species to interact with another one.

Over the last two decades, a number of experimental studies on methoxy over various metal surfaces have been performed using several techniques. Specifically, methoxy on Cu(110) [1-4], Cu(111) [5-7], Cu(100) [8-13], Ag(111) [14], Ni(111) [15], Ni(110) [16,17], Pt(111) [18] has been studied extensively by using X-ray photoelectron diffraction (XPD), reflection absorption infrared spectroscopy (RAIRS), near-edge X-ray absorption fine structure (NEXAFS), temperature-programmed desorption (TPD), low-energy electron diffraction (LEED), scanning tunneling spectroscopy (STM), high-resolution electron energy-loss spectroscopy (HREELS), energy scanned photoelectron diffraction (PED) and surface extended X-ray absorption fine structure (SEXAFS). We note that the XPD [5], SEXAFS [6] and NEXAFS [6] studies for CH_3O/Cu(111) and RAIRS [14] for CH_3O/Ag(111), showed that the CH_3O radical resides in threefold hollow site and the C–O bond is normal to the surface. Whereas, in the PED study [7], it was also found that the CH_3O radical adopted a geometry in which the C–O bond was close to perpendicular to the surface and the O atom occupied a threefold hollow site, fcc. Despite the existence of a large number of studies, conflicting structural assignments still exist. The NEXAFS study of Outka *et al.* [9] shows that methoxy C–O axis will be found with an angle of 20˚ - 40˚ relative to the Cu(100) surface normal. Using the infrared spectroscopy [10,11], Ryberg also found that methoxy is tilted when adsorbed on this surface. Camplin *et al.* [12], using the RAIRS technique, found the C–O methoxy radical bond to be perpendicular to the Cu(100) surface. A later study of Lindner *et al.* [13] with a combined NEXAFS and photoelectron research concluded that the C–O axis is perpendicular to the surface and that a low symmetry adsorption site between the bridge and the 4-fold hollow site is occupied.

Several theoretical studies have also been done on the methoxy—metal surface interactions [19-28]. A many-electron embedding theory, at the *ab initio* configuration interaction level, was used to study the adsorption of

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[*] Corresponding author.

methoxy on the Ni(111) surface [20]. That work showed how CH_3O is adsorbed at 3-fold hollow sites with the C–O axis tilted 5° from the normal to the surface plane. Wang *et al.* [22] used density functional theory (DFT) to determine CH_3O/Ni(111) properties. They found that CH_3O interacts with the surface through oxygen and has a binding energy of 2.58 eV for the threefold fcc hollow site. Witko *et al.* [19,21] have studied the adsorption of CH_3O on Cu(111) surface by performing *ab initio* HF-LCAO calculations. Again it was found that CH_3O is usually adsorbed at 3-fold hollow sites with a slight preference for fcc sites. On Cu(111), the C–O axis lies perpendicular to the metal surface and the calculated adsorption energy is 2.80 eV. Gomes and coworker [23] have studied the same adsorption of CH_3O on Cu(111) surface, using their DFT approach and cluster models. They reported that three-fold hollow sites are the most stable position for methoxy, with fcc and hcp hollows having binding energies of 2.50 eV and 2.18 eV, respectively. Using a DFT approach Greeley and Mavrikakis [24] examined the reaction of CH_3O on Pt(111) top site. They evaluated chemisorption energy around 1.54 eV. Recently, Pang *et al.* [25] have carried out the methoxy adsorption on Ni(111), Ni(110) and Ni(100) surfaces using a DFT method. Very little ab initio and DFT studies have been carried out for methoxy adsorbed on Au. Gomes and Gomes [23] found that CH_3O binds at all high symmetric sites of Au (111) with a preference for the hollow fcc site. The corresponding chemisorption energy for this site was found to be 0.89 eV. With a same surface, Chen *et al.* [26] found that the bridge site is most stable. The corresponding binding energy was calculated to be 0.99 eV. To the best of our knowledge, there is no theoretical study of CH_3O adsorption on the Au(100) surface in the literature.

