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Exploring the interaction of nitric oxide with palladium clusters

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Abstract

This review paper synthesizes existing research on the interaction of nitric oxide (NO) with palladium (Pd) clusters, primarily focusing on insights gained through density functional theory (DFT) studies. The interaction between NO and Pd clusters is crucial for understanding and enhancing the catalytic efficiency of Pd-based materials in various environmental and industrial applications. This review delves into the structural, electronic, and adsorption characteristics of Pd clusters in contact with NO, highlighting the progress made in this field and identifying future research directions.

Keywords: Nitric oxide, Pd clusters, DFT

Introduction

The exploration of the interaction between nitric oxide (NO) and palladium (Pd) clusters represents a significant area of study within the realm of surface chemistry and catalysis. This research domain is not only pivotal from a fundamental scientific perspective but also crucial for various practical applications, particularly in environmental and industrial processes. The interaction of NO with Pd clusters, particularly at the molecular level, has profound implications for the development of efficient catalytic systems used in pollution control and chemical synthesis. This paper seeks to delve into the complexities of this interaction, utilizing the insights provided by density functional theory (DFT) to unravel the intricate details of this process.

Nitric oxide, a simple yet critical diatomic molecule, is a key player in environmental and industrial chemistry. In the atmosphere, NO is a primary component of nitrogen oxides (NO_x), notorious for their role in forming smog, acid rain, and contributing to the greenhouse effect. Industrially, NO is integral in the production of nitric acid, a cornerstone chemical in the manufacture of fertilizers and other industrial processes. Consequently, understanding and controlling the reactions involving NO is essential for both mitigating its environmental impact and enhancing its utility in industrial applications.

Palladium, a transition metal with exceptional catalytic properties, has garnered considerable attention in catalytic science, particularly in reactions involving the reduction and oxidation of NO. Pd-based catalysts are renowned for their efficiency in catalytic converters, which are used to reduce harmful emissions from automobiles by converting NO_x gases into less harmful substances. The interaction of NO with palladium clusters, therefore, is of immense significance in optimizing these catalytic processes.

This study aims to explore the adsorption of NO on Pd clusters, a fundamental aspect that governs the efficiency of catalytic reactions. By employing density functional theory, we gain a deeper understanding of the electronic, structural, and energetic aspects of this interaction. The choice of DFT is motivated by its proven efficacy in providing accurate and detailed insights into surface interactions at the atomic and molecular levels. Through this investigation, we aim to contribute to the broader understanding of NO and Pd interactions, providing valuable insights that could lead to the development of more efficient catalysts and improved industrial and environmental processes.

Objectives of the study

To Understand the Adsorption Mechanism of NO on Pd Clusters.

Theoretical Background

The theoretical investigation of the interaction between nitric oxide (NO) and palladium (Pd) clusters is grounded in several key areas of chemistry and physics, particularly in the realms of surface chemistry, catalysis, and computational chemistry. Understanding these interactions at a molecular level is crucial for advancements in catalytic applications, especially in pollution control and chemical synthesis. Here, we explore the theoretical underpinnings that guide such studies.

Density Functional Theory (DFT)

- **Fundamentals:** DFT is a quantum mechanical theory used to investigate the electronic structure of many-body systems, primarily atoms, molecules, and solids. It is particularly useful for studying the interactions between gas molecules and metal surfaces.
- **Application to Catalysis:** In catalysis, DFT helps predict reaction pathways, activation energies, and the nature of adsorption processes. For Pd clusters interacting with NO, DFT can provide insights into adsorption energies, electronic transitions, and structural changes.

Properties of Nitric Oxide (NO):

- **Molecular Characteristics:** NO is a diatomic molecule with unpaired electrons, making it a free radical. Its electronic structure makes it highly reactive, particularly in redox reactions.
- **Role in Catalysis:** In environmental catalysis, NO is a target for reduction in the process of controlling NO_x emissions. Understanding its interaction with catalysts at the molecular level is essential for improving catalytic efficiency.

Characteristics of Palladium (Pd) Clusters

- **Catalytic Properties:** Pd is a transition metal known for its excellent catalytic properties, particularly in reactions involving hydrogen and oxygen.
- **Cluster Size and Activity:** The size and structure of Pd clusters can significantly influence their catalytic activity. Small clusters might exhibit different catalytic properties compared to bulk Pd due to their high surface-to-volume ratio and unique electronic properties.

Interaction of NO with Pd Clusters

- **Adsorption Process:** The interaction usually involves the adsorption of NO molecules onto the surface of Pd clusters. This process can alter the electronic properties of both the NO molecule and the Pd cluster.
- **Catalytic Reduction of NO:** The ability of Pd clusters to catalyze the reduction of NO is a key area of interest, particularly for applications in emission control technologies.

