Electronic Origin of Catalytic Nitric Oxide Reduction upon Small Rhodium and Copper Clusters

Ryoichi FUKUDA*a,b

*aCenter for the Promotion of Interdisciplinary Education and Research, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Nishikyo-ku, Kyoto 615-8245, Japan
bDepartment of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
*fukuda@esicb.kyoto-u.ac.jp

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Both rhodium and copper show a catalytic activity for nitric oxide (NO) reduction; however, the reaction mechanisms can be different. Herein, we elucidate the difference in the NO reduction mechanisms between Rh and Cu clusters regarding the electronic structures using DFT computations and small cluster models involving four metal atoms. The computational results show that the dissociative adsorption proceeds on the Rh cluster with the reaction barrier of 33 kcal mol\(^{-1}\). The calculated heat of the reaction is almost zero. On the Cu cluster, the calculated reaction barrier reaches to 78 kcal mol\(^{-1}\) indicating that the dissociative adsorption hardly occurs. Instead of the dissociative adsorption, dimerization of NO initiates the catalytic NO reduction on Cu cluster. The calculated energy barrier for the dimerization is 8 kcal mol\(^{-1}\). The adsorbed NO dimer has a similar stability to co-adsorbed two NO molecules. In contrast, the dimerization hardly occurs on the Rh cluster; the reaction pathway is remarkably endothermic, and a stable adsorbed product is not found. The adsorption structures of NO can explain such differences. On Cu cluster, NO takes bent-nitrosyl conformation that acts as an electron acceptor. On Rh cluster, NO acts as an electron donor having linear-nitrosyl conformation.

Keywords: Nitric oxide reduction, Catalytic reaction mechanism, Chemical bond, Transition metal cluster

1 Introduction

A catalytic converter is equipped in the current automobiles for controlling pollutants in the exhaust gas. In gasoline-engine systems, three-way catalyst (TWC) is adopted. The TWC converts nitrogen oxides, carbon monoxide, and hydrocarbon species into nitrogen molecule, carbon dioxide, and water by a series of redox reactions [1]. A frequently used model reaction over the TWC may be written as

\[
2\text{NO} + 2\text{CO} + \text{C}_3\text{H}_6 + (9/2)\text{O}_2 \rightarrow \text{N}_2 + 5\text{CO}_2 + 3\text{H}_2\text{O}. \tag{1}
\]

The catalytic active sites of TWC consist of rhodium, palladium, and platinum. Those platinum group elements are rare and expensive; therefore, replacing them by ubiquitous elements is an urgent issue. The development process of new catalytic systems requires the elucidation of the detailed mechanisms of TWC reactions and its electronic origin for the catalytic activities.

The reduction of nitric oxide (NO) is an important process for discussing the catalytic performance of TWC, and rhodium catalyzes the reduction of NO [1]. Copper-based catalysts also exhibit activity for NO reduction [2–7]. Therefore, copper could be a candidate for an alternative material of Rh in TWCs, and its catalytic mechanism attracts much attention [7–10]. It is known that dissociative adsorption of NO molecule on Rh initiates the NO reduction process [11]. On the other hand, the dissociative adsorption of NO on Cu usually exhibits quite a large energy barrier [8,9]; thus, there should be another reaction mechanism different from the dissociative adsorption [12,13].

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Our previous studies showed that the dimerization of NO is the initial step of NO reduction over Cu catalysts [9,10]. The N-O bond cleavage follows the dimerization [9]. The dimerization of NO also has been found in enzymatic NO reduction of biological systems, in which NO dimer exists as a hyponitrite form (N$_2$O$_2$$_{2−}$) due to the interaction with the environment of enzyme [14–18]. In supported metal catalysts, NO dimer would not have such a multipoint interaction and be weakly adsorbed to the surface as a neutral or monoanion species [9]. It is known that the electronic structure of an isolated cis-ONNO involves a complicated multireference character [10,19,20]. Thus, the electronic structure of the surface NO dimer and the electronic origin of the dimerization process remain unclear.

