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Computational Study of CO Adsorption Potential of MgO, SiO_2, Al_2O_3, and Y_2O_3 Using a Semiempirical Quantum Calculation Method

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Abstract

Air pollution has been a vital subject attracting experts' attention towards the search for ways in which the pollution can better be controlled and minimized to avert the ongoing global warming and climatic changes experienced globally due to the release of poisonous gas regularly release to our environment. The bulk of the discharged gases are traced to the use of fossil fuel and the burning of biomass, which pollutes our environment by the emission of carbon monoxide (CO) to the atmosphere, which has been said to be a dangerous air pollutant with adverse effects on man and its environment. As a way for devising a solution for the better management of air pollution, this study computationally screened and evaluated the CO adsorption potential of different selected metallic oxides, MgO, SiO_2, Al_2O_3, and Y_2O_3 which could be used as an active agent for CO capture and sensation as an adsorbent with the aid of a molecular modeling application called Spartan. The Lewis acidity of the cluster's adsorption sites was equally evaluated using ammonia as a basic molecular probe. Findings from the study reveal that the site acidity has a direct relation to adsorption strength. The study indicates that the metal site of the various clusters was generally more acidic compared to oxygen sites. Moreover, the MgO was of higher acidity, lesser stability, and better adsorption potential for CO than the other metal oxides. Thus, MgO would be more promising for CO adsorption based on the findings from this study.

Keywords: Adsorption, Pollution, Carbon Capture, Adsorbent, Binding Energy, Lewis Acidity.

1. INTRODUCTION

Over the years, interest has arisen in resolving the increased carbon monoxide emission problems, leading to severe air pollution and many detrimental effects on man and its environment (Amirali and Jaber, 2017). The importance of environmental gas monitoring and control is now recognized as a vital area of study. However, much research has focused on developing suitable gas-sensitive materials for continuous monitoring and setting alarms for hazardous materials released to the environment. Chemical vapors (gas) present beyond specification levels affect both humans and the environment resulting in pollutants such as CO (Carbon monoxide), NO (Nitrogen oxide), and H_2S (Hydrogen sulphide) (Javad *et al.*, 2011).

We examined exposure to air pollution caused by households' wood-burning of cooking, generating sets, and vehicle emissions of carbon monoxide (CO) poisonous gas in the most populated urban city of Lagos, Southwestern part of Nigeria. It is a known fact that many families, including children and pregnant women, infant babies, and individuals, lost their lives due to low-quality air control policies and inefficient control of air pollution caused by this deadly gas (Kayode and Kamson, 2013).

The air we breathe is an essential ingredient for our well-being and healthy life. Unfortunately, polluted air is standard throughout the world, especially in developed countries, since the 1960s (Kan, 2009; Arsalan and Mashood, 2011). From these air pollutants, we would be looking at Co (Carbon monoxide) specifically in our research, which is a colorless, odorless, and toxic gas that evolved from our vehicle emission. Air pollution could come from natural and human-made sours; however, global, human-made pollutants from combustion, construction, mining, and agriculture are increasingly significant in air pollution (Mahdi Rezaei and Sahar, 2015). The environment chemistry's main job is to watch the natural environment change due to its interaction with chemicals (Hussein, 2013). In which adsorption could help in managing these pollutants, being a process in which the pollutant known as adsorbate is concentrated from a bulk vapor or liquid phase onto the surface of a porous solid commonly referred to as adsorbent (Sagar *et al.*, 2017).

