

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*



Cite This: <https://doi.org/10.1021/acs.jpca.1c02354>



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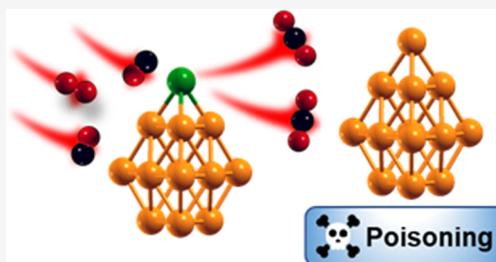


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Supporting Information

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_nCu clusters is unveiled. The search has been initiated with the examination of structural, magnetic, and electronic properties of Ni_{n+1} and Ni_nCu 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_nCu 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 ($2CO + O_2 \rightarrow 2CO_2$) 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-

Received: March 16, 2021

Revised: May 27, 2021



Uncovering the structural, electronic and vibrational properties of atomically precise Pd_mCu_n clusters and their interaction with CO₂ molecule

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ARTICLE INFO

Article history:

Received 1 April 2019

Received in revised form 5 December 2019

Accepted 6 December 2019

Available online xxxx

Keywords:

Icosahedral Pd_mCu_n clusters

Density functional theory

Structural stability

Raman spectra

CO₂ adsorption

ABSTRACT

In this work, we address the structural stability, electronic properties and effect of metal-metal interaction on Raman spectra of icosahedral (*Ih*) Pd_mCu_n ($m + n = 13$) clusters using first principles calculations based on dispersion-corrected density functional theory (DFT-D2). Initially, we investigated the relative stability of *Ih* Pd_mCu_n clusters over monometallic *Ih* Pd₁₃ and Cu₁₃ clusters by calculating the average binding energy per atom, mixing energy, second order energy difference and average bond length. The *Ih* Pd₅Cu₈ is the most stable bimetallic cluster with the 2.88 eV, -0.218 eV and 0.678 eV average binding energy per atom, mixing energy and second order energy difference, respectively. The main goals of the present study are to figure out the chemical enhancement, modulation in electronic properties and Pd-Cu bond length in *Ih* Pd_mCu_n clusters after systematic doping of Cu-atom. Further, to examine the doping effect of Cu atom in Pd cluster, we have also analysed the Raman spectra of *Ih* Pd_mCu_n clusters. In case of *Ih* Cu₁₃ cluster, the contraction of Cu-Cu bond length as compared to its bulk form resulted in a significant blue-shift of characteristic Raman peak (212 cm⁻¹) of *Ih* Pd₁₃ cluster. Finally, the interaction mechanism of the CO₂ gas molecule over Pd-Cu alloy clusters have also been studied to understand the effect of composition on reactivity of CO₂ gas molecule.

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1. Introduction

Palladium (Pd) nanoclusters with precise number of atoms exhibit a range of fascinating structural, electronic, vibrational and catalytic properties, which are unexpected from bulk counterpart [1–5]. This diverse contradiction in properties of Pd nanoclusters from their bulk counterpart is attributed to the variety of factors such as high specific surface area, electronic shell closing (i.e. jellium model), geometric shell enclosing, superatomic character (the sharing of electrons between atoms is not same compared to their bulk systems) and quantum confinement. Due to their low cost and abundance with better thermal stability, Pd nanoclusters are unarguably the most active frontiers for their utilization in the industrial chemistry and heterogeneous catalyst [6–10]. To date, a number of experimental and theoretical studies on Pd nanoclusters [11,12] have been carried out to develop in-depth understanding of their minimum energy configurations for their utilization in hydrogen storage [13], oxidation and reduction processes [14,15] and hydrogenation [16]. The adsorption energetics, dissociation and electron transfer properties of CO, NO, H₂ etc., gas molecules over Pd

nanoclusters have been successfully examined using density functional theory (DFT) based calculations [17–20]. Correspondingly, Sousa et al. [21] revealed that the Pd is a very sensitive catalyst in creating the inter-metallic bonds. Notably, it is observed that the tailoring of catalytic, electronic, magnetic and optical properties can be achieved through the minor changes in the size, varying the chemical composition and order of constituent atoms of Pd bimetallic nanoclusters [22]. For instance, the recent advancement in the DFT calculations and experimental fabrications demonstrated that the impurity/doping can strongly influence the stability and physicochemical properties of the host clusters i.e., Pd-Ag [22], Pd-Co [23], Cu-Ni [24], Cu-V etc. [25]. Mu et al. [26] found that the doping of Mn atom enhances the structural stability and magnetic moment of the Pd clusters. The Pd bimetallic nanoclusters with transition metal such as copper (Cu) with various structural configurations and compositions are being explored by many researchers for their applications in oxygen reduction, oxidation of alcohol, oxidation reactions of formic acid etc. [27–29]. It has been reported by Wu et al. [27] that the Cu atom in the Pd-Cu clusters enhances the catalytic activity. Saputro et al. [30] found that the adsorption strength of CO₂ with pure Pd clusters enhances after the doping of transition metal atoms (M = Ni, Cu, Pt, Rh) and predicted that the Pd₆M clusters facilitate CO₂ hydrogenation for the production of HCOO/COOH. Though,

