

## Calculation of the O<sub>2</sub> Adsorption on FCC(111) Nickel Surface

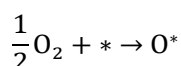
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In this study, the adsorption of oxygen atom at the different sites on the FCC(111) Ni surface were determined using first principle calculations based on the density functional theory (DFT). The different sites that are considered in this study are the top and bridge sites as well as the fcc and hcp hollow sites. Based on the results, adsorption on the bridge site is more favorable than the other sites.

### 1. Introduction

Adsorption is described as the adhesion of atoms, ions or molecules to the surface of a material. In this surface phenomenon, the adsorbent may be chemically bonded on the surface or not. The former is referred to as chemisorption while the latter is referred to as physisorption. Generally, this phenomenon is the basic foundation in surface physic and catalysis. For instance, understanding the underlying concept of the existence of molecular precursors (physisorbed or chemisorbed) is an important concept in describing the adsorption dynamics. Here, the adsorption energy is one of the parameters that can be studied in characterizing the catalytic activities of catalysts, selective functionality of surface, etc. Specifically, the surface energy a molecule having a certain configuration at a certain position on the surface describes the strength of the molecule's interaction with the surface.

To model the isolated adsorbent molecule, the desired molecule is constructed with a certain configuration inside a very large supercell. On the other hand, the adsorption of particles on a certain surface is modelled by cleaving a clean surface from the bulk material and letting the slabs be separated by a large vacuum space. Then the molecules are initially placed by a reasonable distance from the site of interest on the surface and is allowed to be absorbed on one side of the slab. In this work, the oxygen gas molecule O<sub>2</sub> is allowed to be adsorbed at different sites on the FCC(111) Ni surface. In this case, a 4-layer slab separated by 15 Å vacuum and a coverage value of 0.25 ML is used where the bottom two layers are fixed in their bulk positions while the top two layers are allowed to relax. The interaction of O with the surface can generally be described as:



where O\* is an O atom adsorbed on site \*. The different sites that were considered here include the FCC hollow site, HCP hollow site, bridge site and top site. The total energy of the isolated O<sub>2</sub> system (E<sub>O<sub>2</sub></sub>), the slab with

adsorbed molecule (E<sub>O\*</sub>), and the clean FCC(111) facet (E<sub>\*</sub>) Ni slab are all used in determining the adsorption

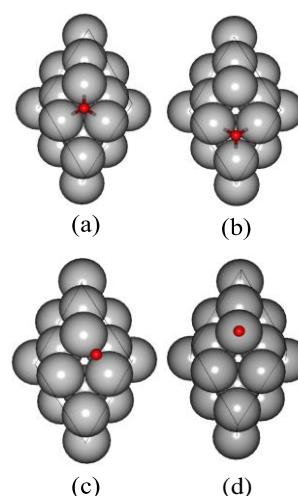


Figure 1. The location of the different sites on the FCC(111) Ni surface: (a) fcc hollow site, (b) hcp hollow site, (c) bridge site and (d) top site.

energy of the molecule at each site. The mentioned sites are located as shown in the following figures:

In calculating the adsorption energy at each site, the following equation is used:

$$E_{\text{ads}} = E_{O^*} - \left( E_* + \frac{1}{2} E_{O_2} \right)$$

where E<sub>O\*</sub> is the energy of the adsorbed O atom on site \*, E<sub>\*</sub> is the energy of the clean surface and E<sub>O<sub>2</sub></sub> is the energy of the isolated O<sub>2</sub> molecule. Basically, the E<sub>\*</sub> and E<sub>O<sub>2</sub></sub> are used the reference energies of the adsorption energy. Smaller adsorption energy corresponds to a stronger adsorption of the atom or molecules on the surface.

### 2. Results and Discussion

The adsorption energies of the O atom at different sites of the FCC(111) Ni surface were calculated and plotted on Figure 2. The data shows that the O atom has the lowest adsorption energy at the bridge site compared to the other

## INTRODUCTION TO DENSITY FUNCTIONAL THEORY CALCULATIONS

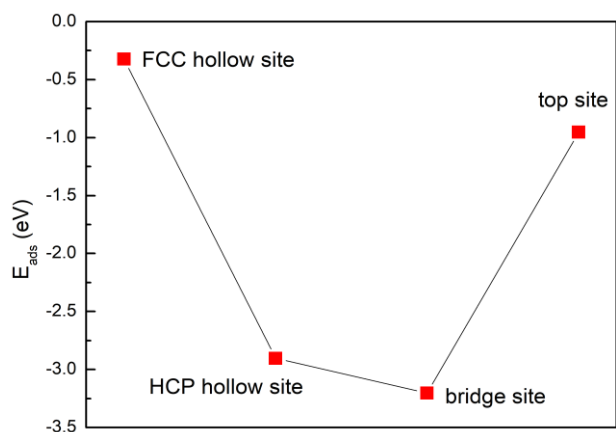


Figure 2. The adsorption energies  $E_{ads}$  in eV of O atom at different sites on the FCC(111) Ni surface.

sites. This means that the strength of interaction between the O atom the Ni surface is strongest at this particular point. A comparison of the  $E_{ads}$  results in this work with previous studies is shown in Table 1.

Based on the tabulated data, there is an observable large Table 1. Comparison of the present result of  $E_{ads}$  with previous calculations in [1-3].

	[1]	[2]	[3]
fcc	-0.32342	-2.36	-2.32
hcp	-2.90342	-2.26	-2.2
bridge	-3.20341	-1.77	1.7
top	-0.95383	-0.48	0.4

discrepancy on the present result with the previous results. This can be due to some factors: (i) different pseudopotentials are used, (ii) different number of layers are used in modeling and (iii) an electric dipole correction is not included in the present study.

