Adsorption Study of Carbon Monoxide on Modified Metal and Non-metallic Surface Using Density Functional Theory: A Short Review Towards Functional Materials

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Abstract. Carbon Monoxide is an established pollutant with high indexed hazard potential for human being and environment and its omnipresence in indoor and outdoor air, has garnered specific research interest for real time detection of the same at trace level of existence. Extensive spectrum of research for development of Carbon Monoxide sensors are therefore being carried out and pursuit for efficient and smart materials constitute the core of such research efforts. The most common technique of sensing these gas molecules is to detect them with various adsorption materials, such as metal, semi-conductor metal oxides like MnO_2, MoS_2, and carbon-based materials, among others. Doping transition metal atoms in adsorbent materials has also been shown to be beneficial in the gas adsorption process. In order to have a predictive command over development of smart functional materials for detection of Carbon Monoxide, the Density Function Theory calculation is still a time-tested tool for analyzing the adsorption properties of pollutant molecules on various materials at the microscale levels to comprehend adsorptive reactions, adsorbents reactivity, and structure activity relationships, that can provide theoretical guidance for scientific experiments. This review presents the adsorption models and surface properties of CO gas molecules on metal and nonmetallic surfaces by Density Function Theory calculations in recent years. This review opens up the theoretical background for DFT based molecular adsorption studies and some of the recent reports of research pertinence.

Keywords: DFT · Carbon Monoxide · Functional Materials

1   Introduction

Deployment of computational aids for modelling of physical systems dates back to the age of World War II, with is prominent role in Manhattan Project. Through an ever-maturing journey of over seventy years, computational algorithms have succeeded to reach a better apex every other day and have attracted researchers from all strata of science and technology towards applications that encompass initial designing of experiments to complex modelling of subatomic regime. Computational tools have allowed to reveal predictive scenario of hitherto unseen and has allowed to design extremely complicated experiments that could be otherwise costed heavily with definite possible errors. They have allowed to do things, that were otherwise difficult to achieve with direct experiment. As on date, computational tools have emerged as first hand cheaper and faster solution to critical problems, which might have required complex machinery to achieve [1]. Computational tools have not only augmented laboratory experiments as potent precursors but has proved its potency towards in-depth understanding of physical and chemical phenomenon through computer simulation derived from numerical analysis and theoretical considerations to solve problems. The scientific computing approach provides understanding, mainly through the analysis of mathematical models.

Among the different potent areas of application, computational simulations have proved to be an indispensable tool to investigate gas molecule adsorption on the sensing materials at molecular or the atomic level. Density functional theory (DFT), a quantum mechanics-based electronic level computational simulation technique, has garnered tremendous attention among researchers in the domain of chemical sensing. It has notable extent of reliability and broad application arena, which is of great value in material computational simulation [2]. In last ten years, Density Functional Theory have been extensively applied to study of the chemical reaction and interfacial chemical reactions [3, 4]. A large gamut of reports have proved the accuracy of DFT calculations by comparing with experiments [5]. Most of the research papers on gas adsorption by DFT calculations have primarily concentrated on low-index surfaces of pure metals and alloys.

Adsorption study of Carbon Monoxide (CO) on different sensor surfaces is appealing from both scientific and technical interest considering the extreme perilous effect and pervasive presence of CO.

This short review presents recent work carried out for CO gas adsorption and diffusion on metals, metal oxides and non-metallic surfaces by DFT calculations. A brief introduction of the density functional theory followed by review of recent work carried out involving dissociative adsorption of gas molecule, adsorption of atom and diffusion of gas molecule by DFT calculations has been provided. Finally, challenges and opportunities with adsorption and diffusion studies of gas molecule on surface has been given.

2   Density Functional Theory

In 1964, Hohenberg and Kohn studied Thomas-Fermi model for the electronic structure of materials and proposed two fundamental theorems that resulted in Density Functional Theory (DFT) [6]. Experimented through time, DFT has proved itself to be an

indispensable tool for theoretical study of solids. Later, Nitya Nanda et.al proposed to derive ground-state energy from Schrodinger equation, which is uniquely determined by the density number of particles [7]. Another theorem is related to condition of constant number of particles, the electron density that minimizes the energy of the overall functional, which is the ground state energy [8]. Thus, by finding charge density wave function in three spatial variables, one can reach to solution of Scrodinger equation. Finally, Scrodinger equation is used to obtain ground-state energy.