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Degrading CO poisoning over foreign atom seized Ag_{12}M icosahedral bimetallic clusters

Cite as: AIP Conference Proceedings **2265**, 030612 (2020); <https://doi.org/10.1063/5.0016620>

Published Online: 05 November 2020

Bhumi A. Baraiya, Venu Mankad, and Prafulla K. Jha



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Cite as: AIP Conference Proceedings **2115**, 030543 (2019); <https://doi.org/10.1063/1.5113382>
Published Online: 12 July 2019

Bhumi A. Baraiya, Venu Mankad, and Prafulla K. Jha



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Benzylic C_{sp}³-H Bond Oxidation on the (111) Facets of Octahedral Cu₂O Nanocrystals

Neelam Gupta, Hiren K. Machhi, Bhumi A. Baraiya, Saurabh S. Soni, Ashutosh V. Bedekar, Prafulla K. Jha, and Hemant P. Soni*



Cite This: <https://doi.org/10.1021/acsanm.1c01169>



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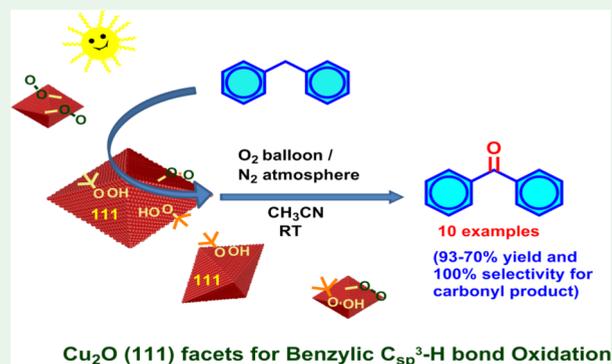


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Supporting Information

ABSTRACT: Octahedral-shaped Cu₂O nanocrystals (o-Cu₂O NCs) have been synthesized by the wet chemical method. By powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), and high-resolution transmission electron microscopy (HRTEM), it was confirmed that the synthesized material was Cu₂O NCs with octahedral morphology with the (111) facets exposed. The synthesized o-Cu₂O NCs have been explored as the catalyst for benzylic sp³ C-H bond oxidation. Reaction parameters like oxidants, solvents, temperature, and reaction time were optimized for the model oxidation reaction involving diphenylmethane (DPM) as a substrate. The results obtained indicate that the substrate having benzylic sp³ C-H bond energy less than 90 kcal/mol can be easily oxidized to the corresponding carbonyl compound in the presence of these nanocrystals at RT with stirring the reaction mixture over the bar magnet (up to 92% conversion). The oxidation of Cu₂O to CuO occurs all together with the progress of the reaction when carried out under typical aerial atmosphere in the presence of light (daylight and mercury compact fluorescent lamp (CFL) tubes prevailing in the laboratory). However, this can be avoided when the reaction was carried out in the dark or inert atmosphere or continuous flow of oxygen gas. A reaction mechanism has been proposed based on the free radical scavenger experiments and other special experiments. Also, the chemical events that occurred in the proposed reaction mechanism have been supported by mass spectral and electrochemical analysis, density functional theory (DFT) calculations, and some other special experiments. Furthermore, Brunauer-Emmett-Teller (BET) surface area analysis was carried out to confirm the catalytic effect due to facets. The experimental results also lead to proving the activation of O₂ molecule through single electron transfer (SET) mechanism on the (111) facets of semiconducting Cu₂O NCs in light.



KEYWORDS: facet-mediated catalysis, Cu₂O octahedral, benzylic C_{sp}³-H oxidation, C-H activation, oxidative valorization

1. INTRODUCTION

Selective functionalization of C-H bonds is challenging since it requires activation of a stubborn C-H bond/s toward the reagents or catalytic systems. This protocol is important in organic synthesis as it can reduce many steps toward the target product in total synthesis and save precious resources and affect the overall cost.¹ Development of the mild reagents or the catalytic systems that can functionalize the desired C-H bonds in the complex molecular framework at any stage of synthesis (late-stage functionalization) without affecting the surrounding molecular environment is the “holy grail” of chemistry.² The situation becomes more complicated when multiple C-H bonds having similar environments are present in a single molecular framework like simple hydrocarbon molecules. Also, it is difficult to predict which C-H bond becomes activated in the presence of multiple functional groups in a complex molecule like natural products.³ Many strategies have been developed for this purpose. The methods involving activation of benzylic sp³ C-H bonds and their

direct oxidation to aromatic carbonyl have particular importance due to their applications in pharmaceutical industries as API, leading to the essential drug molecules and agrochemicals, paint, and pigment industries.⁴

