

Preliminary Investigation on the Screening of Selected Metallic Oxides, M_2O_3 ($M = Fe, La, \text{ and } Gd$) for the Capture of Carbon Monoxide Using a Computational Approach

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Abstract: In our present-day, climate change is often being viewed as a critical challenge that has ever been faced, which has long been traced to be associated with the accelerating processes of anthropogenic greenhouse gas emissions, which carbon monoxide forms are a significant component of it. The pressing global challenge has motivated this study into the evaluation of selected metallic oxides, M_2O_3 ($M = La, Fe, \text{ and } Gd$) such as La_2O_3 , Fe_2O_3 , and Gd_2O_3 for the capture of carbon monoxide from our environment as a way of identifying a feasible material that would best aid the capture of this GHG emitted daily in our surroundings whose the intense effects have already been felt in the form of the extremely violent weather events reported globally. The metallic oxide adsorption strength was evaluated, and the adsorption sites' Lewis acidity of metallic oxides' clusters were investigated via the use of ammonia as a basic molecular probe. In general, a molecular modeling approach was employed in the study with a Spartan molecular modeler's aid. Results from the study reveal that the active site acidity has a direct variation with the adsorption strength. Moreover, the study indicates that the various clusters' metal site was generally more acidic than oxygen sites. Moreover, the Fe_2O_3 showed a higher acidity and better adsorption strength for CO than the

other metallic oxides studied. Thus, in CO adsorption processes, the use of Fe_2O_3 would be more favorable based on the findings from this study.

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

التحقيق الأولي في غربلة أكاسيد معدنية مختارة M_2O_3 (M=Fe, La, Gd) لالتقاط أول أكسيد الكربون باستخدام نهج حسابي

الملخص: في يومنا هذا، غالبًا ما يُنظر إلى تغير المناخ على أنه تحدٍ بالغ الأهمية أكثر من أي وقت مضى، والذي تم تتبعه منذ فترة طويلة ليكون مرتبطًا بالعمليات المتسارعة لانبعاثات غازات الاحتباس الحراري التي منشؤها التدفئة البشرية، والتي يشكلها أول أكسيد الكربون ويعتبر من العوامل الهامة المكون منه. دفع التحدي العالمي الملح هذه الدراسة إلى تقييم أكاسيد معدنية مختارة، M_2O_3 (M=La, Fe, Gd)، مثل La_2O_3 و Fe_2O_3 و Gd_2O_3 لالتقاط أول أكسيد الكربون من بيئتنا كطريقة لتحديد مادة مجدية من شأنه أن يساعد على أفضل وجه في التقاط غازات الدفيئة المنبعثة يوميًا في محيطنا ذات الآثار الشديدة والتي تم الشعور بها بالفعل على شكل أحداث مناخية شديدة العنف تم الإبلاغ عنها عالميًا. تم تقييم قوة امتزاز الأكسيد المعدني، وحموضة لويس من المعدن في مواقع الامتزاز، تم فحص مجموعات الأكاسيد عن طريق استخدام الأمونيا كمسبار جزيئي أساسي. بشكل عام، تم استخدام نهج النمذجة الجزيئية في الدراسة بمساعدة مصمم النماذج الجزيئية المتكشف. تكشف نتائج الدراسة أن حموضة الموقع النشط لها تباين مباشر مع قوة الامتزاز. علاوة على ذلك، تشير الدراسة إلى أن الموقع المعدني للمجموعات المختلفة كان بشكل عام أكثر حمضية من مواقع الأكسجين. علاوة على ذلك، أظهر Fe_2O_3 حموضة أعلى وامتصاصًا أفضل لثاني أكسيد الكربون من الأكاسيد المعدنية الأخرى التي تمت دراستها. وهكذا، في عمليات امتزاز ثاني أكسيد الكربون، استخدام Fe_2O_3 سيكون أكثر ملاءمة بناءً على نتائج هذه الدراسة.

1. Introduction

Fossil fuels have continually been a significant source of financial income to most nations blessed with the resources, like the most populous black nation called Nigeria, where their resource has claimed a more significant fraction of its fuels market likewise its energy mix in general but has long given little attention to the pollution control, waste management and biofuels [1–3]. Globally, these fossil fuels have continued to claim a significant share of the portion of the world's primary energy demand for many years to come, and their consumption is continually increasing. As the demand in the energy market continues to rise across the globe, it has therefore become necessary for both government and private investors to give better attention to the introduction of efficient technical solutions that would aid in better managing the hazardous gaseous products often released by industries and transport media that have been contributing to the demand of the ozone layer which has resulting to an unfriendly climate recently experienced in our various environment across the nations especially the locality dense with the operational process plants [2,4–6]. The importance of environmental gas monitoring and control has now been recognized as a vital area of study. However, much research has been focused on developing suitable gas-sensitive materials for continuous monitoring and setting alarms for hazardous materials released to the environment [7,8]. Some research work has identified households' wood-burning of cooking, generating sets, and vehicle emissions as the significant sources of carbon monoxide (CO) poisonous gas in the most populated urban city of Lagos, the Southwestern part of Nigeria. Moreover, many families, which include pregnant women, infant babies, and individuals, have been reported to have lost their lives as a result of the low-quality air control policies and inefficiency with the control of air pollution caused by this deadly gas [9–11].