Atomic hydrogen (H) is probably one of the most extensively studied adsorbate in a large number of catalytic processes. Details on the H chemisorption on transition metal surfaces (TMS) can be found in the literature [29, 30]. A series of TPD, LEED, STM, and electron energy loss spectroscopy (EELS) studies of H adsorption have performed by several groups on Ni(111) [31-33]. Schick *et al.* have applied HREELS to study H on Ir(111) [31]. Techniques such as LEED [34-37], HREELS [38], LERS [39], UPS [40] and calorimetric measurements [41] have been applied to investigate the adsorption of H on the Pt(100), Pt(110), and Pt(111) surfaces. A number of theoretical studies have also performed for H on TMS. Effective medium theory study for H adsorption on Ni(111), Ni(100), W(100) and W(110) has been reported by Nordlander *et al.* [42]. Jiang and Carter [43] have performed a DFT study of H adsorption on Fe(110). Extensive *ab initio* calculations and the DFT method have been used to investigate the adsorption of hydrogen on Pt(111) [44-47], Pt(110) [47,48], Pt(100) [47,49,50], Ni(100) [49], Ni(111) [51,52] and Cu(001) [53]. To our best knowledge, there are no studies at DFT level of hydrogen adsorption on Au(100) surface.

In this contribution, we present a systematic DFT study of the properties of atomic H and CH_3O radical on the Au(100). Our paper is organized as follows. Section 2 gives the details of the computational method. The results and discussions are followed in Section 3. Section 4 concludes with a short summary.

2. Computational Method

We are based our DFT calculations on the DACAPO ab initio package [54]. A (2 × 2) unit cell is used to construct a four or five-layer Au(100) slab. This corresponds to a surface coverage of 1/4 ML when there is only one adsorbate per unit cell. The unit cell is repeated in super cell with successive slabs separated by a vacuum region of 13 Å. Adsorption is allowed on only one of the two exposed surfaces. The top layers of the slab and the adsorbate were allowed to relax. The maximum force criterion of 0.05 eV/Å was considered for convergence. The surface irreducible Brillouin zone was sampled by 18 special k-points using the $(6\times6\times1)$ Monkhorst-Pack grids.

The Kohn-Sham one-electron valence states are expanded in a basis of plane waves with kinetic energies up to 400 eV, and ionic cores were described by ultra soft pseudo potentials [55]. All calculations were performed non-spin polarized. The exchange-correlation potential and energy are described self-consistently using GGA-PW91 functional [56]. The electron density is determined by iterative diagonalization of the Kohn-Sham Hamiltonian, Fermi-population of the Kohn-Sham states $(k_BT = 0.1\text{eV})$ of the resulting electron density. Total energies are extrapolated to $k_BT = 0$ eV.

Using DFT as described above yields a bulk lattice constant of Au of 4.18 Å, to be compared with the experimental value of 4.08 Å [56]. Our rather high result is in perfect agreement with other theoretical evaluation using similar methods (4.17 Å [58] or 4.19 Å [59]).

3. Results and Discussion

In this section we describe the properties of the adsorbates studied, including the binding energies, site preferences, geometries, and local density of states (LDOS), and we compare these results with theoretical or experimental data available on transition and noble metal surfaces.

3.1. CH_3O Chemisorption on Au(100)

3.1.1. Chemisorption Energies

As usual, the adsorption energy (E_{ads}) is evaluated as:

$$E_{ads} = E_{CH_3O} + E_{slab} - E_{CH_3O/slab} \quad (1)$$

where E_{CH_3O} is the total energy of the free CH_3O radical in the gas phase, E_{slab} is the total energy of the clean Au slab and $E_{CH_3O/slab}$ is the total energy of the CH_3O/Au system. With this definition, a positive E_{ads} corresponds to a stable adsorption on the slab. The energy of the isolated CH_3O radical was determined by performing calculations on a single molecule in a cubic cell with 20 Å parameter.