Direct oxidation of benzylic sp³ C-H to carbonyl is tricky and involves metals like Au,⁵ Pd,⁶ Rh,⁷ Ru,⁸ and Re⁹ (group 4d and 5d metals)-mediating catalysis. The Friedel-Crafts acylation of aromatics is a well-known synthesis protocol for this purpose. However, it involves metal halide-based Lewis acid catalysis. Strong oxidizing agents like acidic solutions of KMnO₄ or CrO₃ can do the same job. However, these protocols produce environmentally toxic by-products during

Received: May 1, 2021

Accepted: July 6, 2021

First-Principles Calculations of the Effects of Edge Functionalization and Size on the Band Gap of Be₃N₂ Nanoribbons: Implications for Nanoelectronic Devices

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Cite This: <https://dx.doi.org/10.1021/acsanm.0c02809>

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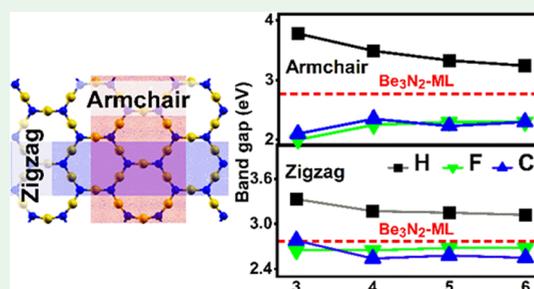
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Supporting Information

ABSTRACT: First-principles calculations are carried out to address the structural stability and width-dependent electronic properties of the hydrogen (H)-, fluorine (F)-, and chlorine (Cl)-passivated armchair and zigzag nanoribbons (NRs) of beryllium nitride (Be₃N₂). The negative value of cohesive and edge formation energies implies the thermodynamic stability of NRs. With regard to the electronic properties, all NRs are direct band gap semiconductors and the band gap (ranging from 2.0 to 3.78 eV) strongly depends on the edge functionalization. The band gap inversely varies with the ribbon width for H-passivated NRs. Interestingly, band gap is almost width-independent for the F- and Cl-passivated NRs. The edge asymmetric effect (σ and π^* orbitals) causes the lower band gap in F- and Cl-passivated NRs. The significant orbital contribution of atoms is analyzed from the projected density of states and partial charge density plots of the valence band maximum and conduction band minimum. The work function (WF) of NRs is quite sensitive to edge functionalization and confirms the tunable emission behavior of the electrons. The adjustable band gap and the WF of NRs approve their efficient applications in nanoelectronics such as field-emission and optoelectronic devices.

KEYWORDS: Be₃N₂ nanoribbons, edge passivation, structural stability and edge formation energy, electronic band structure, work function



1. INTRODUCTION

Two-dimensional (2D) materials hold great promises for their applications in the present and future nanoelectronics and continuously attract more and more attention due to their unlocked phenomena.^{1–4} Two-dimensional honeycomb graphene, originator of the 2D family has received prominence⁵ for its symbolic feature, i.e., Dirac cones at the Fermi level. Graphene has many promising properties like Klein tunneling,^{6,7} the room temperature quantum Hall effect,⁸ ferromagnetism and superconductivity^{9,10} in twisted bilayer graphene with very small angles, ballistic transport,¹¹ and superior thermal conductivity.¹² The gapless nature of graphene restricts its applications in nanoelectronics.¹³ In light of this, etching or patterning of graphene along a specific lattice direction, forms one-dimensional (1D) strips called graphene nanoribbons (GNRs), is considered as an excellent strategy to open up a band gap in graphene.^{1,14,15} The GNRs are categorized into two kinds of edges, namely, the armchair and the zigzag defined by the relative orientation of the hexagons relative to the ribbon length.¹⁵ The low-dimensionality-induced quantum confinement and edge effects, i.e., the presence of dangling bonds are the cause of the modulated electronic, optical, and magnetic properties of GNRs, which makes them different from their corresponding 2D and bulk counterparts.^{16–18} In recent years, the transport properties of the zigzag-edged nanoribbon of graphene-like materials, δ -

graphyne and α -2 graphyne, have been well investigated by Cao et al.¹⁹ and Peng et al.,²⁰ respectively, for their utilization in spin-resolved devices. However, the pristine NRs have in general limited applications. The functionalization is one of the most utilized approaches to engineer desired electronic properties of GNRs, e.g., edge passivation, edge reconstruction, doping, surface adsorption, defect engineering, and strain engineering.^{21–23} It was reported that the coverage-dependent functionalization displays a narrower energy band gap for F-AGNRs and Cl-AGNRs than for H-AGNRs due to structural deformations. While, a reduced band gap observed for OH-AGNRs due to chemical interactions between neighboring OH groups.²⁴

