Carbon Monoxide Adsorption on Os (0001) Surface for Fischer-Tropsch Synthesis

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Abstract:	Crude oil is the most utilized source of energy worldwide today. Gasoline, diesel, and jet fuels are products derived from crude oil which came from fossil fuel. These products were used both in household and industry. As the demand for these products increases, a shortage is expected because of the limited source of fossil fuels. Fischer-Tropsch (FT) synthesis provides a possible solution to resolve this problem. The most commonly used catalysts in FT synthesis are transition metals, which involves iron, cobalt, and ruthenium. On the other hand, osmium belongs to the group 8 elements together with iron and ruthenium and a hexagonal close-packed crystal structure like cobalt and ruthenium with a greater lattice parameter. This study focused on the initiation stage of the FT synthesis where a carbon monoxide (CO) molecule is adsorbed on the Os (0001) surface. This study determined the adsorption energy of CO on osmium (Os) (0001) slab (i.e., CO/Os(0001) system) and the dissociation energy of oxygen (O), with their corresponding density of states (DOS) and charge density difference profiles with the use of Density Functional Theory (DFT) implemented by VASP. The density of states for Os showed symmetry between the spin up and the spin down states, indicating that Os(0001) is non-magnetic. Charge density difference provides a graphical representation of electron distribution and is supported by a Bader charge analysis. Presence of states on the Fermi level was also observed, indicating that Os(0001) is a non-magnetic metal. CO adsorbed on the top site of Os (0001) surface, with an adsorption energy of -2.04 eV.

Key Words: Carbon monoxide adsorption; Fischer-Tropsch Synthesis; Osmium

1. INTRODUCTION

Fossil fuels are currently the world's primary source of energy. Gasoline, diesel, and jet fuels are products derived from crude oil which came from fossil fuels. These products are categorized by hydrocarbon length. Throughout the years, the trend in the number of gasoline-powered vehicles has been going up due to the increasing number of developing countries, resulting in an increase in gasoline demand. As a consequence, the market price of gasoline increases. To avoid a possible shortage in crude oil, researches for other sources of gasoline or higher hydrocarbons have become of great importance for the scientists.

Fischer-Tropsch (FT) synthesis has become a possible candidate alternative source of hydrocarbons developed by Franz Fischer and Hans Tropsch in the 1920s (Mahmoudi et. al., 2017). The process involves the conversion of synthesis gas (a combination of carbon monoxide and hydrogen molecule) to hydrocarbons with the help of a catalyst which is transition metals. The initiation stage of FT synthesis involves carbon monoxide (CO) molecule adsorption and dissociation of oxygen. Iron and cobalt, are among the metals used as a catalyst. Ruthenium is considered as the best catalyst for FT synthesis (Dry, 2002; Davis, 2001; Shetty et. al., 2001, Filot, 2014). Ruthenium is a group 8 element together with Iron, and it has hexagonal closed-packed (HCP) crystal structure as

cobalt with greater lattice parameters. Osmium on the other hand also belongs to the group 8 elements and also has an HCP crystal structure with greater lattice parameter compared to ruthenium and cobalt. Studies on osmium as a catalyst are limited.

2. METHODOLOGY

2.1. Computational Details

Calculations in this study were performed using Viena Ab-initio Simulation Package (VASP) which employs Density Functional Theory for its calculation. Generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional was employed. Frozen-core all electron projector-augmented wave (PAW) method with spin-polarized DFT was used. K-point 9x9x1 using Monkhorst-Pack scheme generation of gamma centered k-points was used for osmium slab. Methfessel-Paxton smearing method with sigma equals 0.2 eV was used for calculations involving osmium. VESTA and Microsoft Excel were used for visualization of the system and analysis of data respectively.

2.2. Initial Parameter Calculations

2.2.1. Adsorbate

The CO bond length was initially set to its experimental value of 1.43 Å. The unit cell was a cube with a length of 20 Å to avoid interaction from neighboring CO molecules. After relaxation, the CO bond length became 1.14 Å which was used in the rest of the calculations.

