



Adsorption of Monoatomic O on Rh(111) Surface

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Heterogeneous catalysis, which is crucial in component in fuel cells and industry, can be done with greater efficiency if there's a *priori* understanding on the surface adsorption of the reactants to the catalyst surface. Periodic density functional theory-based (DFT) first principle calculations were done to determine the adsorption energies (E_{ads}) of monoatomic oxygen at different sites (top, bridge, fcc hollow and hcp hollow sites) of optimized Rh(111) supercell at 0.25 ML adsorbate coverage. Results showed that $E_{\text{ads,top}} = -1.0045$ eV, $E_{\text{ads,bridge}} = -2.5680$ eV, $E_{\text{ads,fcc}} = -2.3974$ eV, $E_{\text{ads,hcp}} = -2.5682$ eV, indicating the preference of O to adsorb at the hcp hollow site. These findings has in agreement with other computational studies in which three-fold hollow sites (hcp and fcc hollow site) is favored for oxygen adsorption compared to top and unoptimized bridge sites.

1. Introduction

Two different materials tend to become attracted when in contact. This degree of attraction can be dependent on many factors, including the polarity of the materials, the exact position and orientation of the material with respect to the other. This process is known as adsorption, which is usually a spontaneous process. Adsorption proceeds to achieve an equilibrium position between these materials at a lower energy than the sum of their individual moieties. Specifically, driving force of adsorption is the reduction of the surface free energy. Much of this phenomenon is occurring in materials of different phases, usually between gas or liquid and solid, wherein the gas or liquid particle (adsorbate) travels to the solid (adsorbent) surface and forms an additional layer to the surface, dependent on the type of adsorption sites.

Adsorption is can be classified by either chemical interaction (chemisorption) or a physical interaction (physisorption). Chemisorption involves the formation of a chemical bond between the adsorbate and the surface. It implies that electrons are redistributed over orbitals of the adsorbing atom or molecule and the atoms that make up the catalytic surface. Hence, atoms and molecules bind on specific sites on surfaces in geometries that correspond to minimum energy configurations. Physisorption involves weaker interactions, mostly with van der Waals attraction, involving the polarization of the adsorbate and surface rather than electron transfer between them. Physisorption is experienced by all molecules which is then masked by any occurring form of chemisorption. Only for rare gases, and very stable molecules such as N_2 and CH_4 , physisorption is usually the dominant interaction. Often, physisorption is the precursor to chemisorption of a molecule¹. Differences between these processes are tabulated in Table 1².

Table 1. Differences between Physisorption (Physical Adsorption) and Chemisorption

Property	Physical adsorption	Chemisorption
Type of bonding forces	Van der Waals	Similar to a chemical bond
Adsorption heat	Low, 10–40 kJ mol ⁻¹	High, 20–400 kJ mol ⁻¹
Chemical change of adsorptive	None	Formation of a surface compound
Reversibility	Fully reversible, i.e. desorption of adsorbate occurs by decreasing the activity of the adsorptive in the fluid surrounding the surface	The process is irreversible; “desorbed compounds” are different from the adsorbed ones
Activation energy	Very low (close to zero)	High, similar to a chemical reaction
Effect of temperature	Negative	In some extent of temperatures positive; so called activated adsorption
Specificity of adsorbate–adsorbent interactions	Very low	High
Formation of multilayers	Yes, in gas phase adsorption usually accompanied by liquefaction in micro- and mesopores	No

Adsorption is essential in heterogeneous catalysis wherein the reactants undergo a mechanism when adsorbed to the active sites of catalytic surface and the chemical products formed undergo desorption. The focus in this study is the adsorption of monoatomic oxygen to different sites of Rh(111) surface. Using first-principle density functional theory calculations, results in this study can be useful in optimizing Rh-catalyzed hydrogenation of CO₂ into methane and other useful products since Rh is found to be one of the transition metal catalyst with highest activity and selectivity³.

In this study, periodic density functional theory-based (DFT) first principle calculations were conducted to calculate the adsorption energies of O atom on different sites of the Rh(111) surface. Four-layered Rh(111) slab supercell models, with high vacuum space at the top and bottom of the slabs, were constructed for each oxygen adsorption sites (see Figure 1): bridge, top, fcc hollow and hcp hollow at an adsorbate coverage of 0.25 ML.