Beyond graphene, the scientific community has successfully predicted and realized several novel 2D nanosystems.^{25–32} The functionalized NRs of these 2D family members seize the attention attributed to their exceptional electronic properties. For instance, the transport properties with negative differential

Received: October 20, 2020

Accepted: December 9, 2020



Nitrogen-decorated borophene: An empowering contestant for hydrogen storage



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ARTICLE INFO

Keywords:

Borophene
N-decoration and doping
DFT-D2
H₂ storage
Gravimetric density

ABSTRACT

Hydrogen (H₂) being, pure source of energy with high energy capacity is an excellent candidate for the energy future resource. In this study, we systematically investigate the H₂ storage capacity of pristine, nitrogen (N)-decorated and N-doped borophene sheets by means of first-principles calculations based on density functional theory (DFT). Semi-empirical dispersion correction (D2) has also been incorporated in all calculations for the consideration of the long-range interaction. The adsorption site, adsorption energy, electronic structure, charge transfer and hydrogen storage performance of pristine, N-decorated and N-doped borophene sheets are discussed in detail. N atom binds strongly with borophene sheet without the issue of clustering. The decoration of N atom significantly enhances the H₂ adsorption strength of borophene sheet compared to the pristine one. Further insight into the interaction of H₂ with considered systems is elaborated by calculating projected density of states (PDOS) and charge density plots. Our calculation shows that N-doped and N-decorated borophene sheets achieve 1.51 wt% and 6.22 wt% gravimetric density, respectively for the H₂ storage.

1. Introduction

Hydrogen (H₂) is considered as an excellent bidder in replacing the non-renewable resources owing to its excellent properties such as its weightlessness, cost-effective, natural abundance, and environment-friendly [1,2]. However, it faces a genuine problem of transportation, security and storage due to its quality of being easily ignited and burns rapidly [3]. Therefore, designing a technology which deals with both high safety and efficiency is important [3]. In this regard, it requires a host material with the high surface-to-volume ratio, higher adsorption energy of H₂ and especially lightweight [4]. The vision of the H₂ economy is approaching to reality with the advancement in technology of the photocatalytic water splitting [5], dissociation of formic acid via metal catalysts [6] and decomposition of NH₃ over defected h-BN [7]. Recent research and evolution in the fabrication of two-dimensional (2D) materials have accelerated their practical and commercial utilization for H₂ storage [8]. Inspired by the fabrication of graphene [9], numerous other 2D materials such as pristine and functionalized boron nitride nanostructures [10,11], phosphorene [12,13], C₂N [14] and MoS₂ [15] have been fabricated experimentally and studied

theoretically in the quest of finding potential host material for H₂ storage. Even though the graphene was foreseen as H₂ storage material due to its advantage of being lightweight and high surface area but pure graphene could not meet the demand of high adsorption enthalpies at room temperature [16,17]. Scientists have developed an effective way to improve the H₂ storage efficiency over 2D materials via decorating/doping the substrate with metallic adatoms and creation of defects [12,14,15,18–21]. Consequently, numerous 2D materials have been comprehensively screening out with decoration of alkali and other metal adatoms with excellent ability towards the H₂ storage capacity [12,14,15,18–20].

For instance, Al and Li decorated graphene has been reported to have an enhancement in adsorption energy of 0.079 eV/H₂ [18] and 0.136 eV/H₂ [19], respectively compared to pristine graphene. Yu et al. [12] reported the 4.40 wt% enhancement in the gravimetric density for Li-decorated phosphorene than the negligible storage capacity in its pristine form. The Li-decorated C₂N [14] and MoS₂ [15] have been reported to have a significantly large 13.0 wt% and 4.4 wt% gravimetric density respectively. The defect engineering is an alternative way to boost the H₂ storage capacity of potential substrates [13,21].