Hohenberg-Kohn theorem described energy function as a single electron wave function as -

$$E[\{\psi\}] = E_{known}[\{\psi i\}] + E_{xc}[\{\psi i\}] \tag{1}$$

where,

$$E_{known}[\{\psi i\}] = \frac{h^2}{m} \sum_i \int \psi i^* \nabla^* \psi i d^3 r + \int v(r) n(r) d^3 r + \frac{e^2}{2} \iint \frac{n(r) n(r^*) d^3 r d^3 r^*}{|r - r^*|} + E_{ion} \tag{2}$$

In above formula, the first term represents the electron kinetic energies, second term represents the coulomb interaction between the electrons and the nuclei, while the third term represents coulomb interaction between pair of electrons and last term represents coulomb interaction between pair of nuclei, respectively.

$E_{xc}[\{\psi i\}]$ represents exchange-correlation functional.

In pursuit to correct electron density, Kohn and Sham solved the problem of finding solution to Scrodinger equation wave function [9].

Final form of equation obtained is as follows:

$$\left[-\frac{h^2}{2m} \nabla^2 + v(r) + v_H(r) + v_{xc}(r) \right] \psi i(r) = \epsilon i \psi i(r) \tag{3}$$

Single electron wave function is obtained by solving kohn-sham equation which depends on three spatial variables ψi (r).

The potential term v, v_H, and v_{xc} are present on left side of the kohn sham equation.

The first term v, represents interaction between an electron and all of atomic nuclei.

The Second term v_H represents Hartee potential, and has form

$$v_H(r) = e^2 \int n(r^*) \frac{d^3 r^*}{|r - r^*|} \tag{4}$$

v_H represents Coulomb interaction between pair of electrons.

The third term v_{xc}, represents exchange to the single electron equations.

It is expressed as '' functional derivative" of exchange correlation energy.

$$v_{xc}(r) = \frac{\delta E_{xc}(r)}{\delta n(r)} \tag{5}$$

An initial charge density, n(r) is applied and solution to Kohn-Sham equation in form of single electron wave function ψi (r).

$n_{ks}(r) = 2 \sum_i \psi i^*(r) \psi i(r)$, single particle wave function is utilized to calculate charge density and calculated charge density nks is compared with initial charge n(r).

If both charge densities are same, it indicates ground state electron density and is used to compute the total energy. If both charge densities are different, then initial electron density is modified in some way [9].

3   Software Packages Based on DFT

Figures and tables should be placed either at the top or bottom of the page and close to the text referring to them if possi In recent years, there have been developments in Computational Technology and improvement of calculation methods. Open- source or Commercial software packages are available that can be used for performing most of the calculations based on DFT. Based upon application, open source software packages such as Quantum Espresso (for investigations with electronic structures, simulation and optimization), ABINIT, SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms), CPMD (Car-Parrinello Molecular Dynamics), MOLPRO and Commercial – Softwares including VASP (Vienna Ab in to Simulation Package), Material Studio (MS), Gaussian, ADF (Amsterdam Density Functional), Crystal or Wien2K are being used by researchers for computation and material simulation [10].

Some software are based on plane waves, whereas, some are based on linear combinations of atomic orbitals. In this paper, we report three programs more frequently used by researchers i.e., VASP, Quantum Espresso, Material Studio, SIESTA. Open source and free software such as Quantum Espresso are used for performing electronic structure calculations and material modelling based on DFT, plane waves (PW)s and pseudopotentials (PPs) [1]. Programming languages such as C++ and Fortran are used in Quantum Espresso. These codes are constructed in such manner that can deal with periodic as well as a periodic boundary conditions. Quantum Espresso can deal with infinite crystal system and treat with efficient convergence of the thermodynamic limit for periodic as well as aperiodic but extended crystal system such as liquids or amorphous materials [11].

As per requirement, open- boundary conditions may be employed by the density-countercharge method. The computations/simulations can be performed using energy for extended/periodic systems or isolated systems, structural optimization of the microscopic (atomic co-ordinates) also macroscopic (unit cell) systems, ground- state condition of magnetic or spin polarized systems, using any arbitrary wavelength second and third derivative of total energy, first principle molecular dynamics study of thermodynamic ensemble, determining transition states and saddle points with help of transition path optimization, calculation of NMR (nuclear magnet resonance) and EPR (electronic paramagnetic resonance) parameters [12].