The adsorption of CH_3O on Au(100) at high-symmetry top, bridge and hollow sites, as shown in **Figure 1**, were investigated. For the bridge site, two different hydrogen orientations were considered: one of the H atoms in the CH_3 group points either toward the nearest-neighbor Au atom (bridge-H top) or toward a fourfold vacancy (bridge-H hollow).

Adsorption energies for CH_3O radical at the hollow, bridge-H top and bridge-H hollow, calculated using different numbers of layers in the slab for methoxy coverage of 0.25 ML are listed in **Table 1**. The top site was found to be unstable, the CH_3O radical moving to the hollow site during geometry optimization. From **Table 1**, it can be found that the adsorption energy of CH_3O increases by 0.586 eV from 4 to 5-layer slab, for all adsorption sites. In addition, one can see from this table that the most stable site for CH_3O adsorption on Au(100) is the bridge site with one of the hydrogen atoms pointing toward a fourfold vacancy (bridge-H hollow), at four or five layers of Au. The corresponding adsorption energy for this site was found 1.727 eV (4-layer slab) and 2.314 eV (5-layer slab). The bridge-H top is significantly less stable by 0.153 eV. The adsorption energy difference between bridge-H hollow and hollow sites is only 30 meV. No calculations of CH_3O radical adsorption on Au(100) have been published. There are theoretical results for adsorption in the bridge site on the Au(111), Ni(111), Ni(110), Ni(100), Cu(111), Cu(110) and Cu(100) surfaces. Gomes and Gomes [23] used a cluster model to study the adsorption of CH_3O on Au(111) surface and predicted a chemisorption energy of 0.471 eV. For the same surface, Chen *et al.* [26], using *ab initio* DFT-GGA calculations with three-layer slab, reported adsorption energy of 0.999 eV for coverage of 1/6 ML. The discrepancy in binding energies may be due to the model effect and the computational methodology (slab vs. cluster). Pang *et al.* [25] have described the methoxy adsorption on Ni(111), Ni(100) and Ni(110) with non-spin-polarized calculations elaborately, and found the adsorption energy of 2.292 eV, 2.478 eV, 2.978 eV (in the short-bridge) and 2.281 eV (in the long-bridge) at 1/6 ML, respectively. In the case of methoxy adsorption on Cu(111) surface, Gomes *et al.* [23] and Chen *et al.* [27] found the adsorption energies of 2.036 eV and 2.363 eV, respectively. For the Cu(100) and Cu(110) surfaces, Pick [28], using *ab initio* DFT-GGA calculations with five-layer Cu slabs, obtained the binding energies of 2.540 eV, 2.690 eV (in the short-bridge) and 2.350 eV (in the long-bridge), respectively. These calculated chemisorption energies are much higher than our results.

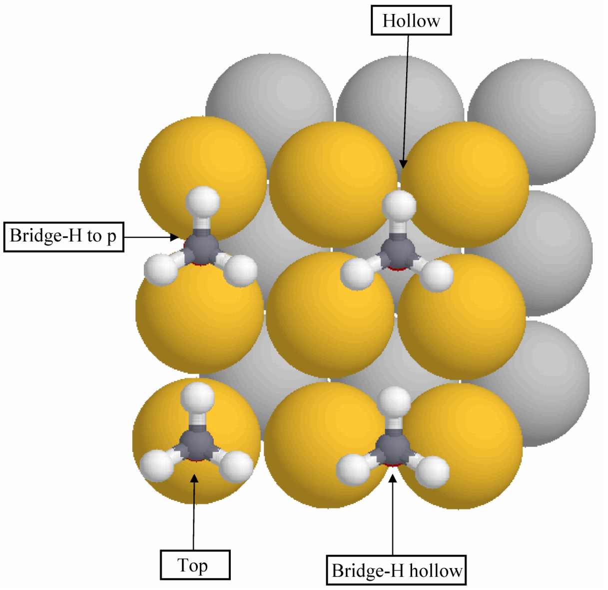

Figure 1. Top view of three high-symmetry adsorption geometries of CH_3O on the Au(100) surface. The indicated adsorption sites are the top, bridge and hollow sites. For the bridge site, two different hydrogen orientations were considered: one of the H atoms in the CH_3 group points either toward the nearest-neighbor Au atom (bridge-H top) or toward a fourfold vacancy (bridge-H hollow) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