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<https://doi.org/10.1016/j.apsusc.2020.146852>

Received 20 February 2020; Received in revised form 20 May 2020; Accepted 30 May 2020

Available online 02 June 2020

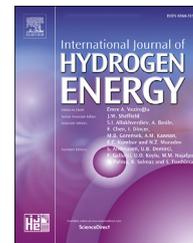
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Catalytic activity and underlying atomic rearrangement in monolayer CoOOH towards HER and OER

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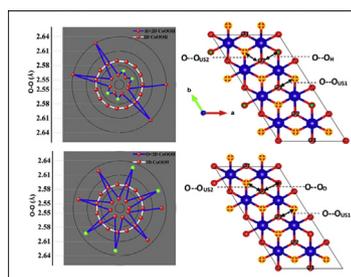
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HIGHLIGHTS

- Activity of 2D CoOOH investigated for HER and OER via DFT calculations.
- Interplanar O–O separation on adsorption of H/O on pristine 2D CoOOH.
- Adsorption of H and O atom turns 2D CoOOH into metallic.
- 2D CoOOH is a potential candidate for better HER activity as compared to OER.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 28 March 2019
Received in revised form
21 February 2020
Accepted 5 March 2020
Available online xxx

Keywords:

2D CoOOH
Adsorption
Hydrogen evolution reaction (HER)
Oxygen evolution reaction (OER)
Electronic density of states

ABSTRACT

For efficient hydrogen and oxygen production, design and synthesis of cost-effective, stable and active materials are inevitable. In this work, the catalytic activity of 2D CoOOH towards hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) has been investigated using first principles calculations based on density functional theory. The adatom induced structural rearrangement have been investigated from structural parameters as well as charge redistribution in 2D CoOOH. The preferred site for hydrogen and oxygen adsorption were found to be the top site of oxygen atom of 2D CoOOH. The catalytic activity of HER and OER towards 2D CoOOH was studied by calculating the Gibbs free energy. Our study revealed that the 2D CoOOH serve better as a catalyst for HER than OER with adsorption energy of -0.45 and -3.68 eV respectively suggesting its efficient use for hydrogen production. We further investigated the changes in electronic properties of 2D CoOOH on adsorption of hydrogen and oxygen atom.

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<https://doi.org/10.1016/j.ijhydene.2020.03.075>

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Incisive study on stability and vibrational properties of NO_x (x = 1 to 3) over Pt surfaces: A comparative analysis

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ARTICLE INFO

Keywords:

NO_x adsorption
Pt surfaces
van der Waals interaction
Adsorption energetics
Vibrational frequencies

ABSTRACT

The catalysts have been extensively investigated for the reduction/oxidation of exhaust gases to reduce the emission of hazardous gases such as nitric oxide (NO) and nitrogen dioxide (NO₂) for the improvement of air quality. In this regard, we have focused on a detailed systematic study of NO_x (where x = 1 to 3) adsorption over platinum (Pt) surfaces within the framework of density functional theory (DFT) calculations. In addition to this, modified van der Waals (vdW) interaction has been taken into account for the consideration of long-range interaction requires for a precise description of adsorption mechanism of gases over metal surfaces. We investigated the adsorption geometries, energetics, electronic properties, and vibrational frequencies of NO_x over Pt(111) and Pt(100) surfaces. Adsorption of NO_x over Pt surfaces with diverse geometries has been considered in search of the optimal adsorption configuration. The inclusion of dispersion correction (D2) strengthens the bonding of gases with the substrate without influencing their geometries and electronic structure. The adsorption energy of NO_x over Pt(100) is found to be higher compared to Pt(111) surface. Thus, our results point out that Pt(100) is the optimal surface for NO_x adsorption and provide a clear and simple way to design novel heterogeneous catalyst for NO to NO₂ conversion.

1. Introduction

Nitric oxide (NO) is a precursor for the smog and acid rain formation on the ground and tropospheric levels that cause a serious environmental threat. The chief sources of the NO on the ground level are automobile exhaust and flue gases from coal-fired boiler plants. With growing concerns for the environmental protection provoked the legislatures to install stringent regulations for pollutant emissions. The reduction of nitrate (NO₃⁻) has recently gained renewed attention in view of its relevance to pollution control. The reduction of NO to nitrogen gas (N₂) in order to meet the environmental regulations have been a major challenge for power plants, process industries, and motor vehicles. In this regard, a catalytic approach is the most direct method for the reduction of NO to N₂ [1,2]. The reduction of NO_x to N₂ encompasses five general steps (1) oxidation of NO to NO₂, (2) sorption of NO₂ and NO leading to nitrite (NO₂⁻) and NO₃⁻ species, (3) reductant evolution, (4) releasing NO_x and (5) reduction of NO_x to N₂ [1–5]. However, the current catalysts are under development and those reported in the literature did not exhibit sufficient activity and deactivation-resistance for the control of NO emission from lean-burn engines and fossil fuel plants.