Material Studio is a commercial software package that offers a platform for computational simulation and modelling. Material Studio helps us in solving important problems in physics, chemistry and material science [13]. CASTEP, $DMOL^3$ modules are used for the first principle quantum mechanics calculations based on DFT. CASTEP is used for solid materials makes full use of the DFT plane-wave prepotentials method and LDA and GGA theoretical methods to explore the exchange correlation energy of electron interaction [13]. Study of band structures, density of states, Mulliken charge distribution, surface chemistry and optical properties (absorption and reflection spectra etc.), study can be performed using CASTEP [13]. Whereas, calculation of surface and solid properties, study of homogenous catalysis, heterogenous catalysis, molecular reaction can be performed using $DMOL^3$. $DMOL^3$ can also be used to predict structures, reaction barriers, reaction energies, thermodynamic properties and vibrational spectra. SIESTA is an open-source software package, which is used for electronic structure calculation

Table 1. Summary of adsorption of CO gas molecules on metal surface

Srno	Gas Molecule	Surface	Doped Element on Surface	Exchange -Corelation	Cutt-off Energy	K Points	Charge Transfer	Adsorption Energy	Equilibrium Distance between molecule and surface	Computational Package	Site	Method	Ref
1.	CO	Cu		GGA-PW91		$8 \times 6 \times 1$		−0.73eV	1.96A	VASP	Cu-C	DFT + U	[17]
2.	CO	Ni		GGA-PBE	500eV	Gamma Points Only		−1.68	4.73	VASP	Ni-C	DFT-PBE + D3	[18]
3.	CO	Au		LSDA			0.25	3.14		Gaussian98	Au-C	DFT	[19]
4.	CO	WO3	-----	B3LYP			−0.338	3.264	2.07	Gaussian	W-C	DFT	[25]
5.	CO	ZnO		GGA-PBE	300 eV	$1 \times 4 \times 1$		0.89eV	2.089A	CASTEP	Zn-C	DFT	[27]
6.	CO	MOS2		PBE	400	$3 \times 3 \times 1$		0.01		VASP	Mo-C	DFT-D2	[26]
7.	CO	Zno (0002)		GGA-PBE	280Ry	$4 \times 4 \times 1$	0.23	−0.76	2.108	Quantum Espresso	Zn-C	DFT-D2	[28]
8.	CO	Co3O4		B3LYP			0.757	−3.36	1.93	Gaussian09	Co-C	DFT	[20]
9.	CO	Co3O4	In	B3LYP			0.1	−5.44	1.93	Gaussian09	In-C	DFT	[20]
10.	CO	Co3O4		GGA-PBE	400			−1.94	1.79	VASP	Co-C	DFT	[20]
11.	CO	Pt (211)		GGA-PBE		$5 \times 3 \times 1$		−2.41	1.83	Material Studio	Pt-C	DFT	[21]
12.	CO	WO3		GGA-PBE		$3 \times 3 \times 6$	0.50	0.35	3.077	DMol3	W-C	DFT	[29]
13.	CO	MgO	Ni	GGA-PBE		Gamma Points	0.557	1.17		DMol3	Ni-C	DFT	[22]

(continued)

Table 1. (*continued*)