3.1.2. Geometric Parameters

Now turn our attention to the geometric parameters. First of all, we checked that the properties of the isolated CH_3O were accurately reproduced. **Table 2** compares our calculated and previous theoretical [25] bond lengths and bond angles of CH_3O. Our results are in good agreement with previous DFT results [26]. Second, we examined the structural parameters, upon adsorption. It can be seen from **Table 1** that the geometric parameters are independent of number of layers in the slab. Similar structural parameters were calculated for the hollow and bridge-H hollow sites. The H–C–H angle is increased from 106.4˚ (shortest H–C–H angle) in isolated methoxy to 108.5˚ (longest H–C–H angle) corresponding to methoxy adsorbed at a bridge-H hollow site. On the bridge-H top site the value of this longest H–C–H angle is 108.7˚. On the bridge-H hollow and bridge-H top sites the longest values of C–O–Au angle are about 120.7˚ and 134.3˚, respectively. Our values are significantly smaller than that the value (179.2˚) obtained par Chen *et al.* [26] for

Table 1. Adsorption energies (E_{ads}) and geometries for CH_3O radical at the hollow, bridge-H top and bridge-H hollow, calculated using different numbers of layers in the slab for methoxy coverage of 0.25 ML. Numbers in parentheses represent the number of bonds with that length or the number of equal angles.

N-layers slabs		4-layer Au	5-layer Au
E_{ads} (eV)	Bridge-H hollow	1.727	2.314
	Bridge-H top	1.575	2.161
	Hollow	1.697	2.283
d_{C-H} (Å)	Bridge-H hollow	1.103(3)	1.103(3)
	Bridge-H top	1.101(1); 1.104(2)	1.102(1); 1.104(2)
	Hollow	1.103(3)	1.103(3)
d_{C-O} (Å)	Bridge-H hollow	1.422	1.424
	Bridge-H top	1.414	1.414
	Hollow	1.422	1.423
d_{O-Au} (Å)	Bridge-H hollow	2.250(2)	2.250(2)
	Bridge-H top	2.195(1); 2.197(1)	2.195(1); 2.197(1)
	Hollow	2.260(2); 3.190(2)	2.260(2); 3.190(2)
H–C–H angle (˚)	Bridge-H hollow	108.3(1); 108.5(2)	108.3(1); 108.5(2)
	Bridge-H top	108.1(2); 108.7(1)	108.1(2); 108.7(1)
	Hollow	108.2(1); 108.5(2)	108.2(1); 108.5(2)
C–O–Au angle (˚)	Bridge-H hollow	120.6(1); 120.7(1)	120.6(2)
	Bridge-H top	132.6(1); 134.3(1)	132.6(1); 134.3(1)
	Hollow	122.0(2); 134.5(2)	122.0(2); 134.6(2)
H–C–O angle (˚)	Bridge-H hollow	109.3(2); 112.9(1)	109.3(2); 112.9(1)
	Bridge-H top	111.0(2); 109.9(1)	111.0(2); 109.9(1)
	Hollow	109.4(2); 112.9(1)	109.4(2); 112.8(1)

Table 2. Comparison between our calculations for geometric parameters for free CH_3O and previous calculated results. Numbers in parentheses represent the number of bonds with that length or the number of equal angles.

Geometric parameters	Our work	DFT(GGA)[a]
H–C–H angle (˚)	106.6(2); 106.4(1)	-
H–C–O angle (˚)	112.3(2); 112.2(1)	-
d_{C-H}(Å)	1.119(3)	1.111
d_{C-O}(Å)	1.341(1)	1.352

(a)Reference [26].

