



Surface Energies of Different Rh Surface Facets

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Understanding the surface characterization and properties gives insight to designing better technologies, e.g. catalysis, fuel cells and manufacturing, with better efficiency in which surface interaction with adsorbates is crucial. Periodic density functional theory-based (DFT) first principle calculations were done to determine the surface energies of Rh in (001), (111), (110) and (211) surfaces. Different structural features contribute to the observed surface energy trends, which includes the occurrence of Smoluchowski smoothing. Results, in agreement with other computational studies, showed that Rh(111) ($\sigma = 1.388 \times 10^{19} \text{ eV/m}^2$) would be the most stable type of surface.

1. Introduction

Heterogeneous chemical reactions are of high importance in consideration of designing technologies such as fuel cells and industrial manufacturing involving catalysis. The key interaction of these reaction types is seen in the interface between the surface and possible adsorbate. The type of surface interacting can affect the mechanism and the reaction rates.

Crystalline surface can be described as cleave patterns done at an arbitrary angle. Different angles would result to different plane surfaces which can be described by Miller indices. Low index planes, e.g. (001), (110), and (111), are considered as the basic building blocks of surface structure as they represent some of the simplest and flattest of the

fundamental planes. Higher indices, e.g. (211), often have open structures that can expose second and even third layer atoms. Both (110) and (211) surfaces are vicinal surfaces (stepped surfaces) with exposed second atomic layers, with additional 3rd layer exposed in (211) surface. This provides additional surface heterogeneity compared to the flat surfaces. Generated plane and surface representations with their corresponding relative atomic surface density are tabulated in Table 1¹⁻³.

The presence of steps as a structural defect have slightly different electronic structure than the terraces as seen in Figure 1³. This is due to the phenomenon called Smoluchowski smoothing which is done by spreading out the electron distribution in a way that makes the discontinuity at the step less abrupt⁴. This leads to different opposing dipole areas within the step surfaces.

Table 1. Hard sphere representations and relative surface atom densities of different surface facets.

| Surface Facet | (001) | (110) | (111) | (211) |
|--|-------|-------|-------|-------|
| Surface planes in fcc lattice | | | | |
| Surface representation | | | | |
| Surface atom density relative to (111) | 0.866 | 0.612 | 1.000 | 0.354 |

This occurrence implies a different chemical reactivity for different abundance of these steps of different surfaces.

The energy needed to cleave the bulk metal producing an intended stabilizing surface is called surface energy, σ . This fundamental quantity is important in understanding surface structure, reconstruction, roughening and the crystal's equilibrium shape. This can be calculated as

$$\sigma = \frac{E_{\text{slab}} - nE_{\text{bulk}}}{2A}$$

where E_{slab} is the total energy of surface slab, n is the number of atoms in the surface slab, E_{bulk} is the bulk energy per atom, and A is the surface area. Calculating this quantity is essential in providing further understanding on the adsorption mechanisms of different adsorbates, which can be related to its whole reactivity.

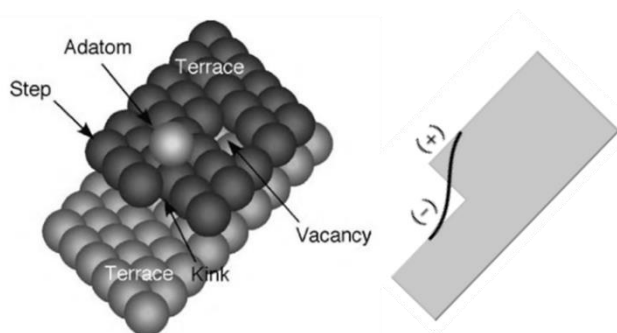


Figure 1. Different structural defects are shown at the left side. The presence of steps creates Smoluchowski smoothing effect that varies the electron distribution as shown on the right side.

In this experiment, different ~4-layered supercell slabs of fcc Rh, with lattice constant of 3.85 Å, are constructed in order to calculate their corresponding surface energies using periodic DFT-based first principle calculations. Insights of this study would be useful in 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 selectivity⁵.

2. Results and Discussion

Different sites of adsorption at atomic level can be identified once the surface is characterized. This can be seen in Figure 2 wherein top sites and different multiple-fold bridge and hollow sites can be found⁶. Considering the Rh surfaces similar to those in Table 1, all of the Rh surfaces in this study can have top sites and two-fold bridge sites. In both of their topmost atomic layer, the (001) surface can have additional four-fold hollow sites whereas (111) surface can have additional three-fold hollow sites. The (110) and (211) surfaces have lower layer bridge sites. Aside from that, (110) surface can have lower layer three-fold hollow sites whereas the (211) surface can have fcc three-fold hollow sites and hcp three-fold hollow sites found in lower layers.