Sr.no	Gas Molecule	Surface	Doped Element on Surface	Exchange -Corelation	Cutt-off Energy	K Points	Charge Transfer	Adsorption Energy	Equilibrium Distance between molecule and surface	Computational Package	Site	Method	Ref
14.	CO	MgO	Pd	GGA-PBE		Gamma Points	0.325	1.61		DMol3	Pd-C	DFT	[22]
15.	CO	MgO	Pt	GGA-PBE		Gamma Points	0.217	2.55		DMol3	Pt-C	DFT	[22]
16.	CO	TiO2 (001)		B3LYP		$8 \times 8 \times 8$		−9.73 kcal/mol		CRYSTAL06	Ti-C	DFT	[30]
17.	CO	TiO2 (101)		B3LYP		$8 \times 8 \times 8$		−6.78 kcal/mol		CRYSTAL06	Ti-C	DFT	[30]
18.	CO	WO3(001)		PW91	400			0.44	2.510	VASP	W-C	DFT	[23]
19.	CO	Alpha-Al2O3		GGA-PBE	400	$5 \times 5 \times 2$		0.45	2.26	CASTEP	Al-C	DFT	[24]
20	CO	WO3		B3LYP			0.062	6.256	1.208	Gaussian 09	O-C	DFT	[25]
21	CO	WO3		B3LYP			−−0.302	0.272	2.07	Gaussian 09	W-C	DFT	[25]
22	CO	WO3	MO	B3LYP			−0.338	3.274	3.07	Gaussian 09	Mo-C	DFT	[25]
23	CO	MOS2	Fe	PBE	400	$3 \times 3 \times 1$	−0.27	1.60		VASP	Fe-C	DFT-D2	[26]
24	CO	MOS2	Co	PBE	400	$3 \times 3 \times 1$	−0.19	1.71		VASP	Co-C	DFT-D2	[26]
25	CO	MOS2	Ni	PBE	400	$3 \times 3 \times 1$	−0.16	1.69		VASP	Ni-C	DFT-D2	[26]
26	CO	MOS2	Cu	PBE	400	$3 \times 3 \times 1$	−0.02	1.27		VASP	Cu-C	DFT-D2	[26]

Table 1. (*continued*)

Sr.no	Gas Molecule	Surface	Doped Element on Surface	Exchange -Corelation	Cutt-off Energy	K Points	Charge Transfer	Adsorption Energy	Equilibrium Distance between molecule and surface	Computational Package	Site	Method	Ref
27	CO	MOS2	Ag	PBE	400	3 × 3 × 1	−0.01	0.79		VASP	Ag-C	DFT-D2	[26]
28	CO	MOS2	Au	PBE	400	3 × 3 × 1	−0.02	1.06		VASP	Au-C	DFT-D2	[26]
29	CO	MOS2	Rh	PBE	400	3 × 3 × 1	−0.16	1.49		VASP	Rh-C	DFT-D2	[26]
30	CO	MOS2	Pd	PBE	400	3 × 3 × 1	−0.06	1.13		VASP	Pd-C	DFT-D2	[26]
31	CO	MOS2	Pt	PBE	400	3 × 3 × 1	−0.08	1.60		VASP	Pt-C	DFT-D2	[26]
32	CO	MOS2	Ir	PBE	400	3 × 3 × 1	−0.16	2.04		VASP	Ir-c	DFT-D2	[26]

and molecular dynamic simulation of molecules, surfaces and solids. SIESTA offers a platform for computational simulation and modelling, based on Density Functional Theory [12]. The basic computation/simulations such as calculation of total energy and local energy, atomic force, stress tensor, electric diploe moment, Mulliken charge distribution, atomic orbital, charge density, energy band and density of states etc. are performed using standard Kohn-Sham method, Local density approximation (LDA) or generalized gradient approximation (GGA) [14]. Two sub-programs of SIESTA code such as FCBUILD and VIBRATOR are used to control phonon frequency of the system. The software programs help us to understand scope of quantum chemistry and enrich the research output based on the density functional theory [12].

In this review, the use of DFT method used to study the adsorption and diffusion behavior of gas molecules on the surface and some examples have been provided (Tables 1 and 2).

4 Adsorption Study of CO Gas Molecules on Metal Surface

Transition metals and precious metals play a significant role in the enhancing catalytic oxidation rate of some gas pollutant molecules such as CO and NOx, and often represents as catalysts with excellent performance [15]. After cleaving the single crystals, the required crystal faces can be obtained, which provides a material basis for the adsorption of the gas molecules. Lattice of the metal is replaced by different forms of crystal planes, which are represented by Miller indices. But on contrary, certain metal oxides may have some properties which are not found in single metal [16]. As a result, study of the adsorption or chemical kinetics mechanism of these pollutants on the surface of pristine metals and their compounds is of great significance for enhancing sensitivity and selectivity of materials for detection of gases. And through last decade, researchers have taken interest in study of the adsorption behaviour of gas molecules on some metal surfaces by DFT theories.

