The Density Functional Theory Study on the Adsorption and Dissociation of NO on Pd (111) Surface

M Y Wang1,2, Q Wu*1,2,3

1Department of Physics, School of Science, Tibet University, Lhasa, 850000
2Institute of Oxygen Supply, Tibet University, Lhasa, 850000
3Center of Tibetan Studies (Everest Research Institute), Tibet University, Lhasa, 850000

*wuqi@utibet.edu.cn
*Corresponding author’s e-mail: wuqi_zangda@163.com

Abstract. Based on the calculation of density functional theory, the adsorption and dissociation of NO on Pd (111) surface were systematically studied. The results show that the most stable adsorption mode of NO was at fcc site with N-terminal downward, followed by hcp site and top site; Bader charge and charge density difference analysis show that there was obvious charge transfer between NO and Pd(111) surface; the analysis of density of states further indicates that there was obvious chemical interaction between them; the dissociation barrier of NO on Pd(111) surface is 2.45eV, which indicates that NO is easy to poison Pd metal surface. Finally, the two dissociation pathways of NO adsorbed on fcc site indicate that NO is very difficult to dissociate on Pd (111) surface.

1. Preface

As one of the main components of automobile exhaust, nitrogen oxides (NOx) pose danger to the ecology, life and human fitness [1]. At present, NO is found able to be decomposed into N2 and O2 on solid catalysts (Rh, Pt and Pd etc.), which is considered a promising method to eliminate the pollutants from automobile exhaust [2,3]. Among these solid catalysts, Pd has brought about wide concern for the experiments and theory research on NO’s adsorption and dissociation on its surface, due to its low cost, high content, good thermal stability and other merits. Various methods are tried to make research on NO’s adsorption and dissociation on Pd surface, such as X-ray photoelectron spectroscopy, infrared reflection absorption spectroscopy and temperature programmed desorption. Understanding NO’s way to be adsorbed and decomposed into N and O on Pd surface is the key to three-way catalyst’s elimination of NO, but now there is no confirming conclusion about NO’s adsorption mechanism and dissociation path on Pd surface.

Based on density functional theory, the direct adsorption and dissociation of NO on Pd(111) surface is on research, the quantum chemistry calculation of NO’s adsorption and decomposition on pd(111) surface is performed, and such significant issues as NO’s optimal adsorption site on Pd surface and the transition state of direct decomposition are solved in this paper.
2. Surface model and calculation methods

2.1. Surface model
To build Pd (111) surface, (2×2) periodic four-layer plate model is applied. During calculation, positions of the Pd atoms on the upper two layers are allowed to change freely, while that on the bottom two layers are fixed completely. Selection of this type of model is suitable for the actual circumstances and saves the calculation time as well. In order to avoid the interaction of periodic plates [4], the thickness of vacuum layer is set 15Å. As shown in Figure 1, 8 possible absorption sites are considered during calculation, among which N-top, N-bridge, N-fcc (face-centered cubic structure) and N-hcp (hexagonal close-packed structure) are the four adsorption configurations that NO is absorbed on Pd(111) surface with the N atom downwards, and O-top, O-bridge, O-fcc, O-hcp are the four configurations that NO is absorbed on Pd(111) surface with the O atom downwards. The initial bond length of adsorbed atoms to the surface is set 1.938Å. As a way to make research on NO’s dissociation on Pd (111) surface and find out the minimal energy path (MEP) and the reaction barrier energy, the CI-NEB method is used to determine the transition state [5].

