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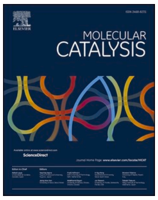

Co Implanted Ψ-graphene: A Non-Noble Metal Single-Atom Catalyst for Proficient CO Oxidation Reaction

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ABSTRACT

Single-Atom Catalysts (SACs) have procured heightened attention of the research community across the globe due to their astounding catalytic behaviour towards some prime chemical reactions. Herein, the catalytic performance of non-noble metal, cobalt single-atom supported over Ψ-graphene (Co@PG) addressed towards CO oxidation reaction by means of first-principles-based, dispersion corrected density functional theory (DFT) calculations. The higher diffusion barrier of Co over Ψ-graphene evidently authenticate the stronger interaction of Co with Ψ-graphene and robust stability of overall system, hence prelude the cluster formation possibility. Further, the temperate interaction of reactants (CO, O_2) affirms that the Co@PG is brilliantly effective in hosting and activating reactants, an indispensable condition to commence any catalytic reaction cycle. The analysis of electronic reactivity descriptors (ERDs) like d-band centre (ϵ_d) and fractional filling of d-band (f_l), by employing improved d-band model, emphasize that the minority-spin states of Co atom would engage predominantly in the interaction with the reactants. Latterly, CO oxidation reaction over Co@PG was carried out with two different mechanisms, viz., Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) pathways for detailed analysis. Computation of minimum energy path (MEP) and activation barriers reveal that the Co@PG favours the ER mechanism, with reaction barrier of 0.19 eV and 0.27 eV for first and second half reactions respectively, both of them being highly exothermic validating the viability of the overall process. Accordingly, present investigation insinuates that Co@PG can be a potent, non-noble metal, practically operational catalyst for CO oxidation reaction.

1. Introduction

The ever-escalating environmental pollution and ultimately the increment in the global warming, attributed to the raising concentration of the exhaust gases (CO_x, NO_x, CH_x) in atmosphere due to major contribution from the incomplete combustion of fossil fuels or petroleum products in industrial processes and automobiles[1–3]. The conversion of these exhaust gases into a relatively benign gases is a crucial societal issue at the global level to be solve. It is the only way to reduce/control the amount of concentration of these gases into the environment and fuel cell poisoning[4]. CO oxidation by molecular oxygen (O_2) has garnered heightened attention not only because it leads to a relatively less detrimental carbon dioxide (CO_2) gas but also because it serves as a fundamental benchmark reaction for assessing the catalyst effectivity and efficiency[5,6]. This dual significance has catapulted CO oxidation reaction into the spotlight in the realm of heterogeneous catalysis.

From decades, traditionally existing catalysts, especially of some noble-metals such as Au[7,8], Pt[9–11], Pd[12–14] are known to display exemplary catalytic activity towards CO oxidation reaction. Given their high cost, high operational temperature, exiguity and CO poisoning effect are hampering their usage in commercial applications [15]. Therefore, complete elimination of these metals in scheming a rational catalyst for catalytic CO oxidation is yet an arduous task for the researchers. The improvement in efficiency and preservation of their catalytic activity could be possible with formation of bimetallic catalysts with low cost transition metals like Fe[16], Cu[17], Ni[18] and reducing the size of catalysts to nanoclusters or even smaller which is the key to proceed in this respect. The approach of downsizing of the particle to atomic scale, leads to amplification in cayalytic activity due to their partially filled d-states and introduction of the quantum confinement [19–22]. In this regard, designing a catalyst wherein the atomically dispersed single atoms act as an active site anchored by some substrates is known as single atom catalysts (SAC). The field of SACs left open by

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Dressing of Cu Atom over Nickel Cluster Stimulating the Poisoning-Free CO Oxidation: An Ab Initio Study