Computational chemistry is rapidly emerging as a sub-field of theoretical chemistry, where the primary focus is on solving chemical-related problems by calculation (Frank, 2007). Computational studies can be carried out to find a starting point for laboratory synthesis data, such as spectroscopic peaks' position and source (DosVesa, 2016). A literature review indicates that researchers have begun to explore the computational chemistry tools' potential to search for the best adsorbent for certain adsorbates. Some of the works are Amirali *et al.* (2017) evaluated the adsorption of CO and NO molecules on the MgO nanotubes (NT) using density functional theory calculations. The authors' study indicated that the NO and CO could be firmly adsorbed on MgO-NT with remarkable adsorption energies. The gas/tube interactions were evaluated using the adsorption energies, Density of States (DOSs), and Molecular Electrostatic Potentials (MEPs) analyses. Beheshtian *et al*. (2011) evaluated the adsorption potential of undoped and doped TiO_2 anatase nanoparticles for COx molecules via the use of DFT calculation. The findings suggest that N-doped nanoparticles were more suitable and energetically favorable than undoped ones. In recent times, Oyegoke *et al.* (2020) confirmed Fe_2O_3 to be better compared to other oxides like Gd_2O_3 and La_2O_3 studied in their report.

However, this study computationally screen and evaluate the carbon monoxide (CO) adsorption capacity of different selected metallic oxides such as MgO, SiO_2, Al_2O_3 and Y_2O_3as a means of identifying potential adsorbate which could be active for CO capture and sensation as an adsorbent via the use of parameterized method 3 (PM3) of semi-empirical calculation approach with the aid of Spartan, application software.

2. METHODOLOGY

2.1 Method of geometry optimization calculations for the clusters and species

The method employed in this study of CO adsorption over different selected metallic oxides is diagrammatically illustrated in Figure 1. The computing machine has a RAM of 4GB, core i3 processor, processor speed of 1.7GHz, and 500GB hard disk. Semi-empirical calculation (PM3 method) was employed for both the energy and geometry optimization calculation in this study using a Spartan molecular modeling application. Considering the computing accuracy and the nature of the available computing machine (i.e., Computational cost), Warren's (2003) report suggests the need to employ the PM3 method due to transition metals and the low-speed computing machine that is available.

2.2 Choice of Adsorbent Structures/Clusters

The choice of adsorbent clusters adopted for this study was obtained from other literature and presented in Table 1. These clusters were employed in CO adsorption study over different selected metallic oxides via a computational approach.

2.3 Method of stability calculations for the clusters and species

The stability of the structure was evaluated using the energy bandgap, which is the absolute difference between the energy of the highest occupied molecular or-