2.2.2. Substrate

Bulk osmium structure optimization was performed and showed its lattice parameters to be **a=b=**2.76 Å and **c=**4.34 Å as shown in figure 1.
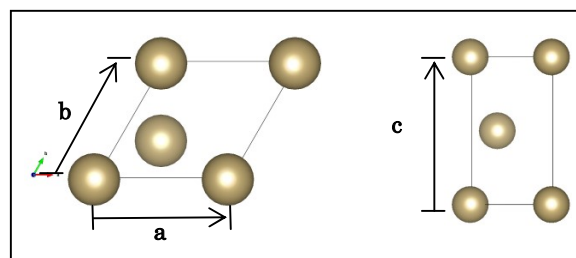

Figure 1. Optimized Bulk Osmium

These values were used for the surface convergence test to determine the number of layers to be used for the substrate. The surface energy varies with the number of layers up to a certain number where the surface energy begins to converge. A realistic slab model requires millions of atomic monolayer which is impossible to model using VASP, therefore a minimum number of layers has to be determined. The convergence of this value ensures that the modeled slab which consists of a few atomic layers will be the same as the realistic model. Here, the surface energy for 3 layers up to 13 layers of osmium with a vacuum of 15 Å was calculated using equation 1. All the atoms were allowed to move except for the atom located at the origin to effect a reduction in the calculation time for relaxation. Figure 2 indicates the results of surface energy calculations.

$$\gamma = \frac{E_{total} - nE_{bulk}}{2A} \quad \text{(Eq. 1)}$$

where:

γ = Surface energy
E_{total} = Total Energy
E_{bulk} = Energy of bulk osmium
n = number of bulk osmium
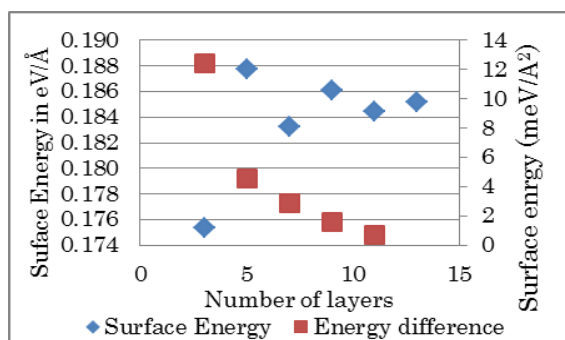A = Area of the slab

Fig. 2 Surface energy convergence

At 5 atomic layers, the surface energy began to converge within 5 meV. The length of the supercell used in this study was determined based on the non-interactive distance between two CO molecules that was determined to be 4.15 Å. The optimized 1x1 unit cell of osmium was only 2.76 Å. This implied that a 2 by 2 unit cell with a length of 5.52 Å must be used. For comparison with other studies, this work considered the top site of Os (0001) surface to be the adsorption site of CO molecule. Figure 3 shows the 2 by 2 Osmium super cell with 5 atomic layers used in the study. The supercell was based on a unit cell that underwent geometry relaxation.
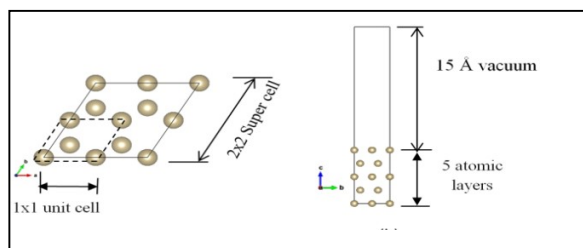

Figure 3. Osmium 2 by 2 supercell

2.2.3. CO/Os(0001) System

Potential energy curve for CO adsorption on Os surface was calculated. The structure was optimized at the configuration of the system which corresponds to the lowest point of the energy curve (figure 4). Adsorption energy was calculated using equation 2 as shown below.

$$E_{ads} = (E_{CO-Os} - E_{CO} - E_{Os}) \qquad \text{(Eq 2.)}$$

where:

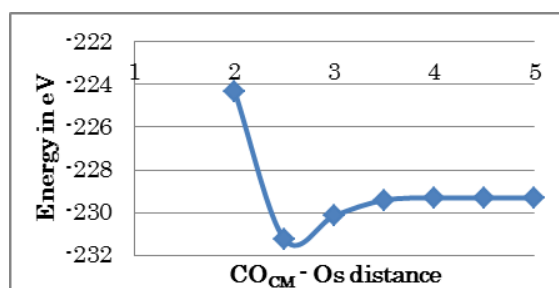|	
E_{ads}	= Adsorption energy
E_{CO-Os}	= Energy of CO-Os system
E_{CO}	= Energy of CO molecule
E_{Os}	= Energy of Osmium slab

Figure 4. Potential energy curve for CO molecule adsorption on osmium slab.