Bhumi A. Baraiya, Hemang Tanna, Venu Mankad, and Prafulla K. Jha*

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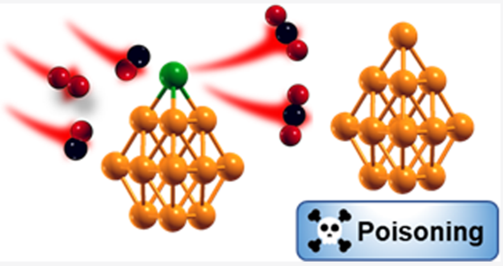
ABSTRACT: In this work using first-principles calculations based on spin-polarized density functional theory (DFT), the role of the Cu atom in degrading the poisoning of carbon monoxide (CO) over Ni$_n$Cu clusters is unveiled. The search has been initiated with the examination of structural, magnetic, and electronic properties of Ni$_{n+1}$ and Ni$_n$Cu clusters ($1 \leq n \leq 12$). X-ray absorption near-edge structure (XANES) spectra of Ni K-edge are computed to extract the information on the oxidation states and coordination environment of metal sites of the clusters. This study is operated with the two forms of dispersion corrections, i.e., D2 and D3, with standard DFT (with LDA and GGA functionals) for the consideration of van der Waals interactions during CO adsorption. The PBE and PBE-D3 approaches are found to be capable of yielding the experimentally observed preferential site for CO adsorption. The effect of spin-polarization on the reactivity of transition metals (TMs) toward CO adsorption is crucially assessed by the electronic reactivity descriptors such as d-band center, d-band width, and fractional filling of d-band using a spin-polarized d-band center model. The effective charge transfer from Cu to Ni atoms makes Ni atoms more efficient of charge and is attributed to the degrading adsorption of CO over Ni$_n$Cu clusters. The Ni$_{12}$Cu cluster stands out with good CO oxidation activity for the Langmuir−Hinshelwood (L−H) reaction pathway.



1. INTRODUCTION

CO oxidation (2CO + O_2 → $2CO_2$) which is crucial in catalytic conversion of automobile exhausts and low-temperature fuel cells for less harmful and environmentally friendly emission is a focus area of interest in the field of fundamental research of various catalytic reactions.[1] Traditionally, platinum group metals (PGMs), e.g., iridium (Ir), rhodium (Rh), platinum (Pt), and palladium (Pd), are in vogue and single out as superior catalysts for CO oxidation and O_2 reduction.[1−3] No matter which size, shape, or dimensionality it possesses, Pt stands out as the irreplaceable and exceptional electrode material for the fuel cells, oxygen reduction reaction, hydrogen evolution reaction, water−gas shift, hydrogenation, and especially for CO oxidation owing to its remarkable catalytic efficiency compared to other transition metals (TMs).[4] To gain molecular-level insights on reactions that occur at Pt surfaces, the nanocluster form of Pt turns out to be a fundamental topic of investigation for CO oxidation.[4,5] Despite all advantages, the major obstacles in the commercialization of Pt-based catalysts are their overprice, scarcity, and especially the higher affinity toward CO which causes rapid deactivation of the catalyst by CO poisoning.[6,7] Thus, the main purpose of designing heterogeneous catalysts by trimming or preventing the usage of traditional PGMs while retaining their catalytic activity has been elevated for years.[8] Principally, two major strategies are available to circumvent the CO poisoning: (1) desorption of CO operating at the elevated temperature and (2) alloying of less reactive metals such as Cu, Ag, and Au with parent material.[8,9] The first strategy appears to be unfeasible and expensive in terms of high reaction temperature which resulted in low coverages for important reactants and the risk of deactivation.[9] In contrast, the second tactic appears convincing due to the higher tolerance to CO poisoning while retaining reasonable activity and cost-effectiveness.[10−12] For that matter, testimonials with optimized performance and design of low-cost catalysts after alloying, count on a fundamental understanding of the electronic structure (in particular the d-states) of an ensemble of surface atoms and its relationship with the energetics of adsorbate−surface interactions.[13,14] The d-band center (ε_d) is a vital electronic reactivity descriptor derived from the d-band model proven to be extremely useful in search of optimal catalytic materials.[15] The number of studies on alloying of Pt-M (M = Ru, Sn, Ge, Mo, and Cu) revealed that the alloying modified the electronic structure of Pt via charge transfer from dopant to Pt and found responsible for the weaker adsorption of CO (lower affinity toward CO).[12,16,17] To avoid poisoning of Pt during CO oxidation reaction, the role of Co, Ni, and Cu doping over free-