Gajdos et al. studied adsorption properties of CO on transition metal Cu (111) and Cu (001) surfaces by first principle calculations [17]. The structural, vibrational and thermodynamic properties of CO on Cu substrate was analyzed within DFT framework. The conventional DFT method along with DFT + U method result were compared with experiments and underlaying advantages of DFT + U method were discovered. The DFT + U method provided correct prediction of site preference and agreement of adsorption energies with experiments. Amorim et al. carried out atomic level study on Ni nanoclusters and CO molecule to determine how the molecular adsorption of CO affects the energetic, structural and chemical properties of Ni. The results depicted those geometric modifications upon molecular adsorption had significant role in structuring molecular interaction. If adsorbed gas molecules have longer internal bond lengths upon adsorption to Ni nanoclusters, stronger chemical bonding resulted with Ni [18]. X.Wu et al. studied binding of CO molecule with small neutral and charged Au clusters using Density Functional theory [19]. It could be observed that CO binding on small gold clusters could be enhanced or decreased by preparing differently charged gold clusters. Nanostructured Co_3O_4 is one of the prominent functional materials with outstanding properties for gas sensing applications. V. Nagarajan et al. studied CO adsorption on

Table 2. Summary of adsorption of CO gas molecules on non-metallic surface

Sr.no	Gas Molecule	Surface	Doped Element on Surface	Exchange -Corelation	Cutt-off Energy	K Points	Charge Transfer	Adsorption Energy	Equilibrium Distance between molecule and surface	Computational Package	Site	Method	Reference
1.	CO	Graphene	Nitrogen,	Pw-91 GGA				−1.04eV	- 3.39 A	GAUSSIAN 09	N-C	DFT	[31]
2.	CO	Graphene	Boron	Pw-91 GGA				−5.68eV	- 3.28 A	GAUSSIAN 09	B-C	DFT	[31]
3.	CO	Graphene	Fe	GGA-PBE			0.13 eV	1.60 eV		ORCA	Fe-C	DFT	[38]
4.	CO	Graphene	Pt	GGA-Pw91	400eV	5 × 5 × 1		−34.3eV		VASP	Pt-C	DFT	[39]
5.	CO	Graphene	Pt,B							VASP	B-C	DFT	[39]
6.	CO	PentaGraphene	Fe	GGA-PBE		2 × 2 × 1	0.094	0.586	1.939	DMol3	Fe-C	DFT-D2	[32]
7.	CO	Graphene		GGA-PBE + Grimme	300	4 × 4 × 2	0.01	−0.131	4.111	CASTEP	C-C	DFT-D2	[33]
8.	CO	Defective Graphene		GGA-PBE + Grimme	300	4 × 4 × 2	0	−2.046	1.301	CASTEP	C-C	DFT-D2	[33]
9.	CO	Graphene	In	GGA-PBE + Grimme	300	4 × 4 × 2	-0.01	−0.021	3.653	CASTEP	In-C	DFT-D2	[33]
10.	CO	Graphene	Sb	GGA-PBE + Grimme	300	4 × 4 × 2	0.01	−0.002	3.165	CASTEP	Sb-C	DFT-D2	[33]
11.	CO	Graphene		B3LYP/LanL2DZ				−1.28	3.576	Gaussian 03	C-C	DFT	[34]
12.	CO	Graphene	Fe	B3LYP/LanL2DZ				−33.77	1.848	Gaussian 03	Fe-C	DFT	[34]
13.	CO	Graphene	Ru	B3LYP/LanL2DZ				−28.07	2.028	Gaussian 03	Ru-C	DFT	[34]
14.	CO	Graphene	Os	B3LYP/LanL2DZ				−41.62	1.997	Gaussian 03	Os-C	DFT	[34]
15.	CO	Graphene	Co	B3LYP/LanL2DZ				−21.74	1.879	Gaussian 03	Co-C	DFT	[34]
16.	CO	Graphene	Rn	B3LYP/LanL2DZ				−23.35	2.016	Gaussian 03	Rn-C	DFT	[34]
17.	CO	Graphene	Ir	B3LYP/LanL2DZ				−36.30	1.959	Gaussian 03	Ir-C	DFT	[34]

(*continued*)

Table 2. (*continued*)