In this paper, we discuss the electronic origin of the NO reduction catalyzed by small metal clusters using a quantum chemical method based on the density functional theory (DFT). We investigated the dissociative adsorption and dimerization of NO on Rh and Cu clusters. We employed Rh$_4$ and Cu$_4$ clusters as a minimal model. Although the particle-size dependence of the catalytic activity has been reported particularly for Cu [4], we believe the present model involves essential electronic origin of the reactions, and this kind of simplest model may help to understand the essence.

2 Computational details

We used the DFT with B3LYP functional [21–23]. For Cu and Rh atoms, the Stuttgart/Dresden (SDD) effective core potentials with basis sets were employed [24,25]. For N and O atoms, the Ahlrichs’ TZVP basis sets were used [26,27]. Broken-symmetry calculations were performed for all singlet states. The partial geometry optimization was performed at fixed N-O or N-N distances with relaxing all other coordinates. Vibrational frequency calculations were performed to confirm the nature of the stationary point (local minimum or transition state). The zero-point energy correction was not considered in the results because it does not affect the discussions for the qualitative reaction mechanisms. The atomic charges, the Wiberg bond indices, and chemical bond characters were evaluated by the NBO (natural bond orbital) method [28] implemented in the Gaussian 09 program. All computations were performed using the Gaussian 09 program [29].

3 Results and discussions

Figure 1 shows the potential energy curves for N-O dissociative adsorption on Rh$_4$ (open circles) and Cu$_4$ (filled circles) clusters with representative molecular structures (blue; nitrogen, red: oxygen).

![Figure 1](image_url)

Figure 1. The potential energy curves for N-O dissociative adsorption on Rh$_4$ (open circles) and Cu$_4$ (filled circles) clusters with representative molecular structures (blue; nitrogen, red: oxygen).
N-O bond length is 1.258 Å; this value is 0.089 Å longer than that of the isolated molecule (1.147 Å by computation). According to the NBO charge, the NO moiety receives −0.443 e charges, and the Wiberg bond index of N-O is 1.44 (that of the isolated NO molecule is 2.11). The electron transfer from the Rh cluster activates the adsorbed NO molecule to weaken N-O bond.

The transition state for the NO bond dissociation was found at N-O = 1.925 Å with the barrier height of 33.3 kcal mol⁻¹. At the transition state, both nitrogen and oxygen atoms take the bridging position between two Rh atoms with sharing one Rh atom by nitrogen and oxygen. Here, the NO moiety takes a charge of −0.872 e, and the Wiberg bond index of N-O becomes 0.55. At the transition state, approximately one electron transfers from the Rh cluster to NO, and it cleaves N-O bond. Additionally, N-Rh and O-Rh bonds become strong during the N-O bond cleavage.

The Rh cluster strongly binds both atomic nitrogen and oxygen as a product of the bond cleavage. The product of the dissociative adsorption corresponds to the geometry at N-O = 2.983 Å. The NO moiety has a charge of −1.000 e (−0.390 e on N and −0.610 e on O). The heat of reaction is calculated to be −0.2 kcal mol⁻¹. In this model, the heat of reaction was almost zero, thus, the dissociation was not thermodynamically unfavorable. The dissociative adsorption of NO on Rh cluster can proceed thermally.

On Cu₄, NO molecule is adsorbed in a side-on structure as the initial state of N-O bond dissociation with relatively small adsorption energy. Both nitrogen and oxygen bind to Cu. The bond lengths were 1.928 and 2.015 Å for N-Cu and O-Cu, respectively. The adsorption energy is calculated to be 11.0 kcal mol⁻¹: about one third of that on Rh₄. The calculated Wiberg bond indices are 0.48 and 0.23 for N-Cu and O-Cu, respectively. We found a relatively weak bonding between the Cu cluster and NO. At this adsorbed state, NO moiety receives −0.518 e charge from the Cu cluster. The N-O bond length is elongated to be 1.242 Å. The adsorption on the Cu cluster also activates the N-O bond.