In general, the literature survey indicates that air pollutions could either come via natural or human-made means. However, human-made pollutants from combustion, construction, mining, and agriculture, are significantly increasing in air pollution globally [12], and environmental researchers have indicated that the bulk of these climatic changes experiment results from the interaction of these pollutants with our environment [13].

Adsorption has long been identified as the potential means to combat this change, as a process that tries to use a material called adsorbent for the attraction or the capture of the adsorbent known as a pollutant in the subject. The adsorbate could be either in the vapor or liquid phase [14]. In this study, carbon monoxide (CO) is the key adsorbate of interest. The potential

adsorbents that were evaluated are Fe_2O_3 , Gd_2O_3 , and La_2O_3 , from which the best adsorbent that displayed the highest adsorption strength for the adsorbate has been searched via the use of the molecular modeling approach, which uses the principle of computational chemistry, where the primary focus is on solving chemically related problems by calculation or computational means [15,16].

A survey of the literature reveals 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 Beheshtian *et al.* [7], who evaluate CO and NO molecules' adsorption 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, DOSs, and MEPs analyses. Abbasi and Sardroodi [17] evaluated the adsorption potential of undoped and doped TiO_2 anatase nanoparticles for CO_x molecules via a DFT calculation. The findings suggest that N-doped nanoparticles were more suitable and energetically favorable than undoped ones. Some other works have employed it to identified research mechanisms in a process [18,19], acidity, and reactivity [20–22] of diverse materials.

This study, therefore, employed the use of computational approach to screen and evaluated the CO adsorption capacity of different selected metallic oxides such as Fe_2O_3 , Gd_2O_3 , and La_2O_3 as 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. The relationship between adsorption capacities and acidities was also investigated. Findings made would provide a preliminary contribution that would ease the search of material for carbon capture.

2. Methodology

2.1 Method of geometry optimization calculations for the clusters and species

The general overview of the computational method employed in this study of CO adsorption over different selected metallic oxides is diagrammatically illustrated in Figure 1.

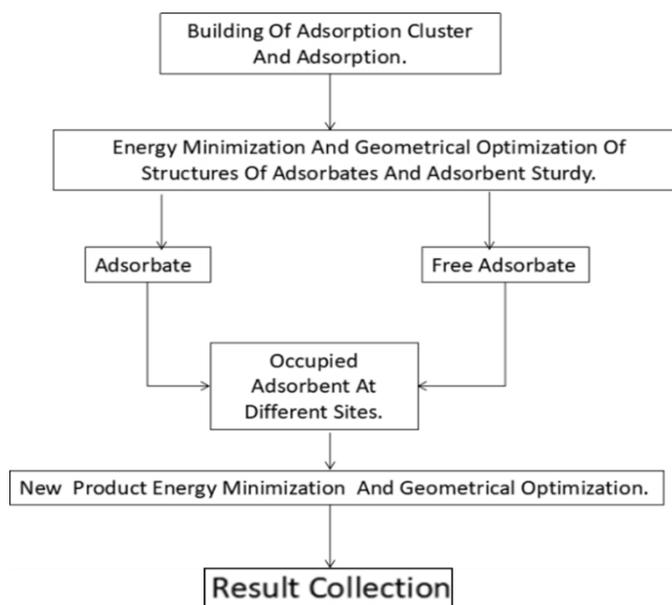


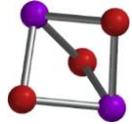
Figure 1. Flowchart Used for the Computational Approach.

The computing machine has a RAM of 4 GB, a core i3 processor, processor speed of 1.7 GHz, and a 500 GB 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. With reference to the literature [18,21], this study considered using the PM3 method due to the presence of transition metals and the available low-speed computing machine.

