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View Article Online PAPER



Cite this: Phys. Chem. Chem. Phys., 2024, 26, 15332

Received 5th April 2024, Accepted 2nd May 2024

DOI: 10.1039/d4cp01398k

rsc.li/pccp

Direct reduction of NO into N₂ catalyzed by fullerene-supported rhodium clusters†

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Catalytic conversion of NO has long been a focus of atmospheric pollution control and diesel vehicle exhaust treatment. Rhodium is one of the most effective metals for catalyzing NO reduction, and understanding the nature of the active sites and underlying mechanisms can help improve the design of Rh-based catalysts towards NO reduction. In this work, we investigated the detailed catalytic mechanisms for the direct reduction of NO to N₂ by fullerene-supported rhodium clusters, C₆₀Rh₄⁺, with density functional theory calculations. We found that the presence of C_{60} facilitates the smooth reduction of NO into N2 and O2, as well as their subsequent desorption, recovering the catalyst $C_{60}Rh_4^+$. Such a process fails to be completed by free Rh_4^+ , emphasizing the critical importance of C_{60} support. We attribute the novel performance of $C_{60}Rh_4^+$ to the electron sponge effect of C_{60} , providing useful guidance for designing efficient catalysts for the direct reduction of NO.

Introduction

Nitric oxide (NO) is an air pollutant associated with severe environmental issues, posing great health risks to human beings. Its treatment has received extensive efforts, 1,2 and current methods for NO control, such as absorption, decomposition, and reduction, always encounter shortcomings such as process complexity and by-product generation.³ The three-way catalyst (TWC), which employs noble metals such as Pt, Pd, and Rh, stands out as an effective catalyst for reducing NO emissions in automobile exhaust. In particular, rhodium excels in NO chemical adsorption and dissociation, showing great activity and selectivity in NO reduction into N2.4,5

Previous studies investigated the dissociation and adsorption of NO on the surfaces of Rh(100), Rh(111), and Rh(110) surfaces and found that N atoms bind and desorb at 450-650 K, and O atoms desorb in O2 form at 1000-1400 K.6-18 It is shown that Rh-doped metal catalysts exhibit more superior catalytic performance than pure metal catalysts for converting NO, emphasizing the critical importance of rhodium. 19,20 However, rhodium is scarce and expensive, limiting its widespread utilization. 1,3,4 In this regard, recently emerged single-atom catalysts (SACs) and single-cluster catalysts (SCCs) that offer high atomic efficiency²¹⁻²³ may provide an interesting approach for employing Rh-based catalysts in NO conversion.

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† Electronic supplementary information (ESI) available: calculated isomers of Rh₄⁺, C₆₀Rh₄⁺, and C₆₀Rh⁺; additional reaction pathways; calculated NBO partial charges; cartesian coordinates. See DOI: https://doi.org/10.1039/d4cp01398k

Mass spectrometric experiments and theoretical calculations on the reactions of free rhodium clusters with NO have elucidated the important role of Rh in N-O bond activation. 24-33 For instance, Ghosh et al. found that Rh clusters containing one to five atoms exhibit stronger bonding with NO compared to Rh(100) and Rh(111), rendering Rh clusters to be good catalysts for NO reduction.²⁵ Xie et al. studied the NO adsorption and reduction on the Rh₇⁺ cluster and found that the reaction follows a three-step process: initial adsorption of NO, subsequent NO decomposition into N and O atoms, and then, the reaction of the N atom with a second adsorbed NO, leading to the formation of N₂ molecules and rhodium oxides.²⁷ Romo-Ávila et al. investigated the NO dissociation on Rh_n^{\pm} clusters (n = 3, 4, 6, and 13) and found that the dissociation of N-O is more feasible on square facets than on triangular atomic environments.28 They also found the energy barrier for breaking the N-O bond depends on the charge states of the rhodium clusters, with cationic clusters being more reactive than neutrals and anions, in agreement with an earlier experimental study.²⁴