The reduction of NO_x is the most promising approach that plays a significant role in three-way catalyst [6] and is applied for the treatment of industrial wastewater, whereby NO₃⁻ is transformed into harmless N₂ with the usage of platinum (Pt) as a heterogeneous catalyst [7]. Usually, metal surfaces are well known to provide a template for reactions to proceed and actively take part in the surface reactions. Up till now, various facets of Pt surfaces have attracted and motivated applied surface scientists due to their benchmarking catalytic activity towards numerous chemical reactions (oxidation/reduction) and potential applications in building nanocatalyst [3,4]. Among them, Pt(111) and Pt(100) surfaces have gained considerable attention which is attributed to the consuming 80% and 20% Wulff surface contribution (the percentage of the area exposed by surface) respectively i.e. strongly influence their performance in sensing, surface-enhanced spectroscopies and catalytic reactions [8]. The “simple” and well-defined NO/Pt(111) system has been widely addressed in experimental [9–14] as well as theoretical [15–26] studies. For instance, in the early 1980s, Masel [27] studied dissociation of NO over a series of stepped Pt surfaces and investigated the strong dependency of this reaction to the surface structure. Getman and Schneider [15] showed that the higher surface coverages favour migration of NO and NO₂. Zeng et al. [16]

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<https://doi.org/10.1016/j.susc.2019.121467>

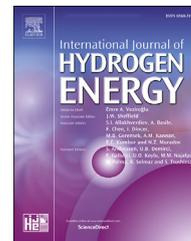
Received 9 April 2019; Received in revised form 3 June 2019; Accepted 19 July 2019

Available online 23 July 2019

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Investigating hydrogen evolution reaction properties of a new honeycomb 2D AlC

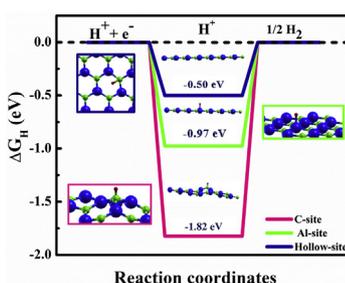
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HIGHLIGHTS

- Investigation is made to shed light on HER activity of h-AlC ML.
- The density of states indicates metallic nature of h-AlC ML.
- Various sites of h-AlC ML play key role in improving HER activity.
- Supercell of h-AlC 4×4 exhibits noteworthy HER activity compared to 3×3 supercell.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 April 2019

Received in revised form

16 September 2019

Accepted 13 October 2019

Available online 13 November 2019

Keywords:

DFT

h-AlC ML

Adsorption

Hydrogen evolution reaction (HER)

Work function

ABSTRACT

The hydrogen due to its high mass energy density is a new renewable, economically viable and clean resource. The most eco-friendly and economical approaches for the generation of hydrogen through hydrogen evolution is electrochemical water splitting. The two-dimensional (2D) nanomaterials have been recently found as potential candidates as non-noble metal catalyst for hydrogen evolution. In this work, we have systematically studied the structural and electronic properties of the newly predicted hexagonal-aluminium carbide monolayer (h-AlC ML) under the framework of dispersion-corrected density functional theory (DFT) calculations. The calculated electronic total density of states (TDOS) of h-AlC ML predict its metallic nature in contrast to other polar honeycomb 2D materials which are either semiconducting or semimetallic. The metallic behavior of h-AlC monolayer which motivates us to investigate its HER activity results due to the presence of delocalized charge density near Fermi level. Thus, we have investigated the HER activity of h-AlC ML by calculating hydrogen (H) adsorption energy (ΔE_H) and Gibbs free energy (ΔG_H) at three different sites of the 3×3 and 4×4 supercells of h-AlC ML; top of carbon atom (E_{H-C}), top of aluminium atom (E_{H-Al}) and hollow site ($E_{H-Hollow}$). Our results show that the hollow site is most catalytically active site in both supercells of h-AlC ML. We believe that our results will inspire experimentalists to fabricate this new 2D material for achieving the desired range of HER activity.

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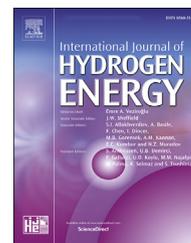
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<https://doi.org/10.1016/j.ijhydene.2019.10.131>

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Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/ije

O-assisted and pristine Au-Pt(100) surfaces: A platform for adsorption and decomposition of H₂O

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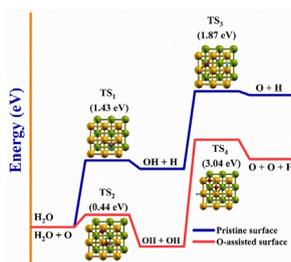
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HIGHLIGHTS

- H₂O adsorption and decomposition were studied on clean and O-aided Au-Pt(100) slabs.
- Added O is a key element and un-availing extra energy for H₂O to OH conversion.
- The co-adsorbed O atom obstruct the dissociation of OH over Au-Pt(100) surface.
- The energy profiles of activation energies with transition states are demonstrated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 21 April 2019

