Density functional theory insights into the bonding of CH$_3$OH and CH$_3$O with Ir(111) surface

Thong Le Minh Pham$^{1,2,*}$, Thanh Khoa Phung$^{3,4}$, Ho Viet Thang$^5$, Anh Thi Le$^{1,6}$, Nguyen Thi Thai An$^{1,6}$

ABSTRACT

Introduction: Understanding the adsorption characteristics of CH$_3$OH and CH$_3$O on the noble metal surfaces is essential for designing better catalysts for the on-board production of hydrogen from CH$_3$OH. 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 CH$_3$OH and CH$_3$O 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 CH$_3$OH and CH$_3$O 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 adsorption of CH$_3$O, resulting in stronger adsorption energy of CH$_3$O (2.23 eV vs. 0.32 eV). In agreement with the adsorption strength, the charge transfer from CH$_3$O to the surface is significantly larger than from CH$_3$OH (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 adsorption strength of CH$_3$OH and CH$_3$O on Ir(111) surface.

Key words: Ir(111), CH$_3$OH, CH$_3$O, adsorption, bonding, charge transfer, DFT

INTRODUCTION

The on-board production of hydrogen from methanol (CH$_3$OH) 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. It has been demonstrated that the most active catalysts for hydrogen production by CH$_3$OH reforming are the noble metals such as Pt, Pd, Ru, and Ir in the form of nanoparticles dispersed on supporting materials. It is widely known that in the mechanism of CH$_3$OH reforming, the dehydrogenation of CH$_3$OH is the key step. Therefore, there have been many experimental and theoretical studies found that CH$_3$OH is molecularly adsorbed on these metal surfaces; then, CH$_3$OH 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 CH$_3$OH dehydrogenation that occurs through CH$_3$O intermediate is the most energetically favourable. The density functional theory (DFT) calculations have provided insights into the adsorption and decomposition mechanism of CH$_3$OH on these metal surfaces. However, all the previous DFT calculations only focused on the energetics of the elementary reactions in the mechanism of CH$_3$OH decomposition and ignored the bonding of CH$_3$OH and the important reaction intermediates such as CH$_3$O with the metal surfaces. Serving as a model for understanding the interaction between CH$_3$OH and CH$_3$O and the noble metal surfaces, the adsorption of CH$_3$OH and CH$_3$O on Ir(111) surface was investigated by performing the DFT calculations. This manuscript presents the adsorption characteristics of CH$_3$OH and CH$_3$O on Ir(111) surface. Moreover, the density of state (DOS) and the Bader charge were analyzed to shed light on the bonding of CH$_3$OH and CH$_3$O with Ir(111) surface.

COMPUTATIONAL METHODS

DFT calculations were performed by the Vienna Ab initio Simulation Package (VASP 5.4.1) which treats the interactions between ions and electrons by the projector augmented wave method (PAW). The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) 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-point grid 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 interaction between the vacuum and the Ir(111) surface.
interactions between the repeated slabs. In the geometry relaxation, CH$_3$OH or CH$_3$O 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 CH$_3$OH and CH$_3$O on Ir(111) surface was calculated as:

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

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

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 CH$_3$OH (CH$_3$O), and $E_{CH_3O/Ir(111)}$ ($E_{CH_3OH/Ir(111)}$) was the total energy of the system consisting of adsorbed CH$_3$OH (CH$_3$O) 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 CH$_3$OH and CH$_3$O on Ir(111) surface.

**Adsorption energy and structural properties**

The adsorptions of CH$_3$OH were calculated at all four high-symmetry sites of Ir(111) surface. CH$_3$OH is a polarized molecule with a negative charge on the O atom. Therefore, the adsorption of CH$_3$OH on the surface occurs by the bonding between Ir and O atoms. The adsorption energy of CH$_3$OH 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 CH$_3$OH, and our finding agrees with the previous DFT results. Moreover, the adsorption energies of CH$_3$OH at the top site are comparable on Ir(111) and Pt(111) surfaces. The adsorption energies obtained by our DFT calculations indicate a weak binding of CH$_3$OH with Ir(111) surface, and the adsorption of CH$_3$OH is physisorption.

After adsorbing on Ir(111) surface in the most stable adsorption configuration, the O–H bond of CH$_3$OH is broken to generate CH$_3$O intermediate. Therefore, it is likely that the newly-formed CH$_3$O 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 CH$_3$O on Ir(111) surface, which is consistent with the finding of the prior DFT study. In a similar way to CH$_3$OH, CH$_3$O 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 CH$_3$O on Ir(111) surface was found to be remarkably larger than that of CH$_3$OH (2.23 eV vs. 0.32 eV). The calculated Ir–O stretching frequencies for the adsorption of CH$_3$OH and CH$_3$O agree well with the respective calculated adsorption energies. Although driven by the same adsorption interaction, the marked difference between the adsorption energy of CH$_3$OH and CH$_3$O is because CH$_3$OH is a closed-shell molecule while CH$_3$O is a radical with an unpaired electron, and CH$_3$O is chemically more active than CH$_3$OH. The adsorption energy indicates that the adsorption of CH$_3$O is chemisorption. The adsorption geometries of CH$_3$OH and CH$_3$O 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 CH$_3$OH and CH$_3$O, demonstrated by the approximately equal values of $\angle$IrOC and $\angle$HCO angles. Moreover, it is important to note that the C–O bonds of CH$_3$OH and CH$_3$O are elongated by 0.02 Å and 0.05 Å by the adsorption.
**Figure 2:** The top view (light) and side view (right) of adsorption geometry of a) CH$_3$OH and b) CH$_3$O 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 CH$_3$OH and CH$_3$O on Ir(111) surface. The Fermi levels ($E_F$) were shifted to 0 eV.
DISCUSSION