![Figure 1. The structure of Pd (111) surface. (a) Top view. (b) Side view. The top site, bridge site, fcc site, hcp site are represented by T, B, F, H. The bulle shows Pd atoms.](image)

2.2. Calculation method
The VASP program package based on density functional theory is applied in all the calculations in the paper [6]. Exchange-correlation functional Perdew-Burke-Ernzerhof (PBE) under generalized gradient approximation (GGA) is selected to describe the system’s exchange-correlation energy (GGA-PBE) [7]. In which the plane wave truncation energy is valued 400eV, the k points of the optimized surface brillouin zone on adsorption structure surface are all 3×3×1. The convergence value of energy is valued 1.0×10⁻⁶ eV/atom, the convergence value of force is valued 0.01 eV/Å. NO’s adsorption energy on Pd (111) surface is calculated as follows:

$$E_{\text{ads}} = E_{\text{NO+Pd(111)}} - E_{\text{NO}} - E_{\text{Pd(111)}}$$

In which $E_{\text{NO+Pd(111)}}$ represents the system’s total energy when NO is adsorbed on Pd(111) surface, $E_{\text{NO}}$ represents the NO molecule’s total energy, $E_{\text{Pd(111)}}$ represents the total energy of the pure Pd(111) surface. The calculation formulas of adsorption energy above show that, the more negative $E_{\text{ads}}$ is, the more reaction exotherm is released. Meanwhile, the greater the absolute value of $E_{\text{ads}}$, the more stable the adsorption.

3. Results and discussion

3.1. adsorption

3.1.1. NO’s adsorption on Pd (111) surface. Before the construction of adsorption model, the structures of the NO molecule and the Pd metal block are needed to be optimized geometrically. The calculation results show the bond length ($d_{\text{N-O}}$) of the optimized NO is 1.163Å, which accords closely with the experiment value 1.154Å. The lattice constant of the optimized Pd structure is transformed to 3.908Å, which approximates to the experiment value of 3.803Å, proving the reliability of the chosen calculation method [4].
On Pd (111) surface, when the adsorption is from the N atom end, the four adsorption sites, top site, bridge site, fcc site, hcp site, are optimized, among which the fcc site is the most stable one. When NO is absorbed at the top site, the N atom interacts with the surface Pd atom to form Pd-N bond, with -1.26eV adsorption energy, as shown in Table 1. When NO is absorbed at the bridge site of Pd (111) surface, the N atom interacts with the closest two Pd atoms to form two Pd-N bonds. But the bridge site’s initial structure will be optimized to a fcc site’s one, which represents the instability of the adsorption structure at bridge site. At the fcc site, the N atom interacts with the nearest three Pd atoms to form three Pd-N bonds, with -2.43eV adsorption energy. At the hcp site, the N atom interacts with the nearest three Pd atoms to form three Pd-N bonds, with -2.38eV adsorption energy. Which indicates that when absorbed on Pd (111) surface from the N end, NO tends to be absorbed at the fcc site of the surface.

When the absorption is from the O atom end, the adsorption energy is 0.01eV and positive at the top site, which indicates that the absorption is unstable at the top site, i.e., the absorption is impossible at the top site. At the bridge site, the O atom interacts with the nearest two Pd atoms to form two Pd-O bonds, with -0.19eV adsorption energy. At the fcc site, the O atom interacts with the nearest three Pd atoms to form three Pd-O bonds, with -0.12eV adsorption energy. At the hcp site, the O atom interacts with the nearest three Pd atoms to form three Pd-O bonds, with -0.15eV adsorption energy. The adsorption energy order is bridge˃hcp˃fcc˃top, and the responding N-O bond length order is N-O_{bridge}˃N-O_{hcp}˃N-O_{fcc}˃N-O_{top}.

The calculation results indicate that, NO’s adsorption energy when absorbed from the O atom is clearly smaller than that when absorbed from the N atom, proving that NO tends to be absorbed on Pd (111) surface from the N end and the absorption at the fcc site is the most stable.