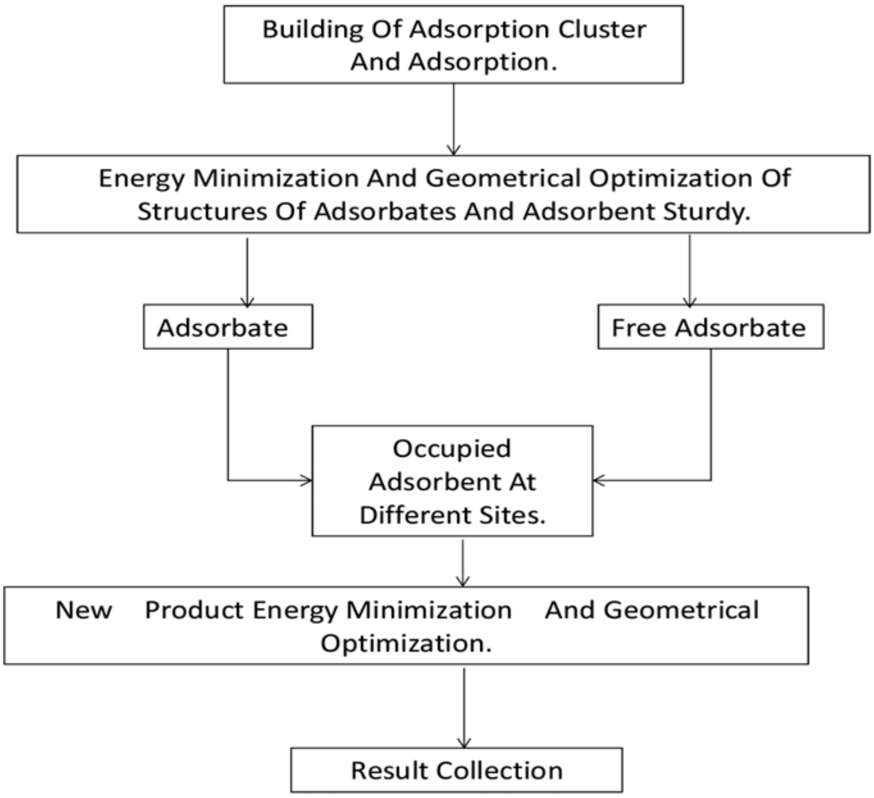


Figure 1: Computational Approach for Adsorption Energy Evaluation

bital (E-HOMO) and energy of the lowest occupied molecular orbital (E-LUMO) as expressed in Equation (1) adopted from (Bendjeddou *et al*., 2016).

$$\text{E-Gab} = |\, E(\text{LUMO}) - E(\text{HOMO}) \,| \qquad (1)$$

Where E-Gab = Band gap energy,
E (LUMO) = Energy of lowest occupied molecular orbital, and E (HOMO) = Energy of highest occupied molecular orbital.

2.4 Method of adsorption calculation

The adsorption energies were evaluated using the expression in equation (2) adapted from Raymond (2010), which has been similarly used in the report of Oyegoke *et al.* (2018), Yu-Jue *et al.* (2013), and Ming-Lei *et al.* (2010).

$$E_{ads} = E(\text{adsorbent/CO}) - E(\text{CO}) - E(\text{adsorbent} \qquad (2)$$

Where E_{ads} = Adsorption energy,
E(CO) = Total energy of the CO adsorbate;
E(adsorbent) = Total energy of the adsorbent (oxide)
and E(adsorbent/CO) = Total energy of the structure for the adsorbent with the adsorbate on its surface.

2.5 Method of Lewis acidity calculation

In this study, ammonia was employed as a molecular probe for the evaluation of the Lewis acidic site in line with the report of Liu (2017) and Oyegoke *et al.* (2018), which identifies it as an excellent potential probe for the evaluation of material acidity via computational approach using the same equation as that of the adsorption energy in equation (2).

3. RESULTS AND DISCUSSION

3.1 Energy computations

Table 2 shows the energy calculation results collated for the selected metal oxide. These energies entail the total potential energy (E), the energies of the HOMO, and LUMO, including the energy gap, while Table 3 shows energies of the carbon monoxide and the basic probe. The energy gap tells us about the structures' stability indicating that the wider the energy gap, the more stable the structure.

The report presented in Table 2 indicates that the SiO_2 was more stable, while MgO was less stable. The clusters were generally less stable than the adsorbate (CO and ammonia) due to their lower energy gab displayed in Tables 2 and 3. According to Oyegoke *et al.* (2018), the MgO with less stability would be expected to be more reactive compared to more stable ones.

3.2 Lewis Acidity Adsorption Sites Using Molecular Basic Probe.

The result of the Lewis acidity is displayed in Table 4 for the different sites (oxygen and metal sites) evaluated on the metal oxide cluster structure via the use of the primary probe that is adsorbed on the metal oxide surface. The probe adsorption energy was used to assess the acidity of the various sites. As a basic molecular probe, the use of ammonia has been proven in previous studies (Oyegoke *et al.,* 2018) to be valid. According to Liu *et al.* (2017) and Oyegoke *et al.* (2018), the higher the probe adsorption

Table 1: Choice of Adsorbent Structure (cluster)

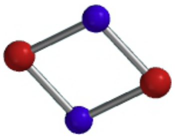
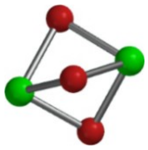
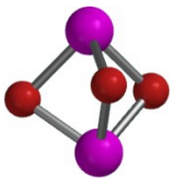
Adsorbent name	Adsorbent cluster structure	Adopted from
Magnesium Oxide$(MgO)_2$		Liang *et al.* (2012).
Yttrium (iii) Oxide(Y_2O_3).		Reed *et al.* (2008).
Silicon (ii) Oxide (SiO_2)		Lu *et al.* *(*2003)
Aluminium (iii) Oxide (Al_2O_3)		Elena *et al.* (2012)

Table 2: Energy minimization and geometrical optimization of adsorbent clusters using MMFF molecular mechanic and the PM3 semi-empirical method.

