

Density functional theory insights into the bonding of CH₃OH and CH₃O with Ir(111) surface

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ABSTRACT

Introduction: Understanding the adsorption characteristics of CH₃OH and CH₃O on the noble metal surfaces is essential for designing better catalysts for the on-board production of hydrogen from CH₃OH. This study aims to provide insights into the adsorption behavior of these molecules on Ir(111) surface. **Methodology:** The adsorption structure, the adsorption energy, and the bonding mechanism of CH₃OH and CH₃O with Ir(111) surface were investigated by means of the density functional theory (DFT) calculations and the Bader charge analysis. **Results:** The DFT results show that the adsorption of CH₃OH and CH₃O is driven by the formation of Ir–O bond at the top site of the surface by the overlap of O-2p and Ir-5d orbitals. The overlap of these orbitals is greater in the absorption of CH₃O, resulting in stronger adsorption energy of CH₃O (2.23 eV vs. 0.32 eV). In agreement with the adsorption strength, the charge transfer from CH₃O to the surface is significantly larger than from CH₃OH (0.386 e vs. 0.073 e). **Conclusion:** Although driven by the same adsorption bond, the difference in the molecular characteristics leads to a marked difference in the absorption strength of CH₃OH and CH₃O on Ir(111) surface.

Key words: Ir(111), CH₃OH, CH₃O, adsorption, bonding, charge transfer, DFT

INTRODUCTION

The on-board production of hydrogen from methanol (CH₃OH) is of paramount importance for the operation of polymer electrolyte membrane fuel cells (PEMFCs), which has been attracted as a promising energy source for various portable applications.^{1,2} It has been demonstrated that the most active catalysts for hydrogen production by CH₃OH reforming are the noble metals such as Pt, Pd, Ru, and Ir in the form of nanoparticles dispersed on supporting materials.³ It is widely known that in the mechanism of CH₃OH reforming, the dehydrogenation of CH₃OH is the key step. Therefore, there have been many experimental^{4–9} and theoretical^{10–15} studies on CH₃OH dehydrogenation over surfaces of the noble metals. The results of experimental studies found that CH₃OH is molecularly adsorbed on these metal surfaces; then, CH₃OH dehydrogenation is initiated by the cleavage of the O–H, the C–H, or the C–O bond. The experimental results also found that the O–H bond cleavage is easiest. The CH₃OH dehydrogenation that occurs through CH₃O intermediate is the most energetically favourable.¹⁶ The density functional theory (DFT) calculations have provided insights into the adsorption and decomposition mechanism of CH₃OH on these metal surfaces. However, all the previous DFT calculations only focused on the energetics of the elementary reactions in the mechanism

of CH₃OH decomposition and ignored the bonding of CH₃OH and the important reaction intermediates such as CH₃O with the metal surfaces. Serving as a model for understanding the interaction between CH₃OH and CH₃O and the noble metal surfaces, the adsorption of CH₃OH and CH₃O on Ir(111) surface was investigated by performing the DFT calculations. This manuscript presents the adsorption characteristics of CH₃OH and CH₃O on Ir(111) surface. Moreover, the density of state (DOS) and the Bader charge were analyzed to shed light on the bonding of CH₃OH and CH₃O with Ir(111) surface.

COMPUTATIONAL METHODS

DFT¹⁷ calculations were performed by the Vienna Ab initio Simulation Package (VASP 5.4.1)^{18–21} which treats the interactions between ions and electrons by the projector augmented wave method (PAW)^{22,23}. The generalized gradient approximation^{24,25} (GGA) with the Perdew–Burke–Ernzerhof (PBE)²⁶ exchange–correlation functional was used in this study with a kinetic cut-off energy of 450 eV. The Brillouin zone was sampled by a gamma-center k-point²⁷ with a grid size of 6×6×1.

The unit cell of bulk Ir (a = b = c = 3.839 Å) was used to construct Ir(111) surface. A vertical vacuum space of 15 Å was included in the surface model to mitigate the

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interactions between the repeated slabs. In the geometry relaxation, CH₃OH or CH₃O molecule and the top 3 layers were allowed to relax while the bottom 3 layers were kept fixed to mimic their bulk positions. The geometry relaxation was stopped when the electronic energy tolerance (10^{-5} eV) was reached, and the residue forces on each atom were less than 0.03 eV/Å. The adsorption energy of CH₃OH and CH₃O on Ir(111) surface was calculated as:

$$E_{CH_3OH} = \left(E_{CH_3OH} + E_{Ir(111)} \right) - E_{CH_3OH/Ir(111)} \quad (1)$$

$$E_{CH_3O} = \left(E_{CH_3O} + E_{Ir(111)} \right) - E_{CH_3O/Ir(111)} \quad (2)$$

where $E_{Ir(111)}$ was the total energy of the clean Ir(111) surface, E_{CH_3O} (E_{CH_3OH}) was total energy of isolated CH₃OH (CH₃O), and $E_{CH_3O/Ir(111)}$ ($E_{CH_3OH/Ir(111)}$) was the total energy of the system consisting of adsorbed CH₃OH (CH₃O) on Ir(111).