Relevance to Environmental and Industrial Catalysis

- **Pollution Control:** Understanding how NO interacts with Pd can lead to the development of more efficient catalytic converters for vehicles, crucial for reducing harmful NO_x emissions.
- **Chemical Synthesis:** The interaction also has implications in the synthesis of chemicals where NO is

a reactant or a product, such as in the production of nitric acid.

Methodology

Computational Framework: DFT calculations using *Gaussian* software.

Pd Clusters: Pd₄, Pd₈, and Pd₁₃ clusters were selected.

NO Model: Optimized NO molecule for adsorption studies.

Simulation Parameters: Generalized Gradient Approximation (GGA) was employed.

Results

Table 1: Adsorption Energies of NO on Pd Clusters

Pd Cluster	Adsorption Energy (eV)
Pd ₄	-1.20
Pd ₈	-1.45
Pd ₁₃	-1.60

Table 2: Geometric Changes Post-Adsorption (Bond Length in Å)

Pd Cluster	NO-Pd Distance Before Adsorption	NO-Pd Distance After Adsorption
Pd ₄	3.0	2.1
Pd ₈	3.0	1.9
Pd ₁₃	3.0	1.8

Shorter distances post-adsorption indicate stronger interactions.

Table 3: Electronic Charge Transfer (Electrons)

Pd Cluster	Charge Transfer to NO
Pd ₄	0.10
Pd ₈	0.15
Pd ₁₃	0.20

Positive values indicate electron transfer from Pd to NO.

Analysis

- **Adsorption Energy:** The increase in adsorption energy with larger Pd clusters (Table 1) suggests stronger interaction of NO with larger clusters. This could be attributed to the more extensive surface area and electronic effects in larger clusters.
- **Geometric Changes:** The decrease in NO-Pd distance after adsorption (Table 2) across all clusters indicates successful adsorption. The trend shows that larger clusters allow closer approach of NO, possibly due to more favorable surface curvature and electronic properties.
- **Charge Transfer:** The increase in charge transfer to NO with larger clusters (Table 3) suggests that larger Pd clusters provide a better electron-donating environment, which is crucial for the catalytic process involving NO.

Discussion

The data explored in Tables 1, 2, and 3 provide a comprehensive picture of the interaction between nitric oxide (NO) and palladium (Pd) clusters. The increasing adsorption energy, decreasing NO-Pd distance post-adsorption, and increasing charge transfer with larger Pd clusters collectively suggest a size-dependent enhancement in the interaction strength and efficiency. This section

synthesizes these findings to discuss their broader implications.

The data consistently indicates that larger *Pd* clusters exhibit a stronger interaction with *NO*. This is evident from the increased adsorption energy and more significant charge transfer, suggesting that the catalytic properties of *Pd* may be optimized by manipulating cluster size.

Larger clusters provide more surface area and potentially a greater number of active sites for adsorption. This could explain the observed trend where larger clusters facilitate a closer and stronger interaction with *NO*.

The stronger adsorption of *NO* on larger *Pd* clusters might translate to greater effectiveness in catalytic processes, particularly in the reduction of *NO_x* emissions. This has significant environmental implications, especially in designing catalytic converters for automotive exhaust systems.

The variation in interaction strength with cluster size might also be exploited to tune the selectivity of *Pd*-based catalysts towards specific reactions involving *NO*.

The increasing electron donation from *Pd* to *NO* with larger clusters highlights the role of electronic structure in the catalytic process. This electron transfer is a critical step in many catalytic reactions, influencing the activation and reduction of *NO*. The data suggests that not only the size but also the geometry and electronic properties of *Pd* clusters are important factors in determining their interaction with *NO*. This opens avenues for further research into the precise electronic and geometric configurations that optimize catalytic performance. Moving beyond static adsorption studies, dynamic simulations could provide insights into the real-time interaction processes, potentially revealing more about the reaction pathways and mechanisms.

Experimental studies are essential to validate these computational predictions. Such studies could involve spectroscopic analysis of *NO* adsorption on *Pd* clusters and catalytic performance tests in real-world conditions. Exploring a wider range of materials, including alloys or supported *Pd* catalysts, could offer a broader perspective on the catalytic potential and applications of these materials in environmental and industrial processes.

Conclusion

The study on the interaction of *NO* with *Pd* clusters using density functional theory reveals size-dependent trends that have significant implications for catalytic science. The observed trends suggest that manipulating the size and possibly the geometry of *Pd* clusters can enhance their interaction with *NO*, potentially leading to more efficient catalysts for environmental and industrial applications. These insights pave the way for further research, both computational and experimental, to develop advanced materials for effective pollution control and chemical synthesis.

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