Sr.no	Gas Molecule	Surface	Doped Element on Surface	Exchange-Corelation	Cutt-off Energy	K Points	Charge Transfer	Adsorption Energy	Equilibrium Distance between molecule and surface	Computational Package	Site	Method	Reference
18.	CO	Graphene	Ni	B3LYP/LanL2DZ				−23.61	1.885	Gaussian 03	Ni-C	DFT	[34]
19.	CO	Graphene	Pd	B3LYP/LanL2DZ				−21.13	2.065	Gaussian 03	Pd-C	DFT	[34]
20.	CO	Graphene	Pt	B3LYP/LanL2DZ				−29.87		Gaussian 03	Pt-C	DFT	[34]
21.	CO	Graphene Pristine		DFTB		5 × 5 × 1		−4.652	3.467	Quantum Espresso	C-C	DFTB	[35]
22.	CO	Graphene-Stone wall Defective		DFTB		5 × 5 × 1		−4.661	3.00	Quantum Espresso	C-C	DFTB	[35]
23.	CO	Graphene-Vacancy Defective		DFTB		5 × 5 × 1	-0.014	−4.652	1.8	Quantum Espresso	C-C	DFTB	[35]
24.	CO	Graphene	In	GGA-PBE		16 × 16 × 1	0.033	−0.219	3.20	DMol3	C-C	DFT-D	[40]
25.	CO	Graphene		GGA-PBE		16 × 16 × 1	0.015	−0.223	3.118	DMol3	In-C	DFT-D	[40]
26.	CO	Graphene	N	GGA-PBE		16 × 16 × 1		−0.152	3.764	DMol3	N-C	DFT-D	[40]
27.	CO	Graphene	Ga	GGA-PBE		5 × 5 × 1	-0.129	−0.674	2.027	DMol3	Ga-C	DFT-T	[41]
28.	CO	Graphene		GGA-PBE		5 × 5 × 1	-0.076	−0.210	3.139	DMol3	C-C	DFT	[41]
29.	CO	Graphene		GGA-PBE	400	4 × 4 × 1	0.015	0.08		VASP	C-C	DFT-D	[36]
30.	CO	Graphene		GGA-PBE	400	4 × 4 × 1	0.155	1.05		VASP	C-C	DFT-D	[36]
31.	CO	Polymorphins	Mn	B3LYP			1.228	−0.468	1.763	Gaussian09	Mn-C	DFT	[37]
32.	CO	Polymorphins	Co	B3LYP			0.985	−0.334	2.045	Gaussian09	Co-C	DFT	[37]
33.	CO	Polymorphins	Fe	B3LYP			0.000	−1.042	1.743	Gaussian09	Fe-C	DFT	[37]
34.	CO	Polymorphins	Cu	B3LYP			0.593	−0.132	3.050	Gaussian09	Cu-C	DFT	[37]
35.	CO	Polymorphins	Ni	B3LYP			0.000	−0.102	3.225	Gaussian09	Ni-C	DFT	[37]
36.	CO	Polymorphins	Zn	B3LYP			0.000	−0.206	2.656	Gaussian09	Zn-C	DFT	[37]

Co_3O_4 nanostructure with substitution impurity and identified favourable sites for CO adsorption [20]. The adsorption properties of CO on CO_3O_4 nanostructures could be enhanced by incorporation of In atoms [20]. Adsorption energies, structures, and C-O stretching vibrational frequencies are explored by evaluating different probable adsorption sites and comparing them with actual data in a DFT analysis of CO Adsorption on Pt (211) surface by Orita et al. [21]. It could be observed that CO adsorption is preferred on atop site on the step edge of Pt (211) at low temperature [21]. Linghuan Zhao et al. conducted DFT investigation of CO Adsorption on O-terminated and WO-terminated WO_3 surface by Density Functional Theory (DFT) calculations [21]. It was found that O terminated surface had higher sensitivity to CO gas molecule as compared to WO terminated surface [21]. Yang et al. carried out DFT investigation to study interaction of CO gas on transition metal doped MgO nanotube [22]. Addition of transition metal dopant could enhance CO adsorption on MgO nanotube while Pt doping demonstrated significant influence on CO adsorption [22]. Jin et al., conducted systematic DFT investigation of CO molecule on the $WO_3(001)$ surfaces for CO sensing [23]. It had been demonstrated that the top oxygen atom converted CO to CO2 for the ideal WO3(001) surface, resulting in the production of a faulty surface with oxygen vacancy at the surface and a drop in surface resistivity[23]. Rohmann et al. studied the adsorption of CO on α-Al_2O_3(0001) using the DFT-GGA computational method and on α- Al_2O_3 powder experimentally by Infra-red spectroscopy [24]. CO adsorption of α- Al_2O_3 layer results in inward relaxation of Al layers and increase or decrease in adsorption energy is in proportion with structural distortion [24]. V.Nagarajan et al. Performed DFT investigation in order to study structural stability, electronic properties, and adsorption characteristics of CO adsorption on WO_3 surfaces [25]. The structural stability of WO_3 nanostructures was discussed with calculated energy. The electronic properties of WO_3 structures were analyzed in terms of HOMO-LUMO gap, ionization potential and electron affinity. The adsorption characteristics CO on WO_3 were reported in terms of adsorbed energy, average energy gap variation, Mulliken population analysis and density of states spectrum. The authors reported that adsorption characteristics of CO could be enhanced with the substitution of Mo impurity in the WO_3 base material. Fan. et al. reported systematic study of structures and electronic properties of diverse transition metal (TM = Fe, Co, Ni, Cu, Ag, Au, Rh, Pd, Pt and Ir)-embedded monolayer of MoS_2 in the S-vacancy and the adsorption of CO molecules using DFT [26].