RESULTS

Structure of Ir(111) surface

Firstly, we present the geometrical structure of Ir(111) surface. In this study, Ir(111) surface was modeled as a periodic slab consisting of 6 atomic layers with 9 Ir atoms on each layer. After the surface relaxation, the Ir–Ir bond length between two adjacent Ir atoms on Ir(111) surface was found to be 2.715 Å. It should be noted that Ir crystallizes in a face-centered cubic lattice. Therefore, there are four high-symmetry positions on the Ir(111) surface, namely one-fold top site, two-fold bridge site, and three-fold hcp and fcc sites, as shown in **Figure 1**. The high-symmetry sites play the binding centers' role for the adsorption of CH₃OH and CH₃O on Ir(111) surface.

Adsorption energy and structural properties

The adsorptions of CH₃OH were calculated at all four high-symmetry sites of Ir(111) surface. CH₃OH is a polarized molecule with a negative charge on the O atom. Therefore, the adsorption of CH₃OH on the surface occurs by the bonding between Ir and O atoms. The adsorption energy of CH₃OH at the bridge, fcc, hcp, and top sites is 0.03 eV, 0.03 eV, 0.04 eV, and 0.32 eV, respectively in **Table 1**. It means that the top site is the most stable site for the adsorption of CH₃OH, and our finding agrees with the previous DFT results.¹¹ Moreover, the adsorption energies of CH₃OH at the top site are comparable on

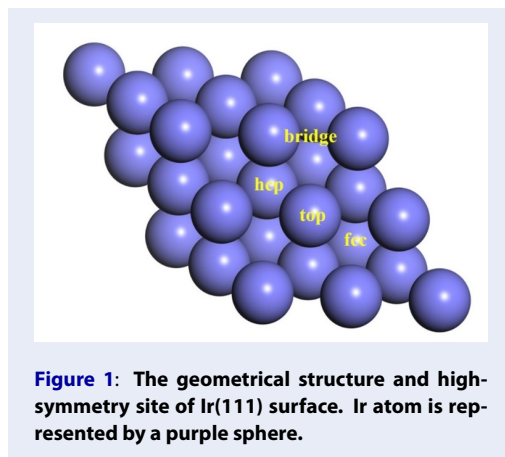


Figure 1: The geometrical structure and high-symmetry site of Ir(111) surface. Ir atom is represented by a purple sphere.

Ir(111) and Pt(111) surfaces.^{12–15} The adsorption energies obtained by our DFT calculations indicate a weak binding of CH₃OH with Ir(111) surface, and the adsorption of CH₃OH is physisorption.

After adsorbing on Ir(111) surface in the most stable adsorption configuration, the O–H bond of CH₃OH is broken to generate CH₃O intermediate. Therefore, it is likely that the newly-formed CH₃O remains at the top site of the surface. Our DFT results verify that the top site is also the most stable site for the adsorption of CH₃O on Ir(111) surface, which is consistent with the finding¹¹ of the prior DFT study. In a similar way to CH₃OH, CH₃O adsorbs on Ir(111) surface by forming Ir–O bond, although the bond length is significantly shorter (1.98 Å vs 2.31 Å). Moreover, the adsorption energy of CH₃O on Ir(111) surface was found to be remarkably larger than that of CH₃OH (2.23 eV vs. 0.32 eV). The calculated Ir–O stretching frequencies for the adsorption of CH₃OH and CH₃O agree well with the respective calculated adsorption energies. Although driven by the same adsorption interaction, the marked difference between the adsorption energy of CH₃OH and CH₃O is because CH₃OH is a closed-shell molecule while CH₃O is a radical with an unpaired electron, and CH₃O is chemically more active than CH₃OH. The adsorption energy indicates that the adsorption of CH₃O is chemisorption.