$CH_3O/Cu(111)$ on the bridge site. For CH_3O on the bridge H-top site, the H-C-O angle, in the range of 109.9˚ - 111.0˚, is smaller than that the free methoxy (112.3˚), and in good agreement with the theoretical results by Pick (109.9˚ - 110.0˚) for the adsorbed CH_3O on Cu(100) on the bridge site [28].

As **Tables 1** and **2** show, the C–H bond is reduced from 1.119 Å of the isolated CH_3O radical to 1.101 Å. The optimized C–H bond is very similar to the C–H bond reported by Pick [28]. The calculated C–O bond length for the adsorbed CH_3O, in the range of 1.414 - 1.424 Å, is longer than that of the free species (1.341 Å), and in excellent agreement with the theoretical results by Pick (1.420 Å) [28] and Chen *et al.* (1.408 Å) [26], and with the experimental results by Hoffmann [7], $1.420(-0.003/+0.0010)$ Å and Amemiya *et al.* [6], 1.460 ± 0.005 Å. Compared with the bridge-H top site, the bridge-H hollow geometry has longer O-Au bonds. In addition, the calculated d_{O-Au} values for the both bridge sites are smaller than the corresponding ones obtained by using DFT/B3LYP for Au_7 cluster [23]. Comparing with the ionic radius of Au^+ and O^{2-}, which are 1.37 and 1.32 Å, respectively, [60]; the values of d_{O-Au} are smaller than the ionic radius sum, indicating the strong interaction between O of CH_3O and the surface Au atom.

3.1.3. Analysis of Local Density of States (LDOS)

We now comment on the evolution of the local electronic structure of the molecule and the surface upon adsorption for the most stable adsorption site. **Figure 2(a)** compares the LDOS of O in CH_3O, adsorbed on a preferred bridge-H hollow site, (continuous curve) to the LDOS of O in CH_3O, when it is in a gas phase (dashed curve), *i.e.* in the case of a free CH_3O radical. The graph obviously falls into two main regions. The first region, from −13 eV to −9 eV, has essentially a mixed $(s + p_z)$ character for O atom. Here, the O density of states can be clearly recognized as they are essentially shifted to lower binding energies by ca. 1.42 eV with respect to the free CH_3O radical. The second region of the graph is the energy range from −9 eV to + 2 eV. The states represented in this region all contain O 2s and O 2p characters. One can see from **Figure 2(a)** that a dramatic change in these orbitals occurs upon adsorption. There is a strong mixing between these orbitals and the 5d states of Au, particularly the d_{xz}-band of the Au surface.

The Au surface is affected by the CH_3O adsorption. By examining the components of the Au-d orbitals, we found that d*xz* is the most affected. **Figure 2(b)** shows the LDOS at a surface gold atom of the bridge-H hollow site (solid line) with the LDOS for a Au atom in the clean surface (dotted line) superimposed. The characters of the two curves are not similar. The LDOS curve for the chemisorption system has a small peak of resonance at ~ −11.36 eV which is due to density in oxygen 2s and 2p-derived orbitals lying within the region of the cut. The other notable differences are the presence of two peaks of resonance at about −6.31 eV and −0.86 eV in the chemisorption system curve. These peaks of resonance correspond to states with O 2s and O 2p characters as described previously. In addition, on can notice there is a clear intensity decrease in the −3.68 eV to −1.46 eV region, and the appearance of continuously distributed states from −0.25 eV up to the Fermi level.