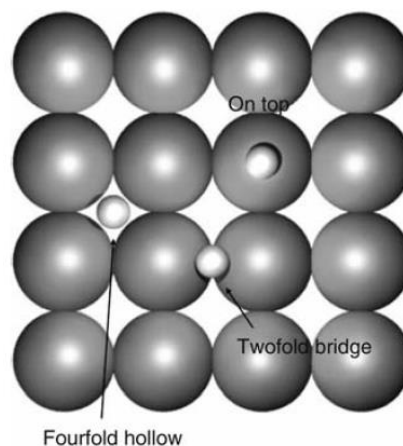


Figure 2. Illustration of different adsorption sites of an atom to a surface, where top, two-fold bridge and four-fold hollow sites are indicated.

Table 2. Data presentation for the calculation of surface energy of each surface facet.

| Surface Facet | (001) | (111) | (110) | (211) |
|-------------------------------|------------------|------------------|------------------|------------------|
| E_{slab} (eV) | -51,130.325 | -102,262.544 | -63,911.909 | -204,516.341 |
| n | 8 | 16 | 10 | 32 |
| A (m ²) | 1.482E-19 | 3.335E-19 | 2.096E-19 | 7.261E-19 |
| E_{bulk} (eV) | -6391.987 | | | |
| σ (eV/m ²) | 1.880E+19 | 1.388E+19 | 1.900E+19 | 1.877E+19 |
| Slab Representation | | | | |

Table 3. Comparison of surface energies calculated in this study in results of different computational studies.

| Surface Facet | Surface Energy, σ (eV/m ²) | | |
|---------------|---|-------------------------|------------|
| | This Study | Literature Values | %Deviation |
| (001) | 1.880E+19 | 1.898E+19 ⁷ | 1% |
| | | 1.808E+19 ⁸ | 4% |
| | | 1.879E+19 ⁹ | 0% |
| | | 1.742E+19 ¹⁰ | 8% |
| | | 1.754E+19 ¹¹ | 7% |
| (111) | 1.388E+19 | 1.667E+19 ⁷ | 17% |
| | | 1.619E+19 ⁸ | 14% |
| | | 1.630E+19 ⁹ | 15% |
| | | 1.542E+19 ¹⁰ | 10% |
| | | 1.579E+19 ¹¹ | 12% |
| (110) | 1.900E+19 | 1.785E+19 ⁷ | 6% |
| | | 1.819E+19 ⁸ | 4% |
| | | 1.921E+19 ⁹ | 1% |
| | | 1.804E+19 ¹⁰ | 5% |
| | | 1.798E+19 ¹¹ | 6% |
| (211) | 1.877E+19 | 1.813E+19 ⁸ | 4% |
| | | 1.874E+19 ⁹ | 0% |

DFT-based first principle calculations were done to determine the surface energy, σ , for each type of Rh slab representing different surfaces. Data summation is tabulated in Table 2. It has been observed that $\sigma_{(111)}$ is the lowest among the group. Likewise, among the low index plane slabs, their decreasing trend on surface atom densities from (111) to (001) to (110) correspond to their increasing trend of surface energies, in which $\sigma_{(111)} < \sigma_{(001)} < \sigma_{(110)}$. These low index plane surface energy trend results are in consonance with other computational studies¹²⁻¹⁴. This indicates that the Rh(111) surface, which is the most closed-packed among the low indices, is the most stable type of flat surface. This means that the lowest energy needed to cleave Rh crystal lattice forms (111) surface.

The presence of stepped and open surfaces has an anisotropic consequence to the work function and eventually to the surface energy. Open surfaces, where lower atomic layers are exposed, found in (110) and (211) can make the relaxation of electrons “smoother” the surface charge. A dipole moment is then built up thus lowering the work function of the surface. Lowering the work function would eventually lead up to increase in its surface energy, as compared to surface energies of (001) and (111). In regards for the (211) surface, which has stepped surfaces, the contributing factors for its relatively high surface energy include its low surface atom density and, in particular, the formation of Smoluchowski smoothing of its step areas which lowers the work function of the surface thus exhibiting an increase of its surface

energy¹⁵. It is then expected that both Rh(110) and Rh(210) surfaces are less stable than Rh(111) in terms of their surface energies.

Literature values of surface energies from different computational studies are being compared to this periodic DFT study as shown in Table 3. Deviations did not exceed to 10% for $\sigma_{(001)}$, $\sigma_{(110)}$ and $\sigma_{(211)}$ whereas deviations ranged from 10-17% for $\sigma_{(111)}$ comparisons. This study and different computational studies agreed that Rh(111) surface would be the most stable based on the calculated surface energy values.

3. Conclusion

In this density functional theory-based first principles calculations, surface energies from constructed Rh supercell surfaces of (001), (111), (110) and (211) are calculated. The Rh(111) facet would form the most stable surface based on its surface energy equal to 1.388×10^{19} eV/m², which is the lowest compared to $\sigma_{(001)}$, $\sigma_{(110)}$, and $\sigma_{(211)}$.

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.

Notes and references

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