Received in revised form

19 June 2019

Accepted 21 June 2019

Available online 25 July 2019

Keywords:

Pristine and O-assisted Au-Pt(100) surfaces

DFT

ABSTRACT

Adsorption and decomposition of water (H₂O) over pristine and oxygen (O) assisted Au-Pt(100) surfaces were systematically explored using *ab initio* calculations based on density functional theory (DFT). To consider the long-range interaction, semi-empirical dispersion correction (D2) was included in all calculations. The most preferable adsorption sites for H₂O and its fragments such as OH, O, and H, over clean and O-assisted Au-Pt(100) surfaces were determined by examining adsorption energy with different configurations. Our calculations showed that the H₂O prefers top site over Au atom while OH, O, and H prefer to be adsorbed over bridge position. In present study, we determine the best possible co-adsorption sets for considered adsorbates. We further investigated the transition states, dehydrogenation process, and activation energies for extracting H from adsorbed H₂O over both pristine and O-aided Au-Pt(100) surfaces. It was found that the O promotes H₂O dissociation significantly by diminishing the barrier energy. The decisive role played by O

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<https://doi.org/10.1016/j.ijhydene.2019.06.201>

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Cite this: *Phys. Chem. Chem. Phys.*,
2019, 21, 17010

Unveiling chemical reactivity and oxidation of 1T-phased group VI disulfides†

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Transition metal dichalcogenides (TMDs) are of particular interest because of their unique electrical and optical properties that evolve from the quantum confinement and surface effects. However, their long-term stability in air is proved to be a main concern for practical applications of the ultrathin materials, especially for TMDs with 1T phased structures. Here, we provide an in-depth understanding of the oxidation and degradation mechanisms of monolayers of group VIB disulfides, including TiS₂, ZrS₂, and HfS₂. As the atomic radius of the transitional metals increases, their air stability significantly decreases and the oxidation mechanisms are quite different from one another. In particular, the oxygen induced oxidations initiated at both the surface vacancy sites and edges of ZrS₂ and HfS₂ are studied, while the oxidation of TiS₂ starts at the edges and water plays a crucial role in the continuous oxidation process. Moreover, the defective sites expose the metals for activation and dissociation of either oxygen or water, causing the breakdown of the systems eventually. Meanwhile, these sites can be used as active centers for specific applications in catalysts and surface functionalized materials.

Received 27th May 2019,
Accepted 13th July 2019

DOI: 10.1039/c9cp02985k

rsc.li/pccp

Introduction

The rise of graphene has inspired intense interest in other two-dimensional semiconducting materials such as boron nitride (BN), black phosphorus (BP) and transition metal dichalcogenides (TMDs).^{1–4} Among them, TMDs, which have a general chemical formula of MX₂, where M is a transition metal (*e.g.*, Mo, Nb, and Hf) and X is a chalcogen, generally, S, Se, or Te, possess transition metal properties based on d-electrons that can be advantageous to modulate a wide variety of material properties.^{5,6} The properties of bulk TMDs are diverse, ranging from semiconductors such as MoS₂ and WS₂, and semimetals such as WTe₂ and TiSe₂, to puremetals such as NbS₂ and VSe₂. Layered TMDs can be produced in bulk form but also as few-layered and monolayered sheets. The fabrication methods have advanced to a state that large-area ultrathin TMD films are routinely prepared on a diverse range of substrates by chemical vapor deposition (CVD).⁵ In particular, layered TMDs have been reported to demonstrate a high electrocatalytic activity towards hydrogen production,

especially with molybdenum sulfide (MoS₂), which has been recently considered as a promising and efficient nonprecious metal catalyst for the hydrogen evolution reaction (HER).^{7–9} Each monolayer consists of a hexagonal metal plane sandwiched between two hexagonal chalcogen planes, with two possible polytypes, namely the trigonal prismatic phase (2H) and the octahedral phase (1T). In general, the ultrathin materials preserve the bulk properties and also lead to additional characteristics due to confinement effects. Therefore, the family of TMD based materials exhibits a unique set of properties, making them potentially useful for many applications including catalysts, batteries, field-effect transistors (FETs), ultra-sensitive chemical sensors, flexible electronics, and spintronics.^{10–14}

Compared with the fast degradation of black phosphorus in air, many TMDs provide much higher stability under ambient conditions. In several cases of TMDs, MoS₂ for example, they can survive under air exposure at room temperature and atmospheric pressure for a considerably long time (maybe up to years) without significant degradation.¹⁵ Still, experiments and theoretical calculations revealed that monolayers of MoS₂ and WS₂ exhibited severe aging effects, including extensive cracking, changes in morphology, and severe quenching of the direct gap photoluminescence.^{15,16} In general, most TMDs suffer from oxidation at different levels depending on the systems, and the specific issue is more obvious for 1T-phased TMDs, such as HfS₂ for example.¹⁷ The oxidized TMDs, can alter the electronic, optical, and tribological properties of the corresponding MX₂ compound consequently.^{16,18} The presence of small bubbles is

