Adsorption and dissociation of carbon monoxide on rhodium surface: AB INITIO study

Zi Yang1*, Cheng-Han Li1, Menglin Zhu1, Yumeng Li2, and Tong Zhang3

1 Department of materials science and engineering, The Ohio State University, Columbus, OH, 43210, USA
2 Department of mechanical and aerospace engineering, The Ohio State University, Columbus, OH, 43210, USA
3 Institute for advanced materials and technology, University of Science and Technology Beijing, Beijing, 10083, China

*Corresponding author’s email: yang.684@osu.edu

Abstract. Ab initio molecular dynamics simulations of carbon monoxide adsorption and dissociation on Rh(100), Rh(110), and Rh(111) surfaces have been performed using projector augmented wave (PAW) pseudopotential and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. The results reveal the C-downward configuration is the most preferable configuration for CO molecules on rhodium surface. CO dissociation energies at Rh(100) hollow site, Rh(110) bridge site, and Rh(111) hollow site are 1.64 eV, 0.05 eV, and 0.91 eV, respectively, which are much lower than that in vacuum (13.19 eV). The minimum energy barrier calculated by nudged elastic band (NEB) method indicates Rh(110) surface provides the highest activity by lowering the energy barrier and dissociation energy by ~13eV.

1. Introduction
Carbon monoxide adsorption and dissociation on metal surfaces plays a vital role in a number of surface-catalyzed electrochemical reactions. For instance, Yang and Garland found three predominant forms of CO absorbed on rhodium surface: linearly bonded form, gem-dicarbonyl form, and bridged form[1]. Studies over the past two decades have provided important information on structural properties and characteristics of CO molecules and individual C and O atoms on rhodium surface. For detailed CO dissociation process however, and particularly on different surfaces, energy barrier exists and the electrochemical environment is different from the stable state. Research to date has not yet provided direct observation of CO adsorption and dissociation on rhodium surface due to experimental limitations. The molecular dynamics simulation method presents an alternative way to analysis the structure and dynamics of materials. It can simulate the CO bond breaking and migration of C and O atoms.

Electrocatalyzed reactions are often designed using transition metals from Pt-group and their alloys. Compared to other catalyst materials such as platinum and palladium, rhodium, the metal of choice in this paper, has by far the highest activity for removal of NOx from the exhaust gas, and it also has significant activity for oxidation of carbon monoxide and hydrocarbon[2]. Approximately 80% of rhodium production throughout the world is used as three-way catalyst, especially in catalytic converters of automobiles[3].
We present a numerical analysis of CO adsorption and dissociation on Rh(100), Rh(110) and Rh(111) surfaces. Considering energy band theory (NEB) we expect structural relaxation in adsorbate complexes.

2. Methods
The molecular dynamics (MD) method in the present study was performed using Vienna Ab Initio Simulation Package (VASP)[4, 5] with projector augmented wave (PAW) pseudopotential[6], Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and a cut-off energy of 212 eV. The bulk face-centered cubic (FCC) lattice parameter for rhodium was 3.846 Å. Rh(100), Rh(110) and Rh(111) surfaces, which contain 108 Rh atoms, 48 Rh atoms and 36 atoms, respectively, were established using CrystalMaker. The k-point mesh for carrying out density functional theory (DFT) calculation was 3x3x1. No constraints to molecular geometry or atomic positions were set, and quantum effects were not taken into account.

To explore the interaction between CO molecules and Rh surfaces, CO molecules were put on top, bridge, and hollow sites on Rh(100) surface, and on bridge, top, hollow, and gap sites on Rh(110) surface, and on bridge, top, hollow B and hollow C sites on (111) surface, as shown in figure 1. Each CO molecule was put with both C-upward and C-downward configurations. The ab initio MD calculation was carried out by changing IBRION flag to 0, and set the temperature using TEBEG and TEEND. Nudged elastic band (NEB) is a method used to determine the saddle point and/or minimum energy path for a reaction. To implement NEB in this study, the reaction pathway was first predicted by positions of reactants and products. Meanwhile, 5 intermediate positions were interpolated along the assumed reaction pathway. Each configuration was relaxed to find the minimum energy while retaining equal distance to others. The spring constant between images was set as -5 and the climbing image algorithm was implemented.

![Diagram of possible sites of CO molecules on Rh(100), Rh(110), and Rh(111) surfaces.](image)

3. Results and discussions

3.1. Molecular dynamics (MD) analysis
During MD analysis (figure 2), C-downward configurations of CO molecules were put at different sites on Rh(100), Rh(110), and Rh(111) surfaces at 400K. Simulation results showed on Rh(100) surface, CO molecule moved from top site toward hollow site; On Rh(110) surface, CO molecule moved from gap site toward top site; On Rh(111) surface, CO molecule left top site and hovered back-and-forth between two hollow sites. Furthermore, all CO molecules kept C-downward configuration during calculation. Another CO molecule with C-upward configuration was set on Rh(110) gap site at 1600K initially, but it flipped over immediately toward C-downward configuration, indicating the C-
downward configuration is the most preferable configuration. This was also proved by energy calculation in Section 3.2.