Previously, Mackenzie and co-workers found that once two NO molecules co-adsorb on Rh_x^{\pm} clusters, NO first dissociates to generate mobile N atoms that can then combine to form N2 molecules; resultant rhodium dioxide clusters $Rh_xO_2^{\pm}$ further adsorb NO, and the process of NO reduction to N2 replicates, yielding higher rhodium oxides.24 In these cases, catalytic reactions stopped with the formation of rhodium oxides and no O2 release, that will, in the end, lead to the deactivation of the catalysts. ^{24,26,27,31,33} Then, a question arises: if a catalytic cycle cannot be completed on free rhodium clusters, how about when supported on certain substrates, considering that in practice most metal catalysts are dispersed on supports like

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metal oxides and porous carbon materials? In this regard, Chen et al. recently showed that Rh-doped anionic clusters, RhCe₂O₃₋₅, with Rh acting as the "active center" and Ce₂O₃₋₅ as the "support", can effectively prompt NO reduction into N2 by introducing CO

In this work, we report the study on the reduction of NO to N₂ catalyzed by C₆₀Rh₄⁺ clusters, with those by free Rh₄⁺ and C₆₀Rh⁺ clusters as comparison. These clusters were chosen because (i) German et al. recently investigated the structures of $C_{60}Rh_n^+$ (n = 1-6) clusters using infrared multiple photon dissociation spectroscopy and found that C₆₀Rh₄⁺ has a square Rh₄⁺ moiety, different from the pyramidal structure for free Rh₄^{+,35} while square Rh₄⁺ has been shown to be more reactive for N-O dissociation than a triangular one²⁸ and (ii) C₆₀ has been shown to have a novel geometric and electronic effect in promoting catalytic reactions.³⁶⁻³⁹ We find that it is more energetically favorable for C₆₀Rh₄⁺ than C₆₀Rh⁺ in catalyzing NO conversion, and the presence of C₆₀ promotes O₂ desorption, allowing the completion of the reaction cycle. We aim to gain insights into the nature of catalytic active sites and reaction mechanisms to guide the improvement of Rh-based catalysts for NO reduction.

Theoretical methods

All DFT calculations were carried out using the Gaussian 09 program⁴⁰ package to investigate the structures of Rh₄⁺, C₆₀Rh⁺, and C₆₀Rh₄⁺ and their reaction mechanisms with NO. Three functionals, BPW91, 41,42 PBE, 43 and B3LYP, 44,45 were tested for optimizing the structures of Rh₄⁺, C₆₀Rh⁺, and C₆₀Rh₄⁺. The 6-31G(d) basis set was used for N, O, and C, and the SDD⁴⁶ basis set for Rh. It was found that PBE and BPW91 could well reproduce the structures of C₆₀Rh⁺ and C₆₀Rh₄⁺ determined previously (see Fig. S1-S4 in ESI†).35 Since BPW91 has been found to be superior in simulating the infrared spectra of fullerene-metal clusters in terms of efficiency and accuracy, 36,37,47,48 it was chosen to optimize all the geometries of transition states and intermediates

during the catalytic NO conversion process. Harmonic frequency analysis was performed to make sure all transition states have only one imaginary frequency and the intermediates have none. Intrinsic reaction coordinate (IRC) calculations were conducted to validate the calculated transition state structures and to confirm the nature and stability of reaction pathways. 49 The natural bond orbital (NBO) analysis was performed with NBO 3.1 as implemented in Gaussian 09.50

Results and discussion

We first confirm that BPW91 can provide reliable structures for Rh₄⁺, C₆₀Rh⁺, and C₆₀Rh₄⁺ as determined from previous experiments (see Fig. S1-S4 in ESI†).35 The most stable structure of $C_{60}Rh_4^+$ has a quartet sate with the four Rh atoms adsorbed on one hexagonal surface of fullerene, forming a square shape parallel to the hexagon, as shown in Fig. 1. The adsorbed NO molecule binds with C₆₀Rh₄⁺ through a Rh-N bond due to the high affinity of small rhodium clusters towards N atoms. 20,25 This step forms the first intermediate IN1 with an exothermic energy of 55.7 kcal mol⁻¹, smaller than the calculated binding energy of 88.8 kcal mol⁻¹ between C₆₀ and Rh₄⁺ in C₆₀Rh₄⁺. Subsequently, the N-O bond undergoes dissociation, which is facilitated by the two adjacent Rh atoms. The energy barrier associated with this process is 49.6 kcal mol⁻¹, resulting in the formation of a Rh-N bond and a Rh-O bond in IN2 (IN1 → TS1 → IN2). Then, a second NO molecule adsorbs on IN2, resulting in the formation of the intermediate IN3 via forming another Rh-N bond. This process exothermically releases an energy of 55.8 kcal mol^{-1} , similar to the energy released by the first NO adsorption. Then, the N-O bond is cleaved by the other two adjacent Rh atoms. Thereafter, all four Rh sites are fully occupied by two N atoms and two O atoms (IN3 \rightarrow TS2 \rightarrow IN4). The energy barrier for this process is 56.8 kcal mol^{-1} , about 7 kcal mol⁻¹ higher than the first N-O bond dissociation, presumably due to the steric effect of the pre-adsorbed N and O