Table 1. NO’s adsorption energy when absorbed on Pd (111) surface, distance ($d_{N-Pd}$) from the adsorbate to the nearest Pd atom to Pd(111) surface, distance($d_{N-O}$) from the N atom to the O atom.

| adsorbate | site | $d_{N-Pd}$ (Å) | $d_{N-O}$ (Å) | $E_{ads}$ (eV) |
|-----------|------|----------------|---------------|---------------|
| Pd (111)  | N    | 1.848          | 1.161         | -1.26         |
|           | B    | —              | —             | —             |
|           | F    | 2.030          | 1.213         | -2.43         |
|           | F    | 2.030          | 1.211         | -2.38         |
|           | T    | 2.132          | 1.154         | 0.01          |
| O         | B    | 2.490          | 1.159         | -0.19         |
|           | F    | 2.578          | 1.157         | -0.12         |
|           | H    | 2.590          | 1.156         | -0.15         |

3.1.2. Differential analysis of Bader charge and charge density. In order to learn more about the electronic transfer when NO is absorbed on Pd (111) surface, the differential calculation of bader charge and charge density is carried out, and the charge difference density diagram is shown in Figure 2. The calculation formula of charge difference is:

$$\rho = \rho(NO/Pd) - \rho(NO) - \rho(Pd)$$

Where, $\rho$ is the differential charge when NO is absorbed on Pd (111) surface, $\rho(NO/Pd)$ is the total charge density when NO is absorbed on Pd (111) surface, $\rho(NO)$ is the total charge density of NO, and $\rho(Pd)$ is the total charge density of Pd (111) surface.

Figure 2. The charge differential density diagram of N atom adsorbed at fcc site. (a) Top view. (b) Side view. The number in the figure represents the number of gain and loss charges. A positive sign indicates that it is obtained and a negative sign indicates that it is lost.
What Figure 2 shows is NO’s charge difference diagram when absorbed on Pd (111) surface from the N end, directly reflecting the electron’s redistribution state caused by the NO molecule’s interaction with Pd (111) surface. There is visible charge transfer between the NO molecule and metal surface. NO’s being absorbed to the surface will lead to obvious interaction between the N atom and the neighboring four atoms, which makes the O atom get electrons and become negative while the N and Pd atoms lose electrons and become positive. Considering bader charge analysis, it is found that the Pd atom loses 0.12 electrons in total, the N atom loses 0.37 electrons in total and the O atom gets 0.67 electrons in total. From the plane average difference density diagram, great change in charge density of where the N atom contacts the Pd (111) surface can be seen, indicating that there has been great interaction between the NO molecule and the Pd basement. The plane average difference density diagram is shown in Figure 3.

![Figure 3. The plane-Average Charge-Density of NO adsorption on Pd (111) surface](image)

3.1.3. State density analysis. To learn more about the electronic structure of NO absorbed on Pd (111) surface, NO’s electronic state density before and after its being absorbed at fcc site from the N end is calculated, as shown in Figure 4, the partial density of state (PDOS) of the Pd, N and O atoms are invisibly different before and after the absorption. There are distinct locality in the PDOS of the Pd, N and O atoms before absorption, the PDOS becomes dispersed after absorption, and the locality declines relatively, in particular that of the Pd atom. The PDOS of the N and O atoms move towards the low-energy direction after absorption, the PDOS of the Pd atom expands to the low-energy direction after absorption, becoming dispersed. These results indicate that there is strong interaction between the NO molecule and Pd (111) surface, which is corresponding to the analysis result of bader charge and charge density difference. The s and p paths’ PDOS of the N and O atoms have changed clearly after absorption, showing that the p path of the N and O atoms from NO has made contribution to the interaction with the d path of the surface Pd atom.
3.2. NO’s dissociation on Pd (111).

NO’s dissociation is a significant basic reaction step in the purification and catalysis of automobile exhaust, which is a key step to reduce NO to N₂. After figuring out NO’s most stable absorption structure on Pd surface, the CI-NEB method is applied to calculate the reactant of NO when it is directly decomposed (NO → N + O) based on the absorption at fcc site of Pd surface, and the structures of the decomposed products are optimized.