5   Adsorption Study of CO Gas Molecules on Non-Metallic surface

In recent years, graphene has garnered specific attention as a prominent sensing material. Lopez et al. conducted a density functional investigation of CO adsorption in B-, N-, and BN-co-doped graphene using a coronene-based model to assess the applicability of these systems as CO-sensors. The results revealed that, while all of the configurations confirmed CO physical adsorption, the relative positions of Nitrogen and Boron gave varied responses to CO adsorption. Since monosubstituted Boron-coronene showed the highest CO adsorption energy, this structure could be potentially a good CO-sensor, as suggested by authors [31]. Arrigada et al. used molecular dynamics to investigate the stability of the FeG-Gas interaction in ambient conditions, as well as the adsorption

stability in aerobic conditions. As a reference, the gas adsorption was also studied onto pristine graphene. Through this study, FeG was suggested to enhance the gas adsorption process of toxic gaseous pollutants with negative effects on human health, flora and fauna [31]. Zhang et al. conducted DFT investigation in order to study the adsorption energy, charge transfer, adsorption distance, charge density, density of states (DOS), and partial density of states (PDOS) of CO gas molecules on Fe-doped Pentagraphene. It was found that adsorption of CO gas could be effectively enhanced by the doping of Fe atom in Fe-doped PG substrate. Adsorption energy and charge transfer for CO on the Fe-doped PG was found to be higher than those on the pristine PG, and different adsorption orientations of CO have different adsorption behaviours [32]. Yang et al. studied adsorptions of CO molecules on the pristine, defective, In-doped and Sb-doped graphene through the density functional theory (DFT) calculations [33]. The results demonstrated that the insertion of defects or dopants into graphene has a significant influence on the stable geometries of graphene-based materials. The pure, In-doped, and Sb-doped graphene surfaces had a modest contact with the adsorbed CO. The inclusion of a C flaw into the sensing material might facilitate interaction between the CO molecule and the faulty graphene substantially. The CO favoured to be chemisorbed on the defective graphene with the C atom above the adsorbent surface in the parallel direction, resulting in the defective graphene's sensing performance towards CO, as revealed by the potent crossover of the spikes in the PDOS of the C atom/O atom in CO and the energetic C atom in the defective graphene [33]. Wanno et al. used density functional theory calculations at the B3LYP/LanL2DZ theoretical level to study CO adsorptions on virgin, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, and Pt doped graphene [34]. This work revealed that the transition metal doped graphene were higher sensitive to CO adsorption than that of pristine graphene. The Os- and Fe-doped graphene displayed the strongest interaction with C and O atoms of CO molecule, respectively [34]. Tit et al. conducted DFT investigation to study adsorption behaviour of CO molecule on Graphene sheet in three forms, namely- (i) pristine graphene, (ii) Stone-Wales defected graphene, and (iii) vacancy-defected graphene. Results showed the occurrence of chemisorption of CO molecules possibly took place on only vacancy-defected graphene, considered to be most active adsorbent one of the highest studied materials. Adsorption of several CO molecules on multiple-vacancy graphene (i.e., which is similar to chemisorption of CO_2 on vG) could be observed was corroborated with rise in total density of states (TDOS) at Fermi level with increase of gas dose. Causing rise of conductance [35]. To investigate the viability of employing Ga-doped graphene for gas sensing, Liang et al. performed DFT calculations on the adsorption of CO gas molecules on pristine graphene and Ga-doped graphene [35]. Because of the poor interaction between graphene electrons and gas molecules, the adsorption of CO gas molecules on pure graphene was weak with little charge transfer. In comparison to virgin graphene, Ga-doped graphene displayed considerably higher affinity for gas molecules. Chemisorption on Ga-doped graphene with relatively high adsorption energies was discovered using the DOS and electron density plots. Adsorption of gas molecules on Ga-doped graphene was discovered to open a significant band gap due to increased electron transport and the creation of strong chemical interactions between the electron cloud and gas molecule orbitals [35]. Ling Ma et al. employed first-principles based on density functional theory (DFT) to investigate sensitivity of pristine