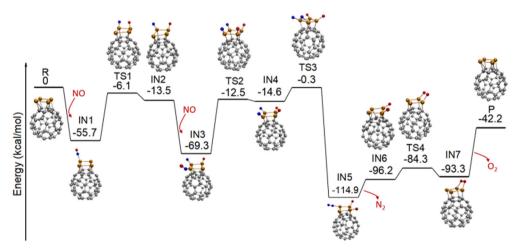


Fig. 1 Reaction pathway of NO reduction on $C_{60}Rh_4^+$ calculated at the BPW91/6-31G(d) θ SDD level of theory. R stands for reactants, IN for intermediates, TS for transition states, and P for products. All energies are provided relative to the energies of the reactants, i.e., C₆₀Rh₄⁺ and two NO molecules.

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atoms from the first NO molecule. This process behaves as the rate-determining step in the catalytic NO reduction by the C₆₀Rh₄⁺ cluster.

Upon combination of the two dissociated nitrogen atoms on the "surface" of the rhodium cluster by overcoming a barrier of 14.3 kcal mol⁻¹, the N₂ moiety forms in a very stable intermediate IN5 that is 114.9 kcal mol⁻¹ below the energy of the reactants. Subsequently, N₂ desorbs from the cluster with an endothermic energy of 18.7 kcal mol^{-1} , forming the intermediate IN6 (IN4 \rightarrow TS3 \rightarrow IN5 → IN6). Then, the two O atoms on the "surface" of the rhodium cluster interact with each other to form an O2 moiety in IN7 through a barrier of 11.9 kcal mol^{-1} (IN6 \rightarrow TS4 \rightarrow IN7). Afterwards, the O₂ molecule desorbs by adsorbing an energy of 51.1 kcal mol⁻¹ completing a reaction cycle for the direct reduction of NO to N2 catalyzed by $C_{60}Rh_4^+$, i.e., $NO + NO \xrightarrow{C_{60}Rh_4^+} N_2 + O_2$. Overall, the calculation shows that this reaction has an exothermic energy of 42.2 kcal mol⁻¹, in excellent agreement with the experimental value of 41.4 kcal mol^{-1,3} During the reaction, the four Rh atoms serve as the active sites for the activation and conversion of two NO

To elucidate the important role of multiple Rh sites for NO reduction, we calculate the reaction pathway of two NO molecules reacting with a C₆₀-fullerene-supported single rhodium atom, i.e., C₆₀Rh⁺ (see Fig. S5, ESI†). It seems that although the reaction cycle can be completed, first and second N-O bond dissociations encounter significant energy barriers, amounting to 103.2 and 89.7 kcal mol⁻¹, respectively. Such barriers are even larger than the calculated binding energy of 82.3 kcal mol⁻¹ between C₆₀ and Rh⁺ in C₆₀Rh⁺, 35 which may result in the destruction of the C₆₀Rh⁺ cluster first before the reaction can proceed, precluding its usefulness in practice.

