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[1] **Biswakarma, N.**, Sarma, P. J., Neog, S., Dutta, P., Dowerah, D., Baruah, S. D., Gour, N. K., and Deka, R. C. Termolecular Eley–Rideal pathway for catalytic oxidation of nitric oxide on $[Pt_2]^{0,\pm}$ dimers using O_2. *International Journal of Quantum Chemistry*, 124:e27390, 2024.

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[1] Sarma, P. J., Dowerah, D., **Biswakarma, N.**, and Deka, R. C. Global Minimum Structures of (MnO) n clusters, n= 1-10 at DFT energy landscape. *Air and Water Quality Assessment, Contamination and our Surroundings: Specific Analysis and Applications,* ISBN: 9788194332169. Walnut Publication, 2019.

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CONFERENCES AND SEMINARS ATTENDED

Oral Presentation

[1] **Biswakarma, N.**, Gour, N. K., and Deka, R. C. *Mechanistic Insight into the Catalytic Oxidation of NO to* NO_2 *on* $[Pt_2]^{0,\pm}$ *Dimers: A DFT Approach.* National Conference on "Research at the Interface of Chemical, Biological and Material Sciences" organized by Tezpur University, Assam, India, 10th March, 2023.

Poster Presentation

[1] **Biswakarma, N.**, Gour, N. K., and Deka, R. C. *Oxidation Pathways of Nitrogen Oxide over* $Au\text{-}M^-$*(M=Pt, Pd) bimetallic dimers: A DFT study.* National Conference on "Theoretical Chemistry Symposium" (TCS-2019), organized by BITS Pilani, Rajasthan, India, 13th-16th February, 2019.

[2] **Biswakarma, N.** and Deka, R. C. *Catalytic oxidation of NO to* NO_2 *on charged and neutral* Pd_2 *dimer: A DFT viewpoint.* National Conference on Recent Advances in Chemistry: Theoretical and Computational Aspects (RAC-TCA), organized by Department of Chemistry, NIT Meghalaya and NEHU, 18th -20th November, 2022.

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RESEARCH ARTICLE

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Termolecular Eley–Rideal pathway for catalytic oxidation of nitric oxide on $[Pt_2]^{0,\pm}$ dimers using O_2

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Abstract

A comprehensive density functional theory (DFT) investigation of the catalytic oxidation of NO to NO_2 on neutral and charged $[Pt_2]^{0,\pm}$ dimers has been considered employing M06L/def2TZVP level of theory. Single as well as co-adsorption energies of NO and O_2 molecules suggest that the traditional Langmuir Hinshelwood (LH) mechanism and less explored termolecular Eley–Rideal (TER) and termolecular Langmuir Hinshelwood (TLH) mechanisms, are suitable for a full catalytic reaction pathway in which two NO molecules are converted to two NO_2 molecules, initiated by an activated O_2 molecule. Activation barrier reveals that the TER mechanism is found to be more reliable in converting two NO molecules into two NO_2 molecules on $[Pt_2]^-$ dimer. In addition to shedding light on the intrinsic characteristics of Pt_2 dimers, the study will serve as a benchmark for investigating the oxidation process of NO to NO_2 utilizing models of termolecular chemical processes.

KEYWORDS
adsorption energy, catalytic oxidation, dimers, M06L, termolecular Eley–Rideal

1 | INTRODUCTION

Nitrogen oxides (NO_x) are one of the main air pollutants responsible for a variety of environmental issues, including acid rain, haze, and photochemical smog. Nitric oxide or nitrogen monoxide (NO) accounts for more than 90% of NO_x. It is a hazardous pollutant that gets released in the exhaust gas of diesel engines [1] and is the cause of serious respiratory ailments [2, 3]. Prior to emission, it is crucial to chemically convert NO to N_2 in order to prevent air pollution. Despite the apparent irony, the catalytic oxidation of NO is a crucial phase in its catalytic reduction. NO_x storage and reduction (NSR), continuously regenerating traps (CRT), and selective catalytic reduction (SCR) are modern day techniques for NO reduction. In NSR, NO is oxidized into nitrogen dioxide (NO_2) and/or nitrate (NO_3) and temporarily retained on the surface of a noble metal before being reduced [4]. In CRT, NO is converted to NO_2, which then oxidizes unburnt hydrocarbons on a diesel particulate filter [5]. Also, the catalytic oxidation of NO is one of the most important steps in the Ostwald process for making nitric acid [6]. The catalytic oxidation of NO and NO_2 is thus established as a crucial reaction for the reduction of detrimental NOx gases, and considerable effort has been put into developing efficient catalysts for NO oxidation.