2.2 Choice of Adsorbent Structures/Clusters

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

Table 1. Choice of Adsorbent Structure (cluster)

Adsorbent name	Adsorbent cluster structure	Adopted from
Iron (III) Oxide (Fe_2O_3)		Nelson et al. [23]
Gadolinium (III) Oxide (Gd_2O_3)		Yuan et al. [24]
Lanthanum (III) Oxide (La_2O_3)		Jing-Heng et al. [25] and Reed et al. [26]

2.3 Method of stability calculations for the clusters and species

The stability of the structures was evaluated using the energy bandgap, which is the difference between the energy of the highest occupied molecular orbital (E-HOMO) and energy of the lowest occupied molecular orbital (E-LUMO) as expressed in equation (1) adapted from literature [20,27].

$$E\text{-}G_{ab} = E(\text{LUMO}) - E(\text{HOMO}) \quad (1)$$

E-Gab is the bandgap energy, E (LUMO) is the lowest occupied molecular orbital energy, while E (HOMO) is the highest occupied molecular orbital energy.

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.* [21], Yu-Jue *et al.* (2013), and Ming-Lei *et al.* [28].

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

Where E_{ads} is the adsorption energy, E (CO) is the total energy of the CO adsorbate, while E (adsorbent) is the total energy of the adsorbent (oxide).

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 [29] and Oyegoke *et al.* [21], which identifies ammonia as an excellent potential probe for the evaluation material acidity via computational approach using the same equation as that of the adsorption energy as in equation (2).

3. Results and Discussions

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.

Table 2: Energy minimization and geometrical optimization of adsorbent clusters using PM3 semi-empirical method

Formula	E (kJ/mol)	E-HOMO (kJ/mol)	E-LUMO (kJ/mol)	E-GAP (kJ/mol)
Fe ₂ O ₃	46.88	-1831.56	-877.57	953.99
Gd ₂ O ₃	-1030.89	-1203.1	-217.75	985.35
La ₂ O ₃	-1745.74	-844.99	60.31	905.30

Table 3: Energy minimization and geometrical optimization of CO and NH₃ using 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 ₃ N	-12.83	-935.48	321.62	1257.10

The report presented in Table 2 indicates that the Gd₂O₃ was more stable, while La₂O₃ was less stable. The clusters were generally less stable than the adsorbate (CO and ammonia) due to their lower energy gap displayed in Tables 2 and 3, in line with the literature [20,22] that reports that the larger an energy bandgap, the higher its stability.

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 alkaline probe that is adsorbed on the metal oxide surface (the molecular structures for the Lewis acidity simulations is presented in Table 7 at the Appendix). The probe adsorption energy was used to assess the acidity of the various sites. As an alkaline molecular probe, the use of ammonia has been proved in previous studies [21] to be valid. According to Liu [29] and Oyegoke et al. [21], the high the probe adsorption energy, the higher the Lewis acidity.

Table 4: Result of Lewis acidity of the clusters adsorption sites using an alkaline molecular probe.

Site Location	Formula	E (kJ/mol)	E HOMO (kJ/mol)	E LUMO (kJ/mol)	E GAP (kJ/mol)	E _{ads}
M-site	H ₃ Fe ₂ NO ₃	-932.1	-817.91	13.5	831.41	-972.69
M-site	H ₃ Gd ₂ NO ₃	-1972.07	-675.03	-66.67	608.36	-185.51
M-site	H ₃ La ₂ NO ₃	-1800.69	-787.12	107.94	895.07	-42.12
O-site	H ₃ Fe ₂ NO ₃	-983.2	-897.39	-89.94	807.45	-957.54
O-site	H ₃ Gd ₂ NO ₃	-1813.38	-560.89	186.03	746.92	-26.82
O-site	H ₃ La ₂ NO ₃	-1037.81	-1286.5	-369.85	916.65	720.76

The findings from the results presented in Table 4 indicates that in all metallic oxides considered in this study, their respective metallic sites were continually found to be more acidic compared to their respective oxygen sites due to the low adsorption energies recorded for the adsorption of ammonia (basic probe) on oxygen sites but higher adsorption energy for the metallic sites. General evaluation of the oxides indicates that iron oxides were found to be more acidic, while lanthanum oxide was found to have shown the lowest adsorption energy following the computational approach reported in the literature [17,20,28].

3.3 Adsorption energy computations

Table 5 shows the adsorption energies results obtained for the carbon monoxide singly bonded on the adsorbate (the molecular structures for the adsorption simulations is presented in Table 8 at the Appendix). The collected results indicate that the iron oxide displays the highest adsorption energies of -754.08, -922.01, and -830.03 kJ/mol, followed by gadolinium oxide reported as -174.60, -306.27, and -444.38 kJ/mol. In contrast, lanthanum oxide has the minimum adsorption energy of 600.27, 602.79, and 405.02 kJ/mol as their adsorption energy for physisorption, chemisorption at the metal site and oxygen sites, respectively.