The above discussion raises an interesting question: What is the role of C₆₀ in the reaction? Can the same reaction cycle be completed without the presence of C₆₀? To answer these questions, we investigated the adsorption and dissociation pathway of two NO molecules on a free Rh₄⁺ cluster and presented it in Fig. 2. The most stable structure of Rh₄⁺ is a pyramid with a doublet state. The first NO molecule is adsorbed on Rh₄⁺ through a Rh-N

bond, forming the intermediate IN1 with an energy release of 62.1 kcal mol⁻¹. Subsequently, the N-O bond undergoes dissociation facilitated by two adjacent Rh sites, resulting in the formation of a Rh-O bond and a Rh-N-Rh ring in IN2 (IN1 \rightarrow TS1 \rightarrow IN2). The energy barrier for this process is calculated to be 29.2 kcal mol⁻¹, consistent with the calculated value of 27.7 kcal mol⁻¹ for N-O bond dissociation of NO on Rh₄⁺ reported by Romo-Ávila et al.²⁸ Then, the cluster adsorbs a second NO molecule, forming a very stable intermediate, IN3, which is about 130 kcal mol⁻¹ below the total energy of reactants and releases an energy of $68.3 \text{ kcal mol}^{-1}$. Similar to the first NO dissociation, a second Rh-N-Rh ring and a Rh-O-Rh ring form in IN4 via TS2. The barrier for this step is 55.4 kcal mol⁻¹, in agreement with the value of 57.7 kcal mol⁻¹ reported for the second N-O bond dissociation.²⁷ This step is the rate-determining step in the reaction of NO molecules with the Rh₄⁺ cluster.

In the following process, the two N atoms on the cluster surface migrate and encounter each other to combine to form a N₂ moiety by overcoming an energy barrier of 39.8 kcal mol⁻¹ (IN4 \rightarrow TS3 \rightarrow IN5). Subsequently, N₂ desorbs from the cluster surface by absorbing 15.6 kcal mol⁻¹ energy, resulting in the formation of the product $Rh_4O_2^+$ (IN5 \rightarrow TS4 \rightarrow IN6 \rightarrow P). Our calculated results on the reaction of Rh₄⁺ with NO match the previous theoretical results on the reaction between NO and Rh_n^+ (n = 4, 6, or 7) clusters. However, due to the geometric constraint, as the two O atoms in Rh₄O₂⁺ are spatially distant, the combination of the two O atoms to form O2 is hindered at normal temperatures. For example, Torres et al. calculated the desorption energy of O_2 from $Rh_6O_2^+$, i.e., $\Delta E = E(Rh_6^+) + E(O_2)$ $- E(Rh_6^+O_2)$, to be approximately 3.07 eV (70.8 kcal mol⁻¹), almost 20 kcal mol⁻¹ higher than that in the presence of C₆₀. ²⁶ Such a process is expected to occur only at high temperatures, for instance, in the range of 1000-1400 K.18 These analyses highlight the unique role of C₆₀ in facilitating the completion of the reaction cycle of NO + NO \rightarrow N₂ + O₂.

To more properly uncover the geometric effect and electronic effect when comparing the catalytic performance of C₆₀Rh₄ and Rh4+, we also calculated the reaction pathway of NO reduction on square Rh₄⁺, a less stable isomer for the Rh₄⁺

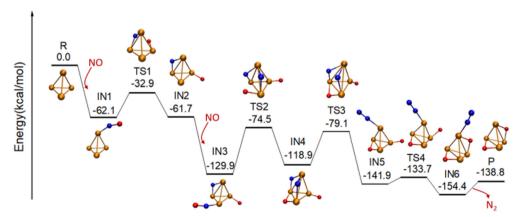
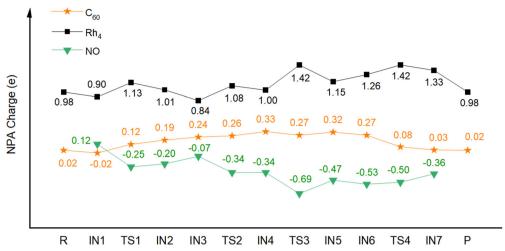


Fig. 2 Reaction pathway of NO reduction on Rh₄⁺ calculated at the BPW91/6-31G(d)&SDD level of theory. R stands for reactants, IN for intermediates, TS for transition states, and P for products. All energies are provided relative to the energies of the reactants, i.e., Rh₄⁺ and two NO molecules.