Figure 5 shows the top view of the osmium slab where the CO molecule is adsorbed via the top site. This configuration of CO molecule adsorbed on osmium surface was referred to as CO on osmium slab (CO/Os(0001)) system.
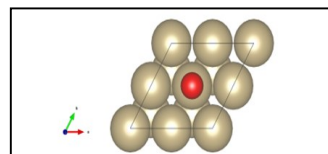

Figure 5. CO on top site of osmium slab

3. RESULTS AND DISCUSSION

3.1. Bulk Osmium

Figure 6 shows the total density of states (TDOS) of the osmium slab. A presence of a state in the Fermi level was observed, indicating that osmium is a metal. There was also symmetry between spin up and spin down states, which indicates that osmium is a non-magnetic metal.
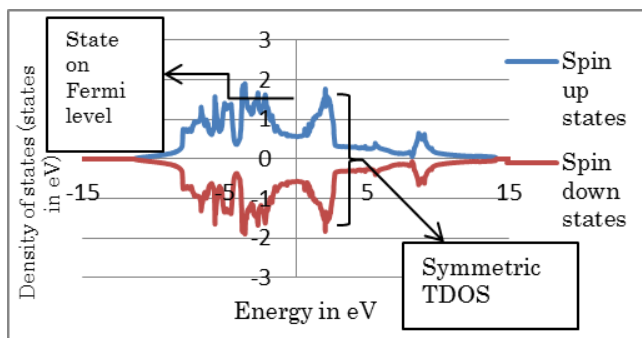
Figure 6. Osmium slab TDOS

3.2.   CO adsorption on Os(0001)

The CO/Os(0001) system was relaxed with the CO molecule's center of mass initially located 2.50 Å from osmium surface. Figure 7 shows the initial (figure 7.a) and final (figure 7.b) configurations of CO on osmium slab. Table 1 shows the results obtained after the optimization. An increase in the CO bond length and a decrease in the distance between the CO molecule center of mass (CO_{CM}) and the osmium slab (Os_{slab}) were observed. The increase in CO bond length indicates adsorption (Bromfield 2005). The calculated adsorption energy was -2.04 eV. This energy is higher compared to the CO adsorption on Ruthenium (Ru) and Cobalt (Co) (Inderwildi et. al., 2007; Ciobica et. al., 2003).
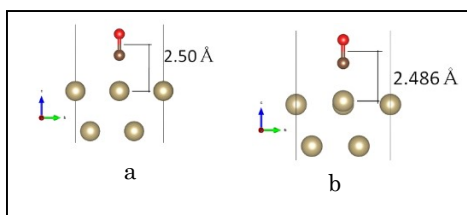

Figure 7. CO adsorption on osmium slab

Table 1. CO adsorption on osmium slab

Initial		Final		
C-O Bond length (Å)	CO_{CM}-Os_{slab} (Å)	C-O Bond length (Å)	CO_{CM}-Os_{slab} distance (Å)	Adsorption energy (eV)
1.14	2.5	1.17	2.49	-2.04

3.3. Charge Analysis

Charge density difference showed that there was a concentration of electron in the region between C atom of the CO molecule and osmium atom. This configuration of electrons was caused by induced charge redistribution as the CO molecule approached the osmium slab. Carbon atom still has a valence shell with lone pair electrons, which caused the attraction of electrons from the osmium atom to its valence shell and establish a covalent bond. This observation was supported by the results from Bader charge analysis. Figure 7 shows the charge density difference of CO/Os(0001).
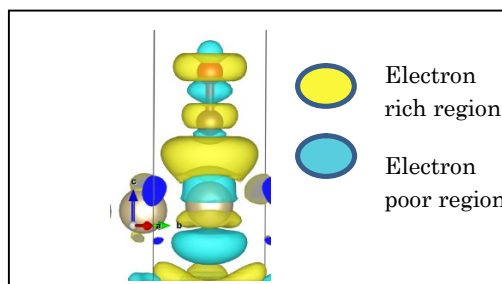

Figure 8. Charge density difference

Table 2. Bader charge analysis

Atom	CO Adsorbed on Osmium Slab (e)	Isolated Osmium Slab and CO Molecule (e)	Charge Transfer (e)
Os	7.84	8.05	-0.20
C atom	3.27	3.03	0.24
O atom	7	6.97	0.03

4. CONCLUSION

This study determined the optimized structure of CO adsorbed on Os(0001) surface. The adsorption energy was calculated to be -2.04 eV. The density of states plot of bulk osmium showed that it was a non-magnetic metal. Charge density difference indicated a covalent bond because of the concentration of electrons in the region between carbon and osmium. Bader charge analysis was performed in which partial charge transfer from osmium atom to carbon atom was observed. The adsorption energy of CO on osmium was higher compared to Ru and Co which only has -1.73 eV and -1.83 eV respectively. Osmium can be considered as a catalyst for FT synthesis.

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