The adsorption geometries of CH₃OH and CH₃O at the top site of Ir(111) surface are depicted in **Figure 2**, and the structural parameters are summarized in **Table 2**. It can be observed that there is quite a close resemblance between the adsorption configuration of CH₃OH and CH₃O, demonstrated by the approximately equal values of ∠IrOC and ∠HCO angles. Moreover, it is important to note that the C–O bonds of CH₃OH and CH₃O are elongated by 0.02 Å and 0.05 Å by the adsorption.

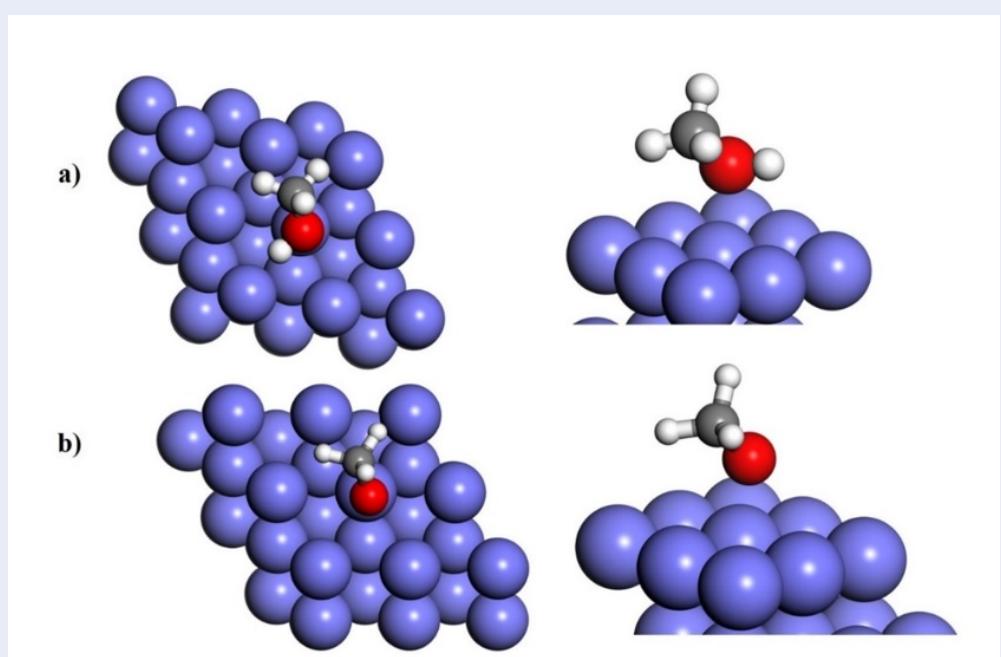


Figure 2: The top view (left) and side view (right) of adsorption geometry of a) CH₃OH and b) CH₃O on the top site of Ir(111) surface. Ir, C, H, and O atoms are represented by a purple, grey, white, and red sphere, respectively