In this part, the nature of the bondings between CH$_3$OH and CH$_3$O 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 CH$_3$OH and CH$_3$O. 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. Thus, it can be seen that the adsorption of CH$_3$O is stronger than CH$_3$OH as the down-shift of the DOS is more pronounced in the adsorption of CH$_3$O. As has been discussed, the adsorption of CH$_3$OH and CH$_3$O on Ir(111) surface is by the bonding between O and Ir atoms. Moreover, the highest occupied orbitals (HOMO) of CH$_3$OH and CH$_3$O 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 CH$_3$O/Ir(111) than the CH$_3$OH/Ir(111), which also supports the finding that the Ir-O bond is much stronger in the adsorption of CH$_3$O than CH$_3$OH. The Bader charge for each atom of adsorbed CH$_3$OH and CH$_3$O 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 CH$_3$OH and CH$_3$O 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, CH$_3$OH and CH$_3$O transfer 0.073e and 0.386e to the surface, respectively by the adsorption. The charge transfer from CH$_3$O is significantly larger than from CH$_3$OH, which also demonstrates that the bonding of CH$_3$O with the surface is stronger than that of CH$_3$OH. It should also be noted that the larger charge transfer from CH$_3$O to the surface results in a less negative charge on O on CH$_3$O.

CONCLUSIONS

By performing DFT calculations, the adsorption geometry, the adsorption energy, and the bonding of CH$_3$OH and CH$_3$O on Ir(111) surface were investigated. The DFT results show that CH$_3$OH and CH$_3$O prefer to adsorb at the top site of Ir(111) surface. Owing to its radical characteristics, the adsorption energy of CH$_3$O is found to be significantly stronger than that of the closed-shell molecule CH$_3$OH. The DOS analyses reveal that the bondings between CH$_3$OH and CH$_3$O and Ir(111) surface is by the overlaps of O-2p and Ir-5d orbitals. By the adsorption, CH$_3$OH and CH$_3$O transfer 0.073e and the 0.386e 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.

### Table 1: The adsorption energy of CH$_3$OH and CH$_3$O 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 CH$_3$OH and CH$_3$O on Ir(111) surface

| Species | Adsorption site | d(Ir–O) (Å) | d(C–O) (Å) | $\angle$IrOC (°) | $\angle$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           |
**ACKNOWLEDGMENT**

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.01-2017.370.

**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.

**REFERENCES**

1. Steele BCH, Heinzel A. Materials for Fuel-Cell Technologies. Nature. 2001;414:345–352. Available from: https://doi.org/10.1038/35104620.
2. Sun Z, Sun Z. Hydrogen Generation from Methanol Reforming for Fuel Cell Applications: A Review. Journal of Central South University. 2020;27:1074–1103. Available from: https://doi.org/10.1007/s11771-020-4352-8.
3. Zhao J, Shi R, Li Z, Zhou C, Zhang T. How to Make Use of Methanol in Green Catalytic Hydrogen Production? Nano Select. 2020;1:12–29. Available from: https://doi.org/10.1002/
Table 3: Bader charge on each atom of adsorbed CH, OH and CH, O 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, OH | CH, 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  |        |

Steam Reforming of Methanol. Applied Catalysis A: General. 2008;341:1-7. Available from: https://doi.org/10.1016/j.apcata.2007.11.006.

Kohn W, Sham LJ. Self-Consistent Equations Including Exchange and Correlation Effects. Physical Review. 1965;140:A1133–A1138. Available from: https://doi.org/10.1013/physrev.140.a1133.

Kresse G, Hafner J. Ab Initio Molecular Dynamics for Liquid Metals. Physical Review B. 1993;47:558–561. Available from: https://doi.org/10.1013/PhysRevB.47.558.

Kresse G, Hafner J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal–Amorphous-Semiconductor Transition in Germanium. Physical Review B. 1994;49:14251–14269. Available from: https://doi.org/10.1013/PhysRevB.49.14251.

Kresse G, Furthmüller J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. Physical Review B. 1996;54:11169–11186. PMID: 9984901.

Kresse G, Furthmüller J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. Computational Materials Science. 1996;6:15–50. Available from: https://doi.org/10.1016/0927-0256(96)00008-0.

Kresse G, Joubert D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. Physical Review B. 1999;59:1758–1775. Available from: https://doi.org/10.1103/PhysRevB.59.1758.

Bloch PE, et al. Projector-Augmented-Wave Method. Physical Review B. 1994;50:17953–17979. PMID: 9976227. Available from: https://doi.org/10.1103/PhysRevB.50.17953.

Perdew JP. Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation. Physical Review B. 1992;46:6671–6687. PMID: 10002368. Available from: https://doi.org/10.1103/PhysRevB.46.6671.

Becke AD. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. Physical Review A. 1988;38:3098–3100. Available from: https://doi.org/10.1103/PhysRevA.38.3098.

Perdew JP, et al. Generalized Gradient Approximation Made Simple. Physical Review Letters. 1996;77:3865–3868. Available from: https://doi.org/10.1103/PhysRevLett.77.3865.

Monkhorst HJ, Pack JD. Special Points for Brillouin-Zone Integrations. Physical Review B. 1976;13:5188–5192. Available from: https://doi.org/10.1103/PhysRevB.13.5188.

Nilsson A, et al. Chapter 2 - Adsorbate Electronic Structure and Bonding on Metal Surfaces. In Chemical Bonding at Surfaces and Interfaces, Nilsson, A.; Pettersson, L. G. M.; Norskov, J. K., Eds. Elsevier: Amsterdam. 2008b, pp. 57–142. PMID: 17562086. Available from: https://doi.org/10.1016/