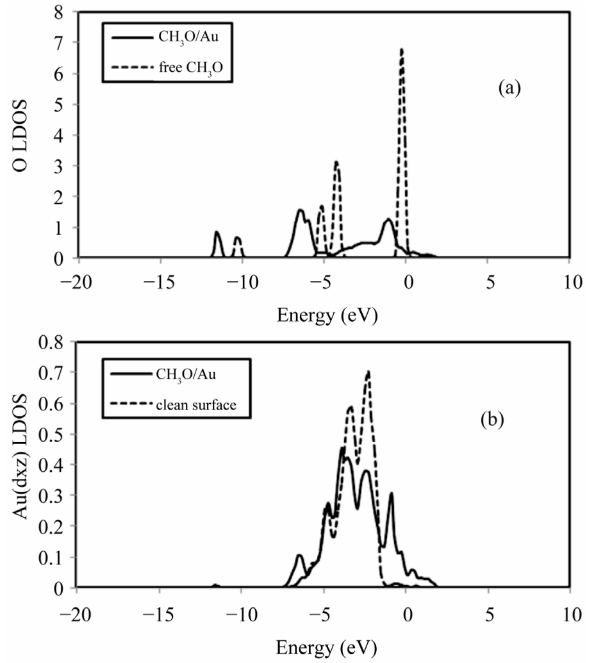

Figure 2. LDOS curves for: (a) O in the free CH_3O and $CH_3O/Au(100)$; (b) d_{xz} orbital of Au. The zero energy corresponds to the Fermi level.

3.2. H Adsorption on Au(100) Surface

3.2.1. Chemisorption Energies and Geometrical Parameters

In this subsection, we investigate the adsorption of H on Au(100) surface. The adsorption energy for atomic hydrogen is calculated by the equation:

$$E_{\text{ads}} = \left[E_{\text{Au(100)}} + n E_{\text{H2}}/2 - E_{n\text{H/Au(100)}} \right] \Big/ n \qquad (2)$$

where n is the number of H atoms in the surface unit, $E_{n\text{H/Au(100)}}$ and $E_{\text{Au(100)}}$ are the energies of the Au(100) system with and without nH absorbates, while E_{H2} is the ground state energy of a free H_2 molecule. The first and last terms are calculated with the same parameters (k-sampling, energy cutoff, etc.). The second term is calculated with only the Γ-point for the Brillouin zone sampling. With this definition, a positive E_{ads} corresponds to a stable adsorption on the slab.

The energy of the free hydrogen molecule was determined from calculations performed on a single hydrogen molecule in a cubic cell with an edge of 15 Å. We made sure that the properties of the free H_2 molecule were accurately reproduced. **Table 3** compares the calculated and experimental bond lengths $d_{\text{H-H}}$ for gas-phase hydrogen. Our calculated result (0.7600 Å) can be compared with the experimental value of 0.7414 Å [57]. Our bigger result is however in excellent agreement with other theoretical evaluation using similar methods [43,61,62].

We start by considering the on-top and bridge adsorption of H on Au(100) for coverages of 0.25 ML and 0.5 ML. The hollow site was found to be unstable, the atom moving to the bridge site during geometry optimization. This phenomenon was also observed by Moussounda *et al.* [49] and Saad *et al.* [47] on the adsorption of H on Pt(100). The adsorption energies for different number of layers in the slab and different coverages are reported in **Table 4**. It might be surprising to find a desorption energy for H in the case of the 4-layer slab for the two coverages, in other terms, the 4-layer slab is predicted to be endothermic with respect to gaseous H_2 and a clean Au surface. These observations are consistent with the theoretical results reported by Sundell *et al.* [53], and Jiang *et al.* [63] and Fabiani *et al.* [64] for $H/Cu(001)$ and $H/Fe(100)$, respectively. Our results reveal that hydrogen preferred adsorbs at the bridge site on Au(100) for the 5-layer slab. The adsorption energy of bridged bonded

Table 3. Comparison between the calculated and experimental bond lengths d_{H-H} of free hydrogen molecule.

	Our work	DFT(GGA)				Experimental value
d_{H-H}	0.7600	0.7557[(a)]	0.7488[(b)]	0.7520[(c)]	0.7500[(d)]	0.7414[(e)]

[(a)]Reference [61], [(b)]Reference [50], [(c)]Reference [43], [(d)]Reference [62], [(e)] Reference [57].