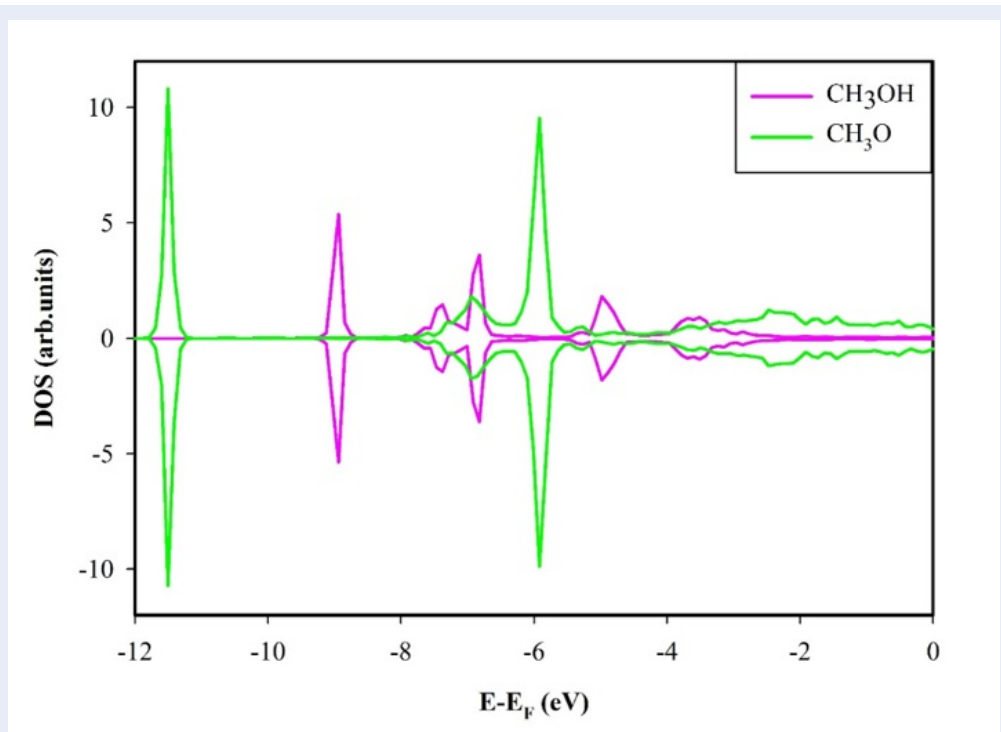


Figure 3: The DOS of adsorbed CH₃OH and CH₃O on Ir(111) surface. The Fermi levels (E_F) were shifted to 0 eV.

Table 1: The adsorption energy of CH₃OH and CH₃O on Ir(111) surface

Species	Method	Adsorption site	Adsorption energy (eV)
CH ₃ OH	DFT	bridge	0.03
		fcc	0.03
		hcp	0.04
		top	0.32
CH ₃ O	DFT	top	2.23

Table 2: The structural parameters of adsorbed CH₃OH and CH₃O on Ir(111) surface

Species	Adsorption site	d(Ir-O) (Å)	d(C-O) (Å)	∠IrOC (°)	∠HCO (°)	v(Ir-O)(cm ⁻¹)
CH ₃ OH	top	2.31	1.45	122.06	108.78	252.09
CH ₃ O	top	1.98	1.41	122.44	110.22	494.22

DISCUSSION

In this part, the nature of the bondings between CH₃OH and CH₃O and Ir(111) surface will be discussed based on the density of states (DOS) calculations and the Bader charge analyses. **Figure 3** displays the DOS of the frontier orbitals of adsorbed CH₃OH and CH₃O. It is widely known that the DOS of an adsorbed molecule is shifted to the lower energy region with respect to the respective free molecule, and the extent of the down-shift reflects the adsorption strength.²⁸ Thus, it can be seen that the adsorption of CH₃O is stronger than CH₃OH as the down-shift of the DOS is more pronounced in the adsorption of CH₃O. As has been discussed, the adsorption of CH₃OH and CH₃O on Ir(111) surface is by the bonding between O and Ir atoms. Moreover, the highest occupied orbitals (HOMO) of CH₃OH and CH₃O are mainly derived from O-2p orbitals, and the valence electrons of Ir atom are in 5d orbitals. Thus, the Ir-O bond is formed by the overlap of O-2p and Ir-5d orbitals, and the extent of the overlap determines the strength of the Ir-O bond. To gain a better understanding of the bonding between Ir and O atoms, the projected density of states (PDOS) of O-2p and Ir-5d orbitals were also calculated and plotted in **Figure 4**. The DOS plots in **Figure 4** show the overlap between the electronic state of O-2p and Ir-5d orbitals. By comparing **Figure 4a** and **Figure 4b**, it can be easily seen that the overlap is much greater for the CH₃O/Ir(111) than the CH₃OH/Ir(111), which also supports the finding that the Ir-O bond is much stronger in the adsorption of CH₃O than CH₃OH.

The Bader charge for each atom of adsorbed CH₃OH and CH₃O on Ir(111) surface are summarized in **Table 3**. Since O is an element with a greater electronegativity than H, the C-O and O-H bonds in

CH₃OH and CH₃O are polarized towards O atom. Accordingly, the results of Bader charge show that O atoms are negatively charged while H atoms are positively charged. Moreover, CH₃OH and CH₃O transfer 0.073e and 0.386 e to the surface, respectively by the adsorption. The charge transfer from CH₃O is significantly larger than from CH₃OH, which also demonstrates that the bonding of CH₃O with the surface is stronger than that of CH₃OH. It should also be noted that the larger charge transfer from CH₃O to the surface results in a less negative charge on O on CH₃O.

CONCLUSIONS

By performing DFT calculations, the adsorption geometry, the adsorption energy, and the bonding of CH₃OH and CH₃O on Ir(111) surface were investigated. The DFT results show that CH₃OH and CH₃O prefer to adsorb at the top site of Ir(111) surface. Owing to its radical characteristics, the adsorption energy of CH₃O is found to be significantly stronger than that of the closed-shell molecule CH₃OH. The DOS analyses reveal that the bondings between CH₃OH and CH₃O and Ir(111) surface is by the overlaps of O-2p and Ir-5d orbitals. By the adsorption, CH₃OH and CH₃O transfer 0.073 e and the 0.386 e to Ir(111), respectively, as demonstrated by Bader charge analysis.