The N-O bond cleavage process exhibits significantly large endothermic feature. The energy rises with increasing the N-O distance. The energy maximum was found around N-O = 2.3–2.4 Å. The calculated dissociation barrier is 78.5 kcal mol⁻¹. Because of such a high energy barrier, we concluded that the dissociative adsorption of NO is unlikely at least on small Cu clusters. At the transition state, nitrogen locates at the bridging position of two Cu atoms. At this state, approximately one electron (−0.988 e) transfers from the Cu cluster to NO moiety. We could not find a stable local structure along this reaction coordinate by the elongation of N-O bond with keeping the cluster shape. This rhombus-shape cluster could not stably bind atomic nitrogen and oxygen simultaneously.

A stable structure for the dissociated product has forms of Cu₃N and Cu₂O with Cu atom inserted between N and O having the energy of 1.6 kcal mol⁻¹ relative to the isolated system, see Figure 1. The geometrical and electronic structures relate to the copper nitride and cuprite. A similar structure was found in the previous study for the NO dissociation on a Cu₁₃₅ cluster [8]. This stable structure cannot smoothly connect with the transi-

| Structure | Reactant | TS       | Product |
|-----------|----------|----------|---------|
| N-O       | 1.258    | 1.925    | 3.000   |
| N-Rh      | 1.969    | 1.768    | 1.794   |
| N-Rh      | 1.970    | 1.893    | 1.812   |
| O-Rh      | 2.243    | 2.002    | 1.835   |
| O-Rh      | 2.704    | 2.096    | 1.941   |

| Structure | Reactant | TS       | Product |
|-----------|----------|----------|---------|
| N-O       | 1.242    | 2.300    | 3.549   |
| N-Cu      | 1.928    | 1.908    | 1.786   |
| N-Cu      | 2.483    | 1.920    |         |
| O-Cu      | 2.015    | 1.769    | 1.769   |

| Structure | Reactant | TS       | Product |
|-----------|----------|----------|---------|
| N-O       | 1.49     | 0.35     | 0.08    |
| N-Cu      | 0.48     | 0.54     | 0.63    |
| N-Cu      | 0.13     | 0.58     |         |
| O-Cu      | 0.23     | 0.68     | 0.63    |

NBO gross charge on NO moiety (in e).

| q(NO) (in e) | -0.443 | -0.872 | -1.00 |
|-------------|--------|--------|-------|
| q(NO) (in e) | -0.518 | -0.988 | -2.565 |

Table 1. The structural parameters (Å) and bond indices for Rh₄NO and Cu₄NO in reactant, product, and transition state (TS) structures.

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tion state because this structure locates far from the transition state. The stable dissociated product is yielded after significant relaxation in the cluster geometry and rearrangement in electronic structure, although such stabilization processes must depend on the cluster-size and shape.

Figure 2 shows the potential energy curves for NO dimerization on the clusters. The energies relative to the isolated systems are plotted against the N-N distance for the lowest spin state (the septet for Rh₄(NO)₂ and the singlet for Cu₄(NO)₂). The molecular structures of the adsorbed state, dissociated state, and transition state (or intermediate state) are given in Figure 2. Table 2 summarizes the structural parameters, bond indices, and atomic charges for those states. A dinitrosyl structure, where two NO molecules are adsorbed on one metal atom, was found to be relatively unstable; therefore, we did not consider dinitrosyl states.

The adsorption energy of two NO molecules on the Cu₄ cluster was calculated to be 31.3 kcal mol⁻¹ for the end-on configuration in the N-end down form. For this structure, the charge of −0.341 e moves to (NO)₂ moiety. The adsorption state may be classified as a so-called bent nitrosyl [30,31]. The N-O distances are 1.170 and 1.174 Å; they are significantly longer than the isolated NO. The N-Cu distances are 1.844 and 1.906 Å, and the Cu-N-O angles are 135.4 and 143.7 degrees. These structural parameters fall within the range of known bent nitrosyl complexes [31].