Table 4. Adsorption energies (E_{ads}) and bond lengths (d_{H-Au}) obtained for hydrogen adsorbed at the top and bridge sites of Au(100).

H coverage		0.25 ML		0.50 ML	
		4-layer Au	5-layer Au	4-layer Au	5-layer Au
E_{ads}(eV)	Top	−0.337	0.234	−0.344	−0.072
	Bridge	−0.030	0.568	−0.030	0.241
d_{H-Au}(Å)	Top	1.609	1.610	1.608	1.610
	Bridge	1.790	1.780	1.790	1.790

H decreases significantly with the increasing H coverage. At the coverage of 0.25 ML, we found an adsorption energy of 0.568 eV. No calculations of hydrogen adsorption on Au(100) have been published. However, comparative values calculated at the same H coverage of 0.25 ML for adsorption in bridge site on Pt(100) and Pt(110) are 0.610 eV [49] and 0.640 eV [64], respectively. Lai *et al.* [50] obtained an adsorption energy of 0.542 eV for $\text{H}/\text{Ni}(100)$. Kresse *et al.* [62] reported an adsorption energy of 0.567 eV for $\text{H}/\text{Ni}(100)$, which is in good agreement with our value.

From **Table 4**, we note the d_{H-Au} bond lengths for both sites. The H–Au distance does not depend on the coverage and increases as usual with the adsorption surface coordination of the adsorbate (1.610 Å and 1.790 Å for top and bridge sites, respectively). Theoretical calculations using similar method for H/Pt(100) [49] found the same result for top and bridge sites (1.572 Å and 1.763 Å, respectively). DFT calculations, using DACAPO package [46], obtained a similar H-Pt bond length for adsorption of H on-top of Pt(111) (1.570 Å). With hydrogen in the unstable top site, our H-Au bond length (1.61 Å) is somewhat higher than the theoretical result published by Haroun *et al.* [52] who have reported 1.46 Å for $\text{H}/\text{Ni}(111)$.

3.2.2. LDOS Calculations

In order to obtain a deeper understanding of the properties of $\text{H}/\text{Au}(100)$, we have also analyzed their local density of states (LDOS), in the most stable energetically site for 0.25 ML. The H LDOS for an adsorbed H on Au(100) for the bridge site is shown in **Figure 3** as well as the corresponding LDOS of a free H atom. We can see that the state situated at ~ −5.30 eV initially is found dispersed on a largest domain of energy (~10 eV). The H 1s band has a strong interaction with Au bands, as seen by the significant change of the Au s, p_y, d_{xx-yy} and d_{yz} LDOS for the bridge site (**Figures 4** and **5**). Several peaks of resonance appear on the Au p_y LDOS (**Figure 4(b)**), the peaks increase in intensity and we can see in **Figures 4(a)** and **5(b)** the strong shift of s and d_{yz} centre of gravity, respectively. This is clearly due to the hybridization between 1s state of H and s-p-d Au states after H adsorption.

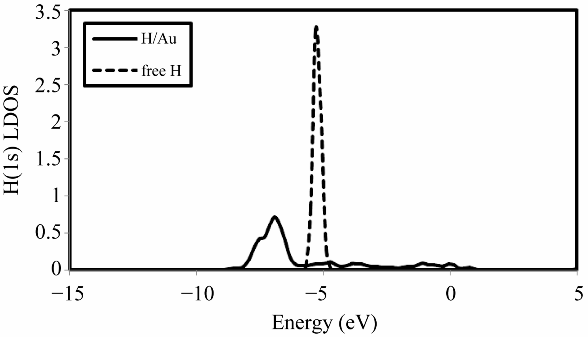

Figure 3. LDOS of H-1s orbital. The zero energy corresponds to the Fermi level.