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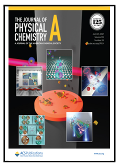

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RESEARCH

A Theoretical Inquest of Atomically Injected Ni-Atom over Graphene and Analogous Substrates for Hydrogen Evolution Reaction

Hemang P. Tanna[1] · **Prafulla K. Jha**[1]

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Abstract

A rational catalyst for electrocatalytic hydrogen evolution reaction (HER) is a long-standing challenge that researchers are confronted with. In view of this, tiny particles of transition metals (TMs) spread over a substrate acting as an active site for the reaction, scientifically known as single-atom catalysts is seen as an efficacious way for designing an efficient catalyst. Herein, we comprehensively investigated catalytic activity of Ni-atoms spread over various kinds of two-dimensional (2D) substrates like graphene, AlC, AlN, h-BN, BeO, and MgO (Ni@2D) towards HER using density functional theory calculations. All the considered 2D substrates have various inequivalent anchoring sites like top, hollow, bridge, and vacancy sites for Ni-atoms. So, there are total 34 anchoring sites, and we computed binding energy (E_b) of Ni-atom over all the sites. Having large number of configurations, we first applied a screener on stability of Ni@2D and only considered those configurations for which the E_b value is <-3.00 eV for further calculations. Out of 34, 17 configurations were falling in this range. Further, we computed the differential Gibbs free energy of H-adsorption (ΔG_H) and generated volcano plot between ΔG_H and exchange current density (i_0) as a prime indicators of HER activity. Then, we screened these configurations based on ΔG_H values that $|\Delta G_H| \leq$ to 0.5 eV, and out of 17, 10 systems were falling in this region. At last, we examined complete reaction profile of HER via Volmer-Heyrovsky (VH) and Volmer-Tafel (VT) mechanisms over the remaining 10 configurations, and the lowest activation energy for HER are 0.12 eV and 0.21 eV for Ni@AlN and 0.28 eV and 0.36 eV for Ni@h-BN via VT and VH mechanism, respectively. Our findings show Ni@AlN and Ni@h-BN could be a non-noble TM candidate for eco-operational HER catalyst.

Keywords Single-atom catalyst · Hydrogen evolution reaction · Density functional theory · Volmer-Heyrovsky mechanism · Volmer-Tafel mechanism

Introduction

The hydrogen evolution reaction (HER) is subject of pervasive research as it is one of those crucial chemical processes that leads to generation of an ecologically clean and sustainable energy source, i.e., hydrogen (H_2) [1]. The versatility of H_2 makes its production a burning need at the moment due to its expediency (i) in fuel for vehicles and spacecrafts with zero-carbon footprint [2], (ii) in fuel cells to generate electricity [3], (iii) as a compact energy carrier due to its high energy density [4], (iv) as a feedstock for various important industrial chemical processes/conversion like in synthesis of ammonia (NH_3) from N_2 [5], in CO_2 reduction to formic acid (HCOOH), hydrocarbons (C_nH_x), alcohols (C_nH_xOH), etc. [6], that sets H_2 an exemplar component in techno-chemical industries. Although, there are various chemical reactions which yield H_2 like water-gas shift reaction [7, 8], coal gasification [9], steam methane reforming [10] etc., either as a main product or by-product, but the HER has the edge among these reactions mainly due to (i) absence of carbon-containing compounds in the whole process of H_2 generation, as an effect improving the longevity of the catalyst used and (ii) decentralized production units deployment attainable at smaller scale reducing the requirements of large-unit setup and soothing the transportation issue [11, 12]. On the flip side, there are some significant issues in HER that require the time and efforts of researchers, like the existing catalyst are mainly comprised of Pt-based systems [13].