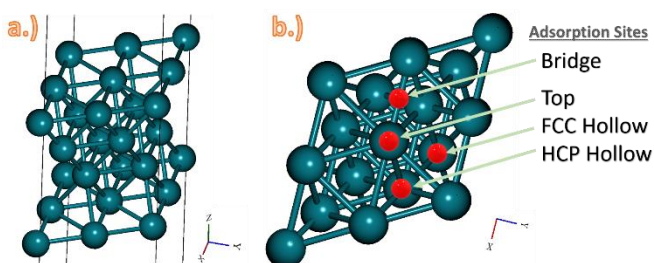
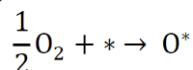


Figure 2. Slab representations for a.) four-layered Rh(111) supercell and b.) different active adsorption sites for monoatomic oxygen

2. Results and Discussion

Calculation of surface adsorption energy is based on the differences of total energies between the products and reactants in the reaction of diatomic oxygen (O₂) gas molecule with Rh(111) slab (represented as *), forming monoatomic oxygen adsorbed to the Rh slab (O*):



Thus, adsorption energy of O* for each adsorption site is calculated as

$$E_{\text{ads}} = E_{\text{O}^*} - (E_* + \frac{1}{2}E_{\text{O}_2})$$

where E_{O^*} is the energy of the system of slab with adsorbed O atom, E_* is the energy of the slab, and E_{O_2} is the energy of an isolated O₂ gas molecule. The E_{ads} is the amount of energy required to pull an O atom off the Rh(111) surface into the gas phase. Based on the reaction given, this quantity is the energy gained (or lost) by pulling two O atoms off the surface and forming an O₂ molecule in the gas phase. In this study, E_{ads} is dependent on the different pre-optimized position of O of different sites.

With only 2 bottom atomic layers' position fixed to represent the bulk part of the material, the rest of the atoms (first 2 atomic layers of Rh and oxygen atom at initially 1.20 Å above the surface) were optimized using DFT calculations for the surface to experience surface relaxation in the presence of oxygen atom by performing an energy minimization as a function of the positions of the atoms in the supercell⁴. Optimized oxygen positions are shown in Figure 2. The bridge site experienced the most significant change in geometrical positioning since the oxygen nearly adapted to the hcp hollow site. It was generally observed that the top layers of Rh atoms at hcp and fcc hollow sites move radially outward from its original position during optimization. This phenomenon has been similarly observed in low-energy electron diffraction (LEED) experiments of adsorbed O on Rh(111)⁵.

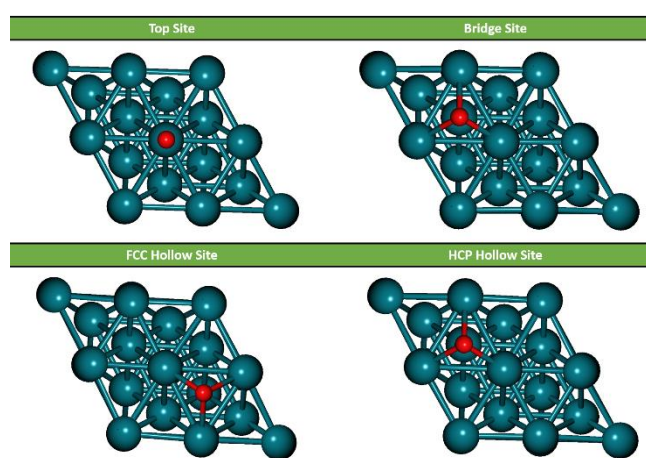


Figure 1. Optimized adsorption configuration of an O adatom on Rh(111) surface

Calculated E_{ads} are tabulated in Table 2. Given that all calculated E_{ads} at different sites are greater than 1 eV in magnitude, monoatomic adsorption to Rh(111) surface is a chemisorption process. Moreover, similar DFT study on oxygen adsorption to Rh(111) by Ganduglia-Pirovano and Scheffler (1999) justified that covalent bond of similar degree is formed between O adsorbate and Rh(111) substrate atoms at hcp and fcc hollow sites⁶. It is observed that the E_{ads} is lowest when oxygen is positioned at the hcp hollow site. It is deemed that due to the similar positioning of oxygen atoms for optimized configurations of oxygen at the bridge and hcp hollow site, as seen in Figure 2, their E_{ads} are expected to be very close to each other. Based on calculations, it is implicit that oxygen atom prefers to bind the Rh(111) at the four-fold hollow sites, specifically hcp at 0.17 eV compared to fcc hollow site, where it has the lowest adsorption energy. This result is in conformance to the observation among (111) metal surfaces that three-fold hollow sites (hcp and fcc hollow sites) have higher coordination number than the unoptimized bridge and top site. Energy is more minimized if oxygen has higher coordination number upon adsorbed.