graphene (PG) and Pd-doped graphene (Pd-G) toward CO gas molecule [36]. It was found that doping graphene with Pd significantly improved the strength of interaction between adsorbed molecules and the modified substrate. The drastic enhancement in adsorption energy and charge transfer of these systems were expected to induce changes in the electrical conductivity of the Pd-G sheet. The results revealed that the sensitivity of graphene-based chemical gas sensors could be significantly enhanced by introducing the Pd dopants, so Pd-G could be concluded to be more suitable for gas molecules detection compared with PG [36]. Ammar et al. investigated the structural stabilities, electronic and optical properties of TM-doped porphyrin (TM = Mn, Co, Fe, Cu, Ni and Zn) using density functional theory (DFT) method. The binding of the CO gas molecules onto the porphyrin was mainly due to electrostatic and van der Waals interactions and thereby physisorption in nature. The CO adsorption nature on TM-doped substrates was found to be dependent on two factors, - (i) the orientation of CO molecule and (ii) species of the doping. The presence of Mn, Fe, Co, and Zn enhanced the adsorption of CO molecule [37].

6 Conclusion

As evidenced by a slew of major discoveries, first-principles calculations, particularly the DFT approach, have proved tremendously effective for understanding the adsorption process of CO gas molecules on various materials.

The adsorption characteristics of CO gas molecules on the surface of several materials have been discussed in this brief overview.

It has been demonstrated that adsorption energy, change in bond length and molecular configuration before and after adsorption, and adsorption charge transfer can be computationally predicted, and the results can be used for sensor fabrication optimised for selectivity, sensitivity, and response towards CO gas molecules, in particular.

According to the findings described here, CO gas molecules may be adsorbed on metals, metal oxides, graphene, and its derivatives. Metals and Semiconductor Metal Oxides (SMOs) are among those that may achieve excellent adsorption without doping. Furthermore, the adsorption impact of pristine graphene has been shown to be modest, but adsorption performance has been extensively reported to be increased by doping the functional groups or metal atoms in graphene, particularly the transition metal atoms. As a result, it is determined that doping transition metal atoms in these adsorption materials enhances CO gas adsorption.

Furthermore, the DFT, in particular, can provide insight into molecule adsorption parameters such as bond angle, energy band, density of state, and magnetic characteristics, which are not described in this study. Despite the fact that DFT-based calculations have been frequently employed in adsorption in recent years, the following issues require systematic attention:

Metal, Semiconductor Metal Oxides, and graphene have been employed to adsorb CO gas molecules, which have been widely used in experimental research and certain applications in practical engineering. However, the use of doped metals, SMOs, and graphene necessitates a thorough knowledge of adsorption processes.

Although it is generally known that noble metal elements have a very good influence on the adsorption behaviour of CO gas molecules, the overall costs of employing these

precious metal materials in the real experiment are very high. As a result, the adsorption behaviour of CO gas molecules on low-cost materials as more attractive adsorbents with trustworthy performance in the development of more cost-effective solutions must be considered.

DFT simulations employ ideal circumstances to simulate molecular behaviour at material surfaces, but real adsorption materials differ from ideal conditions. Furthermore, because the experimental conditions are dynamic and cannot be replicated, the DFT calculation may only reflect an ideal state in some situations. As a result, rigorous optimization is required to get findings that are more compatible with actual tests.

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