Two dissociation paths are considered, due to the similar stability of NO at the fcc and hcp sites, the first dissociation path turns out to be the N and O atoms’ being absorbed at the fcc and hcp sites respectively after the dissociation, and the reaction barrier of the process is 3.23eV. The second dissociation track is the N and O atoms’ combination at the fcc ortho position of Pd (111) in the final state (FS). The reaction barrier of the process is 2.32eV, which is corresponding to other theoretical calculation results [8]. The two dissociation paths are shown in Figure 5. In the transition state TS1, the N-O bond length expands from 1.213Å of the initial structure to 2.082Å, the N and O atoms move respectively to the nearest fcc and top sites, which respectively have distance of 1.901Å and 1.907Å from the nearest Pd atom. In the transition state TS2, the N-O bond length expands from 1.213Å of the initial structure to 1.781Å, the N and O atoms move respectively to the nearest fcc and bridge sites, which respectively have distance of 1.974Å and 2.137Å from the nearest Pd atom. It can be clearly found that, the barrier values of the two dissociation paths are too high, which indicates that NO is
difficult to dissociate on the Pd metal packed-structure surface at a normal temperature. Hence such reducing gases as \( \text{H}_2 \) and CO can be tried to dope or pump on the palladium metal surface, so as to accelerate NO’s dissociation on Pd metal surface and reduce the NO molecule’s intoxication on Pd surface.

Figure 5. The dissociation path of NO on Pd (111) surface. (a) initial state fcc, final state fcc + hcp. (b) initial state fcc, final state fcc + fcc.

4. Conclusion
Based on density functional theory, NO’s possible absorption configuration on Pd (111) surface and possible dissociation path are discussed in this paper, and the calculation results indicate that NO tends to be absorbed at the fcc site of Pd (111) surface from the N end. The analysis of charge density difference and bader charge shows there is obvious chemical interaction between NO and Pd (111) surface, and that there is visible charge transfer which is proved by state density analysis. Transition state calculation shows that NO’s barrier is high when it is directly dissociated on Pd (111), hence transitional metals (Au, Ag, Fe, Pt, Cu, Ni, Ti) are needed to be doped on Pd surface or let such reducing gases as \( \text{H}_2 \) and NO to participate in the reaction to accelerate NO’s dissociation.

Acknowledgments
The work was supported by the Natural Science Foundation of Tibet Autonomous Region (Grant NO. 2016ZR-TU-10), the Scientific Research Foundation for Returned Scholars of Tibet University (Study on the catalytic properties of transition metal oxide clusters) and the Doctoral Development Project of Zhu Feng Scholar of Tibet University.

References
[1] Huai, L.Y., He, C.Z., Wang, H., et al. (2015) NO dissociation and reduction by H2 on Pd (111): A first-principles study. Journal of Catalysis, 322:73-83.
[2] Nakamura, I., Hamada, H., Fujitani, T. (2003) Adsorption and decomposition of NO on K-deposited Pd (1 1 1). Surface Science, 544:45-50.
[3] Brown, W.A., King, D.A. (2000) NO chemisorption and reactions on metal surfaces: A new
perspective. Journal of Physical Chemistry B, 104:2578-2595.

[4] Jiang, Z., Li, L., Xu, J. et al. (2013) Density functional periodic study of the dehydrogenation of methane on Pd (1 1 1) surface. Applied Surface Science, 286:115-120.

[5] Tariq, U., Ming-Qiu, T. (2018) H2S adsorption and dissociation on Rh (110) surface: a first-principles study. Adsorption, 24:563-574.

[6] Chen, P., Zhang, B., Gu, X., et al. (2019) Ethylene adsorption on Ag (111), Rh (111) and Ir (111) by (meta)-GGA based density functional theory calculations. Chinese Journal of Chemical Physics, 32: 437-443.

[7] Nanba, Y., Koyama, M. (2019) NO Adsorption on 4d and 5d Transition-Metal (Rh, Pd, Ag, Ir, and Pt) Nanoparticles: Density Functional Theory Study and Supervised Learning. Journal of Physical Chemistry C, 123: 28114-28122.

[8] Zhang, L., Filot, I.A.W., Su, Y.Q., et al. (2018) Transition metal doping of Pd (111) for the NO+CO reaction. Journal of Catalysis, 363:154-163.