Figure 2. C-downward configurations of CO molecules at different sites on Rh(100), Rh(110), and Rh(111) surfaces.

3.2. Dissociation energy calculation

Based on MD result, possible preferable sites were specified and further explored to determine the surface energy using density functional theory (DFT). CO adsorption energy was calculated by equation (1),

\[ E_{\text{adsorption}} = E_{\text{CO}} - E_{\text{bare}} \] (1)

where \( E_{\text{CO}} \) is relaxation free energy for CO-adsorbed rhodium surface and \( E_{\text{bare}} \) is relaxation free energy for bare rhodium surface. As shown in equation (2), the final state energy of CO dissociation was estimated by setting individual C and O atoms at different sites on Rh(100), Rh(110), and Rh(111) surfaces according to the lowest energy configuration of single atom,

\[ E_{\text{final}} = E_{C} + E_{O} \] (2)

where \( E_{C} \) and \( E_{O} \) are relaxation free energies of C and O atoms on rhodium surface, respectively. Finally, CO dissociation energy was calculated by subtracting the adsorption energy from the final state energy.

\[ E_{\text{dissociation}} = E_{\text{final}} - E_{\text{CO}} \] (3)

Figure 3 summarizes the surface free energy of CO molecule at different sites on Rh(100), Rh(110), and Rh(111) surfaces. It was found the C-downward configuration at hollow site on Rh(100) had the lowest free energy of -761.29 eV. Furthermore, CO molecules were put along <100> and <110> directions, but changed to C-downward configurations after relaxation. This agrees with previous conclusion that C-downward is the dominant configuration. On Rh(110) and Rh(111) surfaces, the lowest energies are bridge site of -262.88 eV and hollow site of -322.13 eV, respectively.

As indicated in table 1, CO dissociation energies at Rh(100) hollow site, Rh(110) bridge site, and Rh(111) hollow site are 1.64 eV, 0.05 eV, and 0.91 eV, respectively, which are much lower than that in vacuum (13.19 eV), indicating rhodium acts as a decent catalyst in lowering the adsorption and dissociation energies for carbon monoxide.
Table 1. CO adsorption and dissociation energies on Rh(100) hollow site, Rh(110) bridge site and Rh(111) hollow site with C-downward configuration.

| Surface       | $E_{\text{adsorption}}$ (eV) | $E_{\text{dissociation}}$ (eV) |
|---------------|-------------------------------|---------------------------------|
| Rh(100) hollow site | -16.20                        | 1.64                            |
| Rh(110) bridge site    | -16.34                        | 0.05                            |
| Rh(111) hollow site    | -16.30                        | 0.91                            |
| CO in Vacuum          | N/A                           | 13.19                           |

3.3. Nudged elastic band (NEB) calculation

Although dissociation energy can be simply calculated by subtracting adsorption energy from final state energy, a reaction often needs to overcome energy barrier, the amplitude of which determines the possibility for a reaction to happen. In order to minimize the energy barrier, nudged elastic band (NEB) method was applied to simulation. More specifically, sites with the lowest CO adsorption energy were assumed to be initial state and sites at which the adsorption energy of carbon and oxygen atoms were separated to the furthest distance were assumed to be final state. Five intermediate states were linearly interpolated between initial and final states.
Figure 4. Minimum energy path calculated by NEB for CO molecule on Rh(100), Rh(110), Rh(111) surfaces and in vacuum with structural changes.

After relaxation of all intermediate states, the minimum energy of each state with the corresponding structure was plotted in Figure 4. It is apparent from this figure that both energy barrier and dissociation energy are lowered by more than 10 eV comparing to CO in the vacuum, and among three low indexed surfaces, Rh(110) surface provides the highest activity by lowering the energy barrier and dissociation energy by ~13eV. These results confirm the capability of rhodium as a catalyst. Additionally, two common transitional states are identified for carbon monoxide on rhodium surface, which agree with literature[7]. The two-peak configuration should attribute to the bonding mechanism of carbon monoxide. The triplets formed between carbon and oxygen atoms are not identical: two of them are common covalent bonds with one electron from each atom and the third one is co-ordinate bond with all electrons from oxygen atom.

4. Conclusion
The main goal of the current study was to determine the active rhodium surface for adsorption and dissociation of carbon monoxide. Three simulation methods were used: molecular dynamics (MD) was implemented to visualize interactions between CO molecules and rhodium surfaces; Density Functional Theory (DFT) was applied to calculate surface adsorption energies for CO molecules at different sites on Rh(100), Rh(110), and Rh(111) surfaces; The reaction pathway and energy barrier for CO dissociation were obtained by Nudged Elastic Band (NEB) method. Based on these three methods, it was found the preferable adsorption sites of CO molecules on Rh(100), Rh(110) and Rh(111) surfaces are hollow, bridge and hollow, respectively, with C-downward configuration. In addition, Rh(100), Rh(110) and Rh(111) surfaces reduce the dissociation energy by ~10 eV and Rh(110) surface exhibits the lowest energy barrier and dissociation energy for CO molecules. Meanwhile rhodium can be recycled and reused with negligible degradation. Overall, rhodium is a cost-effective choice for CO-related catalytic reactions.
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