Platinum is the predominant choice for catalytic oxidation of NO in all of these current approaches due to its high catalytic activity. It is regarded as the model catalyst for NO oxidation and has been extensively investigated in the past years [7–11]. The catalytic activity of platinum catalysts for NO oxidation under different feed containing NO and O_2 have been studied [7, 12].Denton et al. [13] studied the oxidation rate of NO for both Pt/SiO_2 and Pt/Al_2O_3 and found out that Pt particle size was a key reason in controlling the reaction rate while the impact of the support was negligible. Schmitz et al. [9] investigated the impact of precursor, support, loading, and processing conditions on NO oxidation over

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Catalytic Oxidation of NO on $[Au{-}M]^-$ (M = Pd and Pt) Bimetallic Dimers: An Insight from Density Functional Theory Approach

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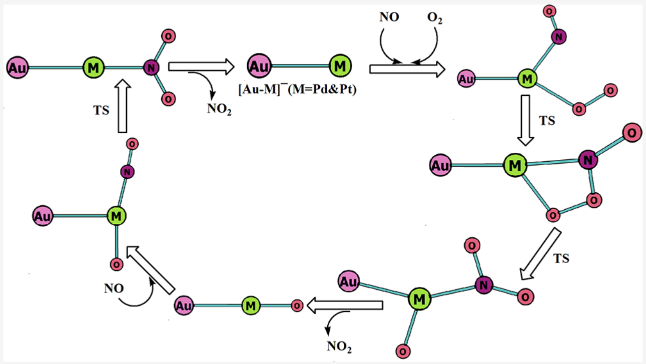
ABSTRACT: Escalation of nitrogen monoxide (NO) concentration into the atmosphere has caused severe environmental problems. So, it is important to prepare or design a suitable catalytic system to understand the oxidation of NO into NO_2 at the molecular level. In this regard, a comprehensive theoretical investigation of the catalytic oxidation of NO on anionic bimetallic dimers $[Au{-}M]^-$ (M = Pd, Pt) has been considered here using the density functional theory method at the M06L functional along with def2TZVP basis set. To refine the energies and electronic properties of all species, single-point energy calculations are further performed with the CCSD(T) method using the same basis set. The adsorption of NO and O_2 on bimetallic dimers is studied, and binding energy has been calculated to understand the stability of the adsorbed species. Our calculations show that M sites are found to be the preferred site for adsorption rather than Au site. Further, full catalytic reaction pathways using the Langmuir−Hinshelwood mechanism are investigated in which two NO molecules are converted into two NO_2 molecules in the presence of an activated O_2 molecule. Moreover, an energetic span model has justified that conversion on $[Au{-}Pd]^-$ catalyst possesses a lower apparent activation energy than that on $[Au{-}Pt]^-$ which makes $[Au{-}Pd]^-$ a more efficient catalyst toward the catalytic conversion of NO into NO_2. Thus, the present study will convey an understanding of the mechanism of NO oxidation at the molecular level as well as designing better catalysts for future prospects.



1. INTRODUCTION

Nitrogen oxides (NO_x) abatement is one of the important steps for minimizing the harmful emissions which are released into the environment owing to the growth in the automobile industry. Automobiles are a significant source of carbon monoxide (CO) as well as NO_x. NO_x includes nitrogen monoxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O), and the release of these gases causes environmental hazards such as photochemical smog and acid rain. Controlling NO_x emission has been made possible by introducing various methods such as three-way catalysis (TWC), NO_x storage reduction (NSR), continuously regenerating trap (CRT), and selective catalytic reduction (SCR).[1−3] In CRT, soot, a harmful byproduct of incomplete combustion, is collected on a diesel particulate filter. Therefore, NO is oxidized to NO_2, which in turn oxidizes soot.[4] It was found that the soot oxidation by NO_2 occurs at a much lower reaction temperature (greater than 300 °C)[5] than that of oxygen (500−600 °C)[6,7] In a lean exhaust environment, SCR catalysts can control NO_x emission using an additional reductant. In the NH_3-SCR process, it was found that reaction rate is greatly enhanced upon retaining the equimolar feed of NO/NO_2 reaction mixture. When a fraction of NO is converted to NO_2 represented as $4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$, the rate of reaction was found to be 10 times faster than standard SCR reaction ($4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$) at a temperature range of 200−300 °C.[8,9] In normal conditions, the NO oxidation efficiency is observed to be slow as a result of the complex nature of fuel gas and different particulate size distributions.[10] Thus, focus has to be on developing eligible catalyst for NO oxidation that could enhance NO conversion rate. It has been observed that nanoparticles of precious metals such as Au, Pd, and Pt are extensively used in this regard due to their higher catalytic activity.[4,11−14]

Consequently, considerable interest has been shown from both the industrial and scientific communities toward nanosized gold clusters.[15−18] Gold nanoparticles exhibit catalytic activity on reactions such as low-temperature CO oxidation,[19,20] water gas shift reaction,[21,22] and direct propylene epoxidation using H_2 and O_2.[23,24] The catalytic activity of gold

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