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Calculated NBO partial charges (e) of the Rh₄⁺ cluster (black square) and C₆₀ (orange star) of NO reduction catalyzed by C₆₀Rh₄⁺.

cluster but possessing a similar geometry of the Rh₄⁺ moiety in C₆₀Rh₄⁺. Fig. S6 in the ESI† presents the result, and it can be seen that although it seems the NO reduction into N₂ and O₂ on square Rh₄⁺ can be fulfilled, the energy barriers for the two-NO-bond cleavage are 54.5 and 61.6 kcal mol⁻¹, both about 5 kcal mol⁻¹ higher than the barriers on C₆₀Rh₄⁺. This clearly shows that the electronic effect is in play. Overall, both geometric and electronic effects play roles in the catalytic NO reduction by C₆₀Rh₄⁺, as the most stable Rh₄⁺ becomes square from pyramidal when it is supported on C₆₀, demonstrating the important support effect.

To uncover why C₆₀ can have such a role in the catalytic reduction of NO to N2, we conducted natural bond orbital (NBO) analysis. Fig. 3 shows the calculated NBO partial charges of the Rh₄⁺ moiety and C₆₀ of NO reduction catalyzed by C₆₀Rh₄⁺, and the charge changes for the catalytic reactions of NO by pyramid Rh₄⁺, square Rh₄⁺ and C₆₀Rh⁺ are shown in Fig. S7-S9 (ESI†), respectively. It can be seen that the metal moiety shows alternating charges increasing and decreasing due to the cooperative effect of the electrophilic reactant NO, its dissociated N and O atoms, and the C₆₀ support. Before the formation of IN4, the C₆₀ support progressively donates electrons to metal and the reactant and reaches a maximum positive charge of 0.33 e; afterwards, before releasing the N₂ molecule (IN6), the charges on Rh₄ and C₆₀ show exactly reverse trends; then, the positive charge on C₆₀ keeps decreasing, meaning that C₆₀ has been accepting electrons from metal and/or the reactant. Thus, during the whole process, C₆₀ alternatively donates and accepts electrons, behaving as an "electron sponge", as we previously proposed. 37,38 Specifically, for the O₂ desorption process, the charge changes seem to reduce the interaction between Rh₄⁺ and O atoms and simultaneously increase the binding energy between Rh₄⁺ and C₆₀. Hence, the presence of C₆₀ enables the O atoms to become "surface" O rather than "lattice" O, making the desorption of the O2 molecule easier. In the case of free Rh₄⁺, the reactant seems to extract electrons from metal due to their higher electron negativity compared to metal, thus increasing the binding strength between metal and reactant. Without the electronic buffering effect of C₆₀, such an enhanced

binding strength would make desorption of the formed molecules difficult.

Conclusions

In summary, we studied the catalytic NO reduction into N₂ by rhodium clusters, in particular Rh₄⁺, with and without the presence of C₆₀-fullerene support. The Rh atoms serve as the active sites for the reduction of two NO molecules, and the C60 support plays an important role in regenerating the Rh₄⁺ catalyst with relatively smooth O2 desorption, which is difficult for free Rh₄⁺ without the presence of C₆₀ as it forms a stable rhodium oxide cluster, Rh₄O₂⁺. The introduction of C₆₀ support not only induces a geometric transformation for the ground state of free Rh₄ from a trigonal pyramid to a square form but also can donate to or accept from the metal electrons during the NO catalytic reduction. This work demonstrates the electron sponge behavior of C₆₀, and the ability of C₆₀ to donate and accept charges at distinct steps within the reaction between NO and Rh clusters sheds light on the intricate electronic interactions involved, offering valuable insights for designing efficient catalysts in the realm of direct reduction of NO.

Author contributions

G.-L. H. conceived and designed the research. R. L., Y.-K. L., and J. X. performed the research. R. L., Y.-L., and G.-L. H. wrote the manuscript. All authors approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (92261101), Innovation Capability **PCCP** Paper

Support Program of Shaanxi Province (2023-CX-TD-49), and Research Foundation-Flanders FWO (G033724N). G.-L. H. acknowledges the support from the Fundamental Research Funds for Central Universities, China. Part of the computational resources and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by the Research Foundation-Flanders (FWO) and Flemish Government-Department EWI.

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