Formula	E (kJ/Mol)	E HOMO (kJ/mol)	E LUMO (KJ/Mol)	E GAP(KJ/Mol)
MgO	476.2	-723. 4	-494. 79	228.61
O_3Y_2	-438. 84	-659. 14	-37. 26	621.88
O_2Si	-372. 03	-981. 25	21.59	1002.84
Al_2O_3	-557. 19	-975. 04	-260. 37	714.67

Table 3: Energy minimization and geometrical optimization of CO and NH_3 using the MMFF molecular mechanic and the PM3 semi-empirical method.

Formula	E (KJ/Mol)	E HOMO (KJ/Mol)	E LUMO (KJ/Mol)	E GAP (KJ/Mol)
CO	-82.61	-1256.99	96.48	1353.47
H_3N	-12.83	-935.48	321.62	1257.10

Table 4: Result of Lewis acidity of the clusters adsorption sites using a basic molecular probe

Site Location	Formula	E (KJ/Mol)	HOMO (KJ/Mol)	LUMO (KJ/Mol)	E GAP (KJ/Mol)	E_{ads} (KJ/Mol)
M-site	H_3MgNO	-154. 43	-847. 98	-107. 71	740.27	-617. 8
M-site	$H_3NO_3Y_2$	-508. 72	-610. 23	4.6	614.83	-57. 05
M-site	H_3NO_2Si	-485. 03	-874. 14	54.65	928.79	-100. 17
M-site	$H_3Al_2NO_3$	-800. 76	-860. 71	-146. 74	713.97	-230. 74
O-site	H_3MgNO	-49. 91	-624. 72	0.33	625.04	-513. 28
O-site	$H_3NO_3Y_2$	-498. 49	-689. 54	-58. 51	631.03	-46. 82
O-site	H_3NO_2Si	545.2	-1195. 24	-499. 82	695.41	930.06
O-site	$H_3Al_2NO_3$	-590. 3	-767. 91	-165. 48	602.44	-20. 28

[Key: Physio = Physisorption; Chem.(M) = Chemisorption metal site; Chem. (O) = Chemisorption oxygen site]

Table 5: Minimization and geometrical optimization of adsorbent clusters with CO on their surfaces using MMFF molecular mechanic and the PM3 semi-empirical method via Single bonded CO Adsorption

Type of Adsorption	Formula	E (KJ/Mol)	HOMO (KJ/Mol)	LUMO (KJ/Mol)	E GAP (KJ/Mol)	E_{ads} (KJ/Mol)
Physio.	CO.MgO	-59. 52	-964. 94	-204. 68	760.25	-453. 11
Physio.	$CO.O_3Y_2$	-922. 95	-694. 35	-66. 01	628.35	-401. 5
Physio.	$CO.O_2Si$	-498. 15	-924. 2	-22. 68	901.52	-43. 51
Physio.	$Al_2O_3.CO$	-640. 17	-976. 13	-261. 33	714.8	-0. 37
Chem. (M)	$CMgO_2$	-148. 3	-912. 91	-102. 84	810.07	-541. 89
Chem. (M)	CO_4Y_2	-922. 95	-694. 86	-65. 96	628.9	-401. 5
Chem. (M)	CO_3Si	-498. 15	-924. 21	-22. 63	901.59	-43. 51
Chem. (M)	CAl_2O_4	-763. 65	-906. 65	-185. 22	721.43	-123. 85
Chem. (O)	$CMgO_2$	-273. 83	-733. 35	-122	611.35	-667. 42
Chem. (O)	CO_4Y_2	-922. 95	-694. 72	-65. 97	628.75	-401. 5
Chem. (O)	CO_3Si	-509. 53	-796. 45	-63. 63	732.81	-54. 89
Chem. (O)	CAl_2O_4	-763. 65	-906. 65	-185. 22	721.43	-123. 85

[Key: Physio= Physisorption; Chem.(M)=Chemisorption metal site; Chem. (O)=Chemisorption oxygen site] energy (i.e., the most negative values), the higher the Lewis acidity.