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9cp02985k

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Catalysis

Adsorption Energetics of Atoms and Diatomic Gases with Electrocatalysis Approach towards Hydrogen and Oxygen Evolution Reaction on Pt Surfaces

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The computational study of chemisorption of atoms and gases intends to provide a great insight in the developing of an up-to-date elusive assessment of a correct choice of the site for the adsorption on platinum surfaces i.e. a key step for many chemical processes in catalysis and surface sciences. A density functional theory (DFT) calculation using generalized gradient approximation (GGA) scheme and supercell model with the inclusion of modified dispersion correction (DFT–D2) has been performed to explore the adsorption trends and evaluate adsorption energies of H, C, N, O, and S (atoms) and H₂, C₂, N₂, O₂, and S₂ (homonuclear diatomic molecules) on Pt(111) and Pt(100) surfaces for multiple sites, in search of the most active catalytic site. Our chemisorption data revealed that the

incorporation of DFT–D2 correction strengthens the adsorption energy by the amount of 0.05 eV to 0.67 eV for atoms and gases. Finally, this study focuses on unveiling catalytic activity of the two seemingly simplest electrochemical reactions; the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) on numerous sites of Pt surfaces using the adsorption strength of H and O with the inclusion of DFT–D2 correction, which shows the good consistency with the results of standard DFT calculations. The highest catalytic activity towards HER is shown by Pt(100) in contrast to the best OER catalytic activity by Pt(111) surface with their respective most favorable 4fh and top sites.

1. Introduction

Platinum and platinum-based alloys serve as the brilliant catalyst for the catalytic oxidation and reduction activity with carbon monoxide and nitric oxide, respectively.^[1] Since the development of sustainable energy solutions represents one of the most important scientific and technical challenges of our time, heterogeneous catalysis is at the heart of the problem. These are the key reactions for improving air quality, especially in the automotive industries, where platinum is used as the active metal in three-way catalyst.^[2–5] Over the past few decades, the interaction of atoms or molecules with the platinum surfaces are intensively studied in surface science and achieved a great deal of attention both experimentally^[6–14] as well as computationally^[15–34] majorly due to its scientific and industrial importance in chemical and petroleum applications.

Furthermore, the chemisorption of atoms (H, C, N, O, and S) takes an important role in the reactions of the chemical industries mainly contained in the reactions of hydrocarbon production, ammonia synthesis, oxidation, corrosion, and petroleum re-forming.^[6–34] The intrinsically fundamental interest of the interaction of atoms with metal surfaces is relevant to

catalytic chemistry. The adsorption properties of many atoms and small molecules on transition metals have been studied by Hammer and Nørskov^[15] which primarily depends on the electronic structure of the surface, which in turn is determined by its geometric structure and chemical composition. Nevertheless, platinum is one of the most expensive metal and consequently, our main interest is to modify its properties to achieve higher activity or selectivity in a catalytic reaction so that less metal would be required. In this regard, computational simulations can deliver useful and rational perspectives into chemical reactions by predicting a system's geometric and/or electronic structure at the atomic scale.^[15–34]

Atomic and molecular interactions of hydrogen^[8–9,17–23,29–32] and oxygen^[10–11,24–28,30] are most intensively and extensively studied on platinum surfaces which play an important role in numerous processes central to clean energy sources. Simultaneously, it will provide a platform to study the hydrogen/oxygen bonding between intermediates for the many chemical reactions which are performed on the transition metal surfaces. In the past few decades, countless experimental and DFT studies have been carried out for atomic hydrogen^[8–9,17–22,29–32] and oxygen^[10–11,24–28,30] adsorption on platinum surfaces and found that the fcc hollow is the most stable adsorption site on Pt(111) surface whereas hcp and top are less stable for the adsorption of H and O. However, for the Pt(100) surface bridge site is the most promising site. Further, sulfur and its compounds are of considerable interest due to their wide applications in hydrodesulfurization of hydrocarbons and use as a prototype system to develop the better understanding of the poisoning of metal by sulfur compounds. Studies on the

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/slct.201802072>

Vibrational properties of III-V semiconductor in wurtzite phase: A comparative density functional theory study

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Citation: [AIP Conference Proceedings](#) **1832**, 090043 (2017); doi: 10.1063/1.4980596

View online: <http://dx.doi.org/10.1063/1.4980596>

View Table of Contents: <http://aip.scitation.org/toc/apc/1832/1>

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