We found the transition state for the NO dimerization with forming an N-N bond at N-N = 2.1 Å. The energy barrier for NO dimerization was calculated to be 8.4 kcal mol⁻¹. At this structure, N-Cu bonds become weak. The N-Cu distances become 1.926 and 1.984 Å, and the Wiberg bond indices for N-Cu decrease to 0.42 and 0.39. Here, ONNO moiety receives −0.419 e charge that drives the N-N bond formation.

The stable structure of the product, adsorbed ONNO, was

| Structure | Reactant | TS/Int | Product |
|-----------|----------|--------|---------|
| N-N       | 3.655    | 2.000  | 1.400   |
| N-Rh      | 1.787    | 1.938  | 2.121   |
| N-Rh      | 1.787    | 1.938  | 1.918   |
| N-O       | 1.158    | 1.179  | 1.223   |
| N-O       | 1.158    | 1.179  | 1.226   |
| Rh-N-O    | 163.6    | 123.0  | 122.7   |
| Rh-N-O    | 163.6    | 123.0  | 139.9   |

| Bond indices | N-N | N-Rh | N-Rh | N-O | N-O | q(ONNO)² |
|--------------|-----|------|------|-----|-----|---------|
| N-N          | 0.06| 1.24 | 1.24 | 1.84| 1.84| 0.011   |
| N-Rh         | 0.296| 0.80 | 0.80 | 1.77| 1.77| −0.270  |
| N-Rh         | 1.07 | 0.37 | 0.69 | 1.55| 1.49| −0.397  |
| N-O          | 1.84 | 1.216| 1.216| 1.213 | 133.6|
| N-O          | 1.170| 1.174| 1.174| 1.213 | 137.4|

²NBO gross charge on (NO)₂ moiety (in e).
found at N-N = 1.459 Å. This N-N bond length is much shorter than that of isolated ONNO (2.2–2.3 Å by experiment and computation [19,20]). The electronic structure of adsorbed ONNO significantly differs from that of the isolated ones mainly due to the electron transfer from the metal cluster. The ONNO moiety has the gross charge of −0.534 e; thus ONNO may be classified as an anion dimer, not as hyponitrite. The relative energy of the product was calculated to be −31.8 kcal mol⁻¹, indicating the similar thermodynamic stability for the reactant and product. The dimerization reaction can proceed thermally.

The situation of the co-adsorption of two NO molecules on the Rh₄ cluster differs from that on the Cu₄ cluster significantly. The adsorption energy of two NO molecules on the Rh₄ cluster was calculated to be 72.5 kcal mol⁻¹ for the end-on configuration in the N-end down form. At this structure, NO is almost neutral; the charge on (NO)₂ was calculated to be +0.011 e. Two adsorbed NO were symmetric. The adsorption state may be classified as a linear nitrosyl [30]. The N-Rh and N-O distances are 1.787 and 1.158 Å, respectively. The Rh-N-O angle is 163.6 degrees. This relatively short N-O distance and open Rh-N-O angle agree with those of known linear nitrosyl complexes [31]. The Wiberg bond index for the N-Rh bond was calculated to be 1.24; NO molecules strongly bind to Rh with multiple interactions of donation/back-donation mechanisms [30].

The energy rises significantly with decreasing the N-N distance. The extent of the destabilization is remarkable. The adsorption structure and electronic structure drastically change with decreasing the N-N distance. At the geometry of N-N = 2.0 Å, N-Rh distance becomes 1.938 Å; the bond is about 0.15 Å longer than the initial co-adsorption state. Additionally, the Wiberg bond index decreases to 0.80. The N-Rh bonds become weak significantly. The N-O distances elongate to 1.179 Å, and Rh-N-O angles decrease to 123.0 degrees. The adsorbed state of NO molecules varies to a bent nitrosyl with receiving electron of −0.270 e from the Rh₄ cluster.