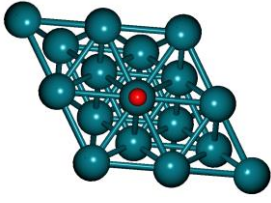
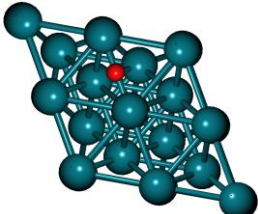
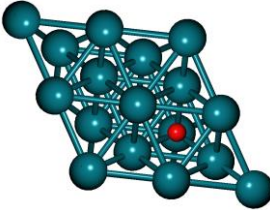
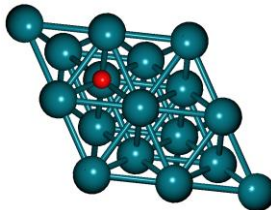
Rh Surface Site	Top	Bridge	FCC Hollow	HCP Hollow
E_{O^*} (eV)	-102,826.1344	-102,827.6978	-102,827.5272	-102,827.6980
E_* (eV)	-102,262.5443			
E_{O_2} (eV)	-1,125.1711			
E_{ads} (eV)	-1.0045	-2.5680	-2.3974	-2.5682
Slab Representation (Before optimization; top view)				

Table 2. Calculated energies of needed for the determining adsorption energies of oxygen at different Rh(111) surface sites

The preference of hcp hollow site in this study has been in good agreement with the study of Loffreda et. al (1998) but differs with the study of Mavrikakis et. al (2002) wherein fcc hollow site has the lowest E_{ads} , as seen in Table 3^{7,8}. Discrepancies of values of this study to other studies might be explained by differences between that calculation and theirs, which can include the functionals, the treatment of core electrons, the inclusion/exclusion of electric dipole correction and the approximations for surface dynamics (inclusion/exclusion of surface relaxation). Nevertheless, these studies agree that three-fold hollow sites (hcp and fcc hollow) would be more stable than the top and bridge sites.

Table 3. Adsorption energy comparison of this study compared to other DFT studies

Rh(111) Surface Sites	Adsorption Energy, E_{ads} (eV)		
	This Study	Loffreda et. al. (1998)	Mavrikakis et al (2002)
Top	-1.0045	-1.38	-3.58
Bridge	-2.5680	-1.97	-4.43
FCC Hollow	-2.3974	-2.14	-4.88
HCP Hollow	-2.5682	-2.18	-4.85

3. Conclusion

In this density functional theory-based first principles calculations, adsorption energies (E_{ads}) of monoatomic O to different sites of Rh(111) supercell surfaces are determined ($E_{ads,top} = -1.0045$ eV, $E_{ads,bridge} = -2.5680$ eV, $E_{ads,fcc} = -2.3974$ eV, $E_{ads,hcp} = -2.5682$ eV). Based on this result, monoatomic oxygen preferred to adsorbed at the hcp hollow site of Rh(111).

Computational Model

DFT calculations were 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 were described using the projector augmented wave (PAW) method. Plane wave basis sets were employed with an energy cut-off of 400 eV. The surface Brillouin zone integrations were performed on a grid of 4x4x1 Monkhorst-Pack k-points using Methfessel-Paxton smearing of $\sigma=0.2$ eV. Electric dipole correction is included along the direction of the vacuum space.

Notes and references

- (1) *Catalysis: An Integrated Textbook for Students*; Hanefeld, U., Lefferts, L., Eds.; Wiley-VCH: Weinheim, 2018.
- (2) Králik, M. Adsorption, Chemisorption, and Catalysis. *Chemical Papers* **2014**, *68* (12). <https://doi.org/10.2478/s11696-014-0624-9>.
- (3) Erdőhelyi, A. Hydrogenation of Carbon Dioxide on Supported Rh Catalysts. *Catalysts* **2020**, *10* (2), 155. <https://doi.org/10.3390/catal10020155>.
- (4) Sholl, D. S.; Steckel, J. A. *Density Functional Theory: A Practical Introduction*; Wiley: Hoboken, N.J, 2009.
- (5) Schwegmann, S.; Over, H.; De Renzi, V.; Ertl, G. The Atomic Geometry of the O and CO + O Phases on Rh(111). *Surface Science* **1997**, *375* (1), 91–106. [https://doi.org/10.1016/S0039-6028\(97\)01249-1](https://doi.org/10.1016/S0039-6028(97)01249-1).
- (6) Ganduglia-Pirovano, M. V.; Scheffler, M. Structural and Electronic Properties of Chemisorbed Oxygen on Rh(111). *Phys. Rev. B* **1999**, *59* (23), 15533–15543. <https://doi.org/10.1103/PhysRevB.59.15533>.
- (7) Loffreda, D.; Simon, D.; Sautet, P. Molecular and Dissociative Chemisorption of NO on Palladium and Rhodium (100) and (111) Surfaces: A Density-Functional Periodic Study. *The Journal of Chemical Physics* **1998**, *108* (15), 6447–6457. <https://doi.org/10.1063/1.476051>.
- (8) Mavrikakis, M.; Rempel, J.; Greeley, J.; Hansen, L. B.; Nørskov, J. K. Atomic and Molecular Adsorption on Rh(111). *The Journal of Chemical Physics* **2002**, *117* (14), 6737–6744. <https://doi.org/10.1063/1.1507104>.