Now, the electronic density of states of the surface atoms and the O atom on the different sites are shown on the figures below. Each of these cases reveals an overlapping valence and conducting bonds and hybridization of the Ni-3d and O-2p states.

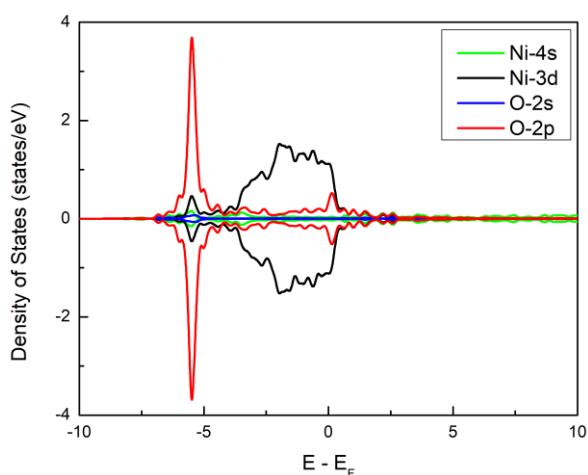


Figure 3. Local density of states of O and the surface atoms on the bridge site.

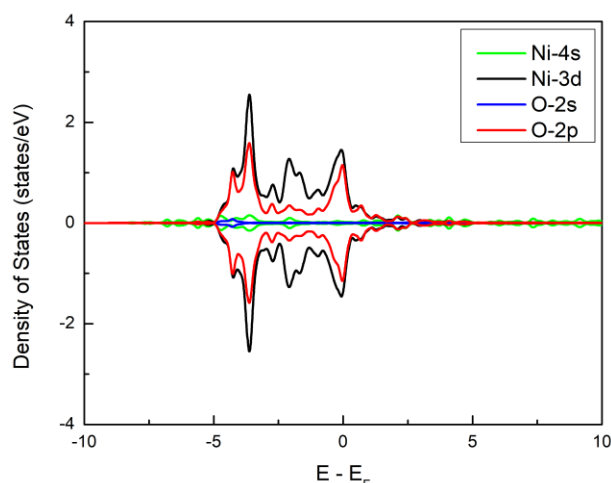


Figure 4. Local density of states of O and the surface atoms on the top site.

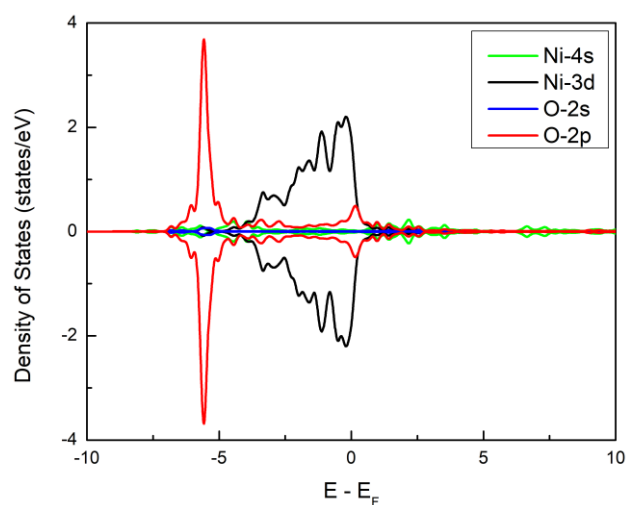


Figure 5. Local density of states of O and the surface atoms on the hcp hollow site.

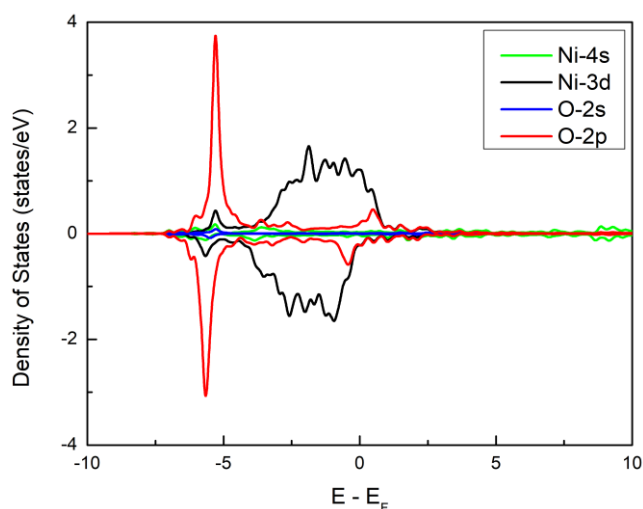


Figure 6. Local density of states of O and the surface atoms on the fcc hollow site.

### 3. Conclusion

The strength of the interactions between an O atom with the surface atoms at different high symmetry sites of fcc(111) Ni surface were quantified using the adsorption energy. The results have shown that the interaction in O/Ni system is more favorable in the bridge site.

### Computational Model

DFT calculations was implemented using Quantum Espresso with exchange-correlation term described using the generalized gradient approximation (GGA) based on Perdew-Burke-Ernzerhof (PBE) functional. The interaction between ions and electrons was described using the ultrasoft pseudopotential. Plane wave basis sets was employed with an energy cut-off of 25 Ry. The surface Brillouin zone integrations was performed on a grid of  $6 \times 6 \times 6$  Monkhorst-Pack k-points for the fcc bulk structure,  $4 \times 4 \times 1$  for the surfaces and  $1 \times 1 \times 1$  for the isolated O<sub>2</sub> gas molecule using Gaussian smearing of  $\sigma = 0.2$  Ry.

### Notes and references

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