A stable local structure of adsorbed ONNO could not be found with the present model and computational condition, although a flat region of potential energy curve was found around N-N = 1.4 Å. A broken-symmetry structure was obtained for N-N = 1.4 Å, where two NO groups are not equivalent. Here, the ONNO moiety has the gross charge of −0.397 e. The N-O distances increase to 1.223 and 1.226 Å. The adsorbed structure of ONNO moiety is similar to that on the Cu₄ cluster. Even if we find a stable local structure around here, the NO dimerization reaction on Rh cluster results in endothermic about 34 kcal mol⁻¹. Consequently, the NO dimerization on Rh cannot proceed thermally.

Figure 3 exhibits the isosurface plots of NBOs for bonding between metal and NO in Cu₄(NO)₂ (a, b) and Rh₄(NO)₂ (d, e, f) at the reactant structure and for N-N bond in Cu₄(NO)₂ (c) at the transition state structure.

Figure 3. The isosurface plots (isovalue = 0.04) of several NBOs for bonding between metal and NO in Cu₄(NO)₂ (a, b) and Rh₄(NO)₂ (d, e, f) at the reactant structure and for N-N bond in Cu₄(NO)₂ (c) at the transition state structure.
For Rh$_4$(NO)$_2$, one σ-bonding (Figure 3 (d)) and two π-backbonding (Figure 3 (e) and (f)) interactions were found in NBOs. The HOMO of Rh$_4$ clusters is composed of Rh (4d) characters, and the orbital energy levels of Rh (4d) are close to that of Cu (3s). Thus, Rh (4d) and NO (π*) form strong π-backbondings, similar to those in metal-CO complexes. Here, NO moiety acts as an electron donor and may be considered as NO$^-$: an isoelectric system of CO. The strong π-backbonding interaction favors the linear Rh-N-O conformation. Such strong Rh-NO bonds inhibit the N-N bond formation during the dimerization. The N-N bond formation requires an in-phase interaction between two NO (π*) orbitals similar to Figure 3 (c). In Rh$_4$(NO)$_4$ system, the π-backbondings of Rh-NO use the NO (π*) orbitals as shown in Figure 3 (e) and (f); thus, the NO (π*) component has to be extracted from the orbital of Figure 3 (f) to make the N-N binding orbital. However, such interaction is unfavorable; consequently, the dimerization reaction pathway becomes remarkably endothermic, and the dimerization hardly occurs on the Rh cluster.

4 Conclusions

The present DFT calculations with a small cluster model clearly shows that the reduction of NO molecule on Rh cluster proceeds by the dissociative adsorption, and the NO dimerization process is unfavorable by thermodynamic and kinetic point of views. On the other hand, the dissociative adsorption of NO on Cu is kinetically unfavorable. Also, the dissociative adsorption was calculated to be thermodynamically unfavorable at least on the small cluster used in the present study. The reduction of NO on Cu cluster proceeds from the dimerization of co-adsorbed NO molecules. The Rh cluster strongly binds both NO molecule and atomic nitrogen and oxygen. The stabilization of reactant and product states may reduce the dissociation barrier. The binding of NO on Cu cluster is less strong. A copper nitride-like and cuprite-like structure and electronic states are necessary for stabilizing the dissociated products on Cu cluster. Thus, significant geometrical and electronic structural relaxations are required for the dissociative adsorption, and therefore it would be unfavorable.

The co-adsorbed structures between Cu$_4$(NO)$_2$ and Rh$_4$(NO)$_2$ are significantly different. Cu$_4$(NO)$_2$ takes a bent nitrosyl conformation and electronic structure. In this structure, NO acts as an electron acceptor, and receives one electron from cluster. The excess electron occupied NO (π*) orbitals that can form an N-N binding orbital, and it promotes the dimerization of NO. On the other hand, Rh$_4$(NO)$_2$ takes a linear nitrosyl conformation and electronic structure, where NO acts as an electron donor. The strong Rh-NO interaction inhibits the N-N bond formation and destabilizes the NO dimer significantly. The present results suggest that the metal-nitrosyl bonding character controls the reaction pathways of catalytic NO reduction. We believe this control factor may be generalized to other metals and materials.

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