4. Conclusion

We performed all-electron periodic DFT-GGA calculations of the adsorption of CH_3O and H on Au(100). For methoxy radical, we found that the CH_3O adsorption energy depends strongly on number of layers in the slab and increases with increases in number of layers in the slab. The electronic structure analysis of the adsorbed CH_3O shows that there is a pronounced hybridization between the O 2s, 2p orbitals and d_{xz}-band of the Au surface. For atomic hydrogen, the desorption is found to be favorable for the 4-layer slab. The local density of states curves around H of the adsorbed hydrogen show dispersed states below the metal Fermi level indicating an

H–Au mixing demonstrating a chemical interaction.

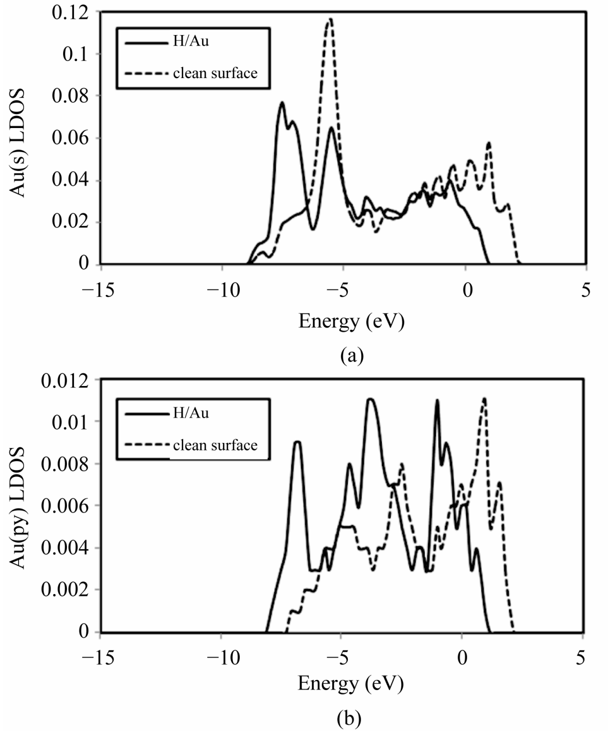

Figure 4. LDOS of Au band after H adsorption on Au(100): (a) s; (b) p_y [solid curves]. The dashed curves indicate the Au orbitals before adsorption of H. The Fermi level lies at 0 eV.

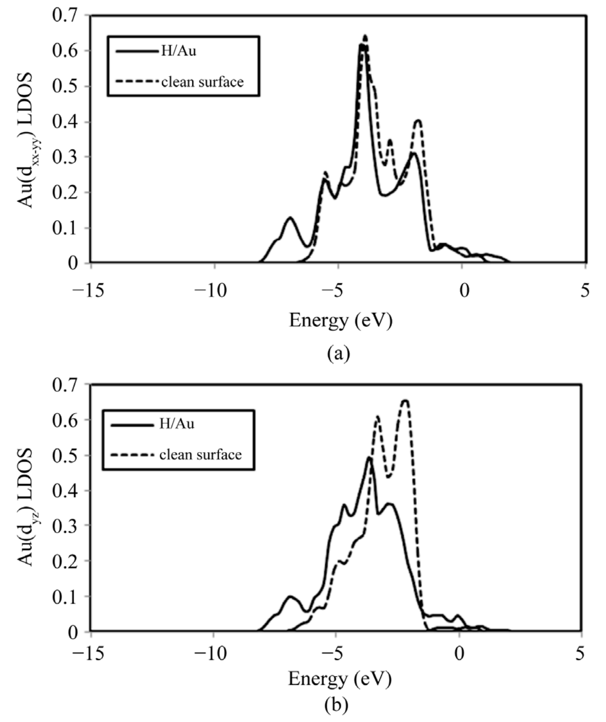

Figure 5. LDOS of Au band after H adsorption on Au(100): (a) d_{xx-yy}, (b) d_{yz} [solid curves]. The dashed curves indicate the Au orbitals before adsorption of H. The Fermi level lies at 0 eV.

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