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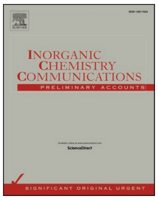

Short communication

Water-gas shift activity of atomically embedded transition-metals on AlN support: A DFT investigation

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Keywords:
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ABSTRACT

Single-Atom Catalysts (SACs) have piqued the interest of the global research community due to their remarkable catalytic activity in some key industrial chemical reactions. Herein, the catalytic efficacy of transition metals (TMs) embedded AlN (M@AlN; M = Ni, Pd, Pt, Cu, Ag, Au) are examined towards water–gas shift (WGS) reaction by employing first-principles-based, spin-polarized, van der Waals corrected, density functional theory (DFT) calculations. The strong interactions between M-atoms and AlN substrate (at Al-d site) and the higher diffusion barrier of M-atoms over AlN specifies the steadfast-stability of M@AlN. Further, the abstemious interplay between reactants (CO, OH, H_2O, CO + OH and CO + H_2O) corroborates the potency of M@AlN in harbouring the reactants. Then, to contemplate the activity of M@AlN towards WGS reaction, a well-established formate mechanism and a fairly novel OH-assistive mechanism, were considered. Predominantly, the OH-assistive mechanism determined to be more favourable than the formate mechanism. Precisely, the Au@AlN and Cu@AlN systems are deemed as most active and competent SACs for WGS reaction via OH-assistive mechanism with the required activation energy (E_a) of rate determining step (RDS) reckoned to be 0.14 eV and 0.21 eV, respectively. Moreover, the linearity of E_a with co-adsorption energy of CO–OH molecules (E_{ads}(CO + OH)) and d-band centre (ε_d) substantiate the findings. Also, the comparison between E_a and reaction energy (E_R) certifies the workability of Au/Cu@AlN towards WGS reaction. Wherefore, the investigation under discussion connotes Au/Cu@AlN can be a cogent, practicably applicable SACs for WGS reaction.

1. Introduction

The global quest of renewable and sustainable energy sources and ozone-friendly industrial exercises has reinforced the chase for ingenious catalytic operations to produce green energy sources in heap [1]. Hydrogen gas (H_2) is been viewed as a shoo-in due to its ample abundancy, high energy value, compliance in usage and ecosystem and zero-carbon footprint. One of many ways to generate ultra-pure H_2 in plenty is water–gas shift (WGS) reaction, fundamentally a reversible reaction involving carbon monoxide (CO) and water vapour (H_2O) to produce carbon dioxide (CO_2) and H_2, represented as $CO + H_2O \rightleftarrows CO_2 + H_2$ [2,3]. The WGS reaction has reaped heightened emphasis from the research community and industries across globe due to its significance in production and purification of hydrogen, in syngas conditioning to maintain CO/H_2 ratio and its environmental impact as it converts detrimental CO gas into benign CO_2 gas, placing it amongst the prime chemical reactions [4]. Howbeit, the cardinal challenges in WGS reaction are (i) to manage its slow reaction kinetics and high thermodynamics of the reaction, (ii) to avert the CO poisoning effect of the catalyst, (iii) to oversee the selectivity of the catalyst towards forming H_2 as a product and not any other CH-products (like CH_3, CH_3OH etc.) and (iv) to implement large-scaled commercialization of such catalyst [5]. Thus, the WGS reaction, owing such an essentiality from environmental and industrial point of view, and having handful of complications, requires an auxiliary attention to study it's reaction kinetics and design an efficacious and potent catalyst for functional aspect [6–8].

Historically, TMs based catalysts like Ni(1 1 1), Ni(1 0 0), Ni(1 1 0), Ni (2 1 1) [9,10] Pt-nanotubes [11], $Au_{32}M_6$ (M = Cu, Pt, Pd, Rh, Ir) nanoclusters (NCs) [12], Ag NCs [13] etc., are perceived to evince superior catalytic behaviour towards WGS reaction. However, their high cost, paucity and effectively low-metal-atom-utilization efficiency of the precious metals calls on us to look for an alternative approach to design a catalyst addressing the above issue at least without compromising the activity and selectivity for the WGS reaction. In that direction, an approach of retrenching the catalyst particle size from bulk to 2D to NCs

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