Table 5. Minimization and geometrical optimization of adsorbent clusters with CO on their surfaces using 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)	Eads
Physio.	CO.Fe ₂ O ₃	-789.81	-1697.08	-598.31	1098.77	-754.08
Physio.	CO.Gd ₂ O ₃	-1288.1	-1129.41	-372.66	756.76	-174.60
Physio.	CO.La ₂ O ₃	-1228.08	-1391.28	-372.87	1018.41	600.27
Chem.(M)	CFe ₂ O ₄	-957.74	-989.07	-178.78	810.29	-922.01
Chem.(M)	CGd ₂ O ₄	-1419.77	-1371.26	-547.76	823.5	-306.27
Chem.(M)	CLa ₂ O ₄	-1225.56	-1449.1	-385.78	1063.32	602.79
Chem.(O)	CFe ₂ O ₄	-865.76	-1692.65	-613.12	1079.53	-830.03
Chem.(O)	CGd ₂ O ₄	-1557.88	-1216.95	-260.41	956.54	-444.38
Chem.(O)	CLa ₂ O ₄	-1423.13	-1294.35	-471.65	822.7	405.22

Key: Physio= Physisorption, Chem. (M)=Chemisorption Metal Site,
Chem. (O)=Chemisorption Oxygen Sit

Table 6. Energy minimization and geometrical optimization of adsorbent clusters with CO on their surfaces using PM3 semi-empirical method via Double bonded CO Adsorption.

Type of Adsorption	Formula	E (kJ/mol)	HOMO (kJ/mol)	LUMO (kJ/mol)	E-GAP (kJ/mol)	Eads
Physio.	CO.Fe ₂ O ₃	-317.29	-1642.34	-757.9	884.43	-508.82
Physio.	CO.Gd ₂ O ₃	-2023.43	-692.38	-73.85	618.53	-167.09
Physio.	CO.La ₂ O ₃	-1423.13	-1294.27	-471.69	822.58	-381.05
Chem. (M)	CFe ₂ O ₄	-742.14	-1646.54	-762.35	884.2	-933.67
Chem.(M)	CGd ₂ O ₄	-2150.71	-668.72	-6.43	662.29	-294.37
Chem.(M)	CLa ₂ O ₄	-1964.28	-612.48	-42.18	654.66	-922.20
Chem. (O)	CFe ₂ O ₄	-523.27	-1690.76	-833.54	857.21	-714.80
Chem. (O)	CGd ₂ O ₄	-2023.4	-692.34	-73.81	618.53	-167.06
Chem. (O)	CLa ₂ O ₄	-1970.72	-852.29	-61.12	913.41	-928.64

Key: Physio= Physisorption, Chem. (M)=Chemisorption Metal Site,
Chem. (O)=Chemisorption Oxygen Site

Considering the result obtained from the CO singly bonded adsorption strength, the iron oxide was found to be the strongest metal oxide for absorbing carbon monoxide. The result obtained for the double-bonded CO adsorption on the metal oxide was presented in Table 6. The results show that iron oxide has the highest adsorption energy with -508.82, -933.67, and -714.8 kJ/mol, followed by lanthanum oxide with -381.05, -922.2, and -928.64 kJ/mol, while Gadolinium oxide has the lowest adsorption energy of -167.09, -294.37 and -167.06 kJ/mol for the physisorption, adsorption at metal and oxygen sites, respectively. The adsorption energy trend was similar to that made for the singly bond CO adsorption studies, indicating that the metal oxide with the highest adsorption energy is iron oxide. The findings deduced for the iron oxide potential for the capture of carbon monoxide was found to be similar to the report of Cho *et al.* [30] that identifies iron oxide to be the second-best in among the oxide (of iron-, nickel-, copper-and manganese-based oxygen) considered in the study experimentally.

The general evaluation of the Table 5 and 6 indicated that the iron oxide (adsorbent) displayed the highest adsorption strength (with the highest negative values) at both singly and doubly bonded carbon monoxide adsorption evaluation. The emergency of iron oxide as the best oxide compared to other oxides evaluated for the adsorption of carbon monoxide was found to be in good agreement with the literature [31–33] reports, where iron oxide was experimentally confirmed to be suitable for carbon capture. These findings indicated that iron oxide shows a better adsorption potential for carbon capture than other oxides used in this study.

4. Conclusions

The study of the Lewis acidity unveils that the adsorbent studied, that is, the iron oxide, gadolinium oxide, and lanthanum oxide displayed a higher Lewis acidity at the metal site, which implies that the site is the most electron pair acceptor site, 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. Moreover, the iron oxide was found to have shown the highest Lewis acidity and CO adsorption energies than other oxides considered in the study. From all the results obtained from this study, it can thus be concluded that iron oxide would be more promising for carbon capture due to its high affinity and binding strength for the CO reported in this study.

5. Acknowledgement