ABBREVIATIONS

PEMFCs: polymer electrolyte membrane fuel cells

DFT: density functional theory

VASP: Vienna Ab initio Simulation Package

COMPETING INTERESTS

The authors declare that there are no conflicts of interest regarding the publication of this paper.

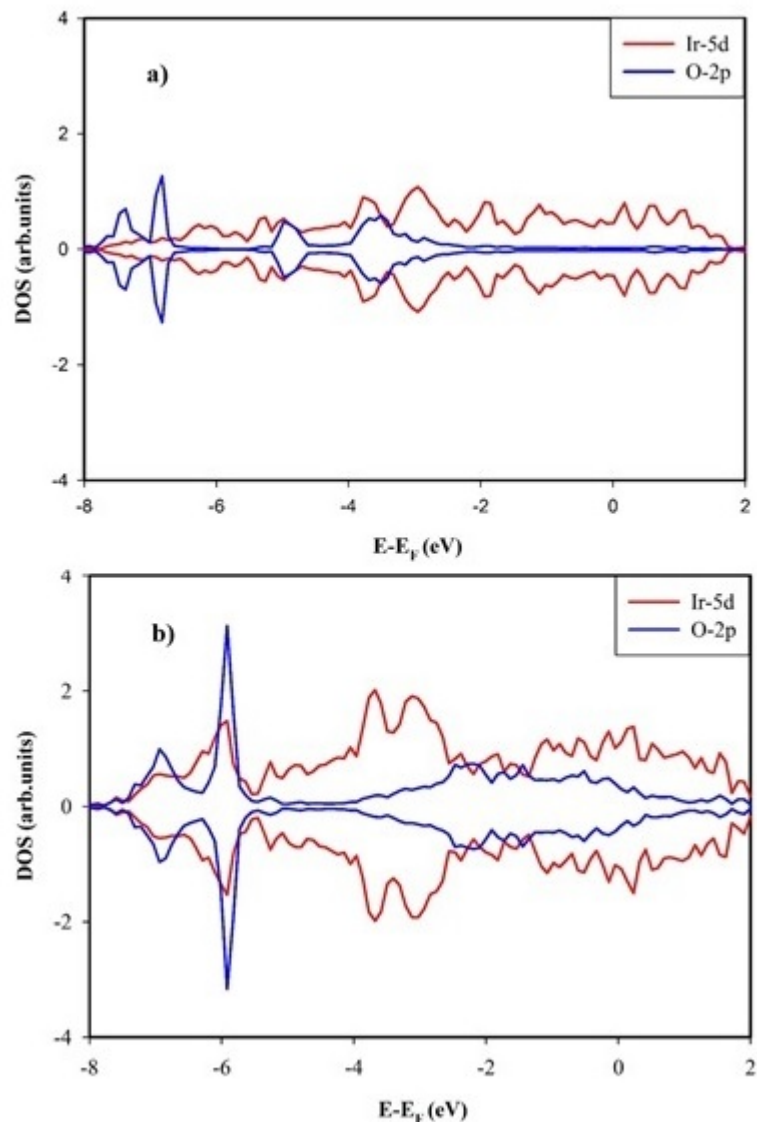


Figure 4: Projected DOS of Ir-5d and O-2p orbitals for: (a) CH₃OH/Ir(111) and (b) CH₃O/Ir(111). The Fermi levels (E_F) were shifted to 0 eV.

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AUTHOR'S CONTRIBUTION

Thong Le Minh Pham conceptualized the study and did all the DFT calculations. Anh Thi Le and Nguyen Thi Thai An interpreted the data and did the proof reading. Thong Le Minh Pham, Thanh Khoa Phung and Ho Viet Thang participated in the writing of the

manuscript. All the authors read and approved the manuscript.

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Table 3: Bader charge on each atom of adsorbed CH₃OH and CH₃O on Ir(111) surface. The first three H atoms are bound to C, and the last H atom is bound to O

Atom	Bader charge (e)	
	CH ₃ OH	CH ₃ O
C	0.356	0.427
H	0.046	0.053
H	0.069	0.019
H	0.068	0.054
H	0.628	/
O	-1.094	-0.906
Sum	0.073	0.386

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