The results presented in Table 4 indicate that in all metallic oxides considered in this study, the metallic site on MgO was seen to have displayed a higher ammonia adsorption energy than other adsorption across their respective oxygen site, which recorded lower energy across the respective oxides. Similar observations were made for other oxides studied. Moreover, these findings imply that all the analyzed oxide's metallic sites were more acidic than their respective oxygen sites using ammonia as the basic probe due to higher adsorption energy recorded for the metallic sites. General evaluation of the oxides (MgO, SiO_2, Al_2O_3, and Y_2O_3) indicates that iron oxides were found to be more acidic, while lanthanum oxide was found to have shown the lowest acidity.

3.3 Adsorption energy computations

Table 5 shows the adsorption energy results obtained to evaluate carbon monoxide singly bonded on the adsorbent. The result obtained for the CO physisorption for the selected metal oxide indicated a trend that goes thus: MgO> Y_2O_3> SiO_2> Al_2O_3. The CO chemisorption singly bonded to the metal sites results obtained followed the trend: MgO> Y_2O_3> Al_2O_3> SiO_2 while the oxygen sites chemisorption evaluation for the singly bond CO was found to be MgO> Y_2O_3> Al_2O_3> SiO_2 in decreasing order of their adsorption energy.

The obtained results indicate that the magnesium oxide (MgO) displays the highest adsorption energies of -453.11, -541.89, and -667.42 kJ/mol for physisorption, chemisorption at the metal site and oxygen sites, respectively. The deduction of the singly bonded CO adsorption study to selected oxide indicates that MgO would better capture the CO while SiO_2 would potentially display the least potential.

The result obtained for the double-bonded CO adsorption on the metal oxide was presented in Table 6. A similar trend was equally obtained for the physisorption and chemisorption of CO to the selected metal oxides displaying MgO> Y_2O_3> SiO_2> Al_2O_3 (physio.) and MgO> Y_2O_3> Al_2O_3> SiO_2 (chem. for both metal and oxygen sites) in order of their adsorption energy. The results show magnesium oxide has the highest adsorption energy with -455.07, -667.42, and -544.32 kJ/mol for the physisorption, adsorption at metal, and oxygen sites, respectively.

These findings indicate that both studies investigating the singly and doubly bonded CO adsorption in screening the metallic oxides' adsorption strength for the carbon monoxide capture confirmed MgO to be the best oxides out of the selected metal oxides. Likewise, other works like Yuliusman *et al*. (2020) report showed an agreement with this study finding indicating that the introduction of MgO on an activated carbon significantly improves its carbon capture capacity, which agrees with Gan *et al.* report (2015).

4. CONCLUSIONS

A study that computationally evaluates the carbon monoxide (CO) adsorption capacity of different selected metallic oxides such as MgO, SiO_2, Al_2O_3, and Y_2O_3as a means of identifying potential adsorbate which could be active for CO capture and sensation as an adsorbent was carried out using PM3 of semi-empirical calculation approach with the aid of Spartan application software.

The Lewis acidity study unveils that the potential adsorbents (MgO, SiO_2, Al_2O_3, and Y_2O_3) displayed a higher Lewis acidity at the metal site, which implies that the site is the most electron pair acceptor sites, unlike their oxygen site that indicated a low potential. Similarly, the metallic sites were found to have shown the highest adsorption strength for the carbon monoxide, unlike the oxygen sites. However, the order of the adsorption potential for CO was found to be MgO> Y_2O_3> Al_2O_3> SiO_2.

Moreover, the magnesium oxide was found to have shown the highest Lewis acidity, lesser stability, and CO adsorption energies than other oxides considered in this study, which confirms it to be the best oxide out of all the oxides studied. Therefore, this study suggests using the MgO as a potential material for improving carbon capture from our environment due to the higher CO adsorption energy recorded for the oxide.

CONFLICT OF INTEREST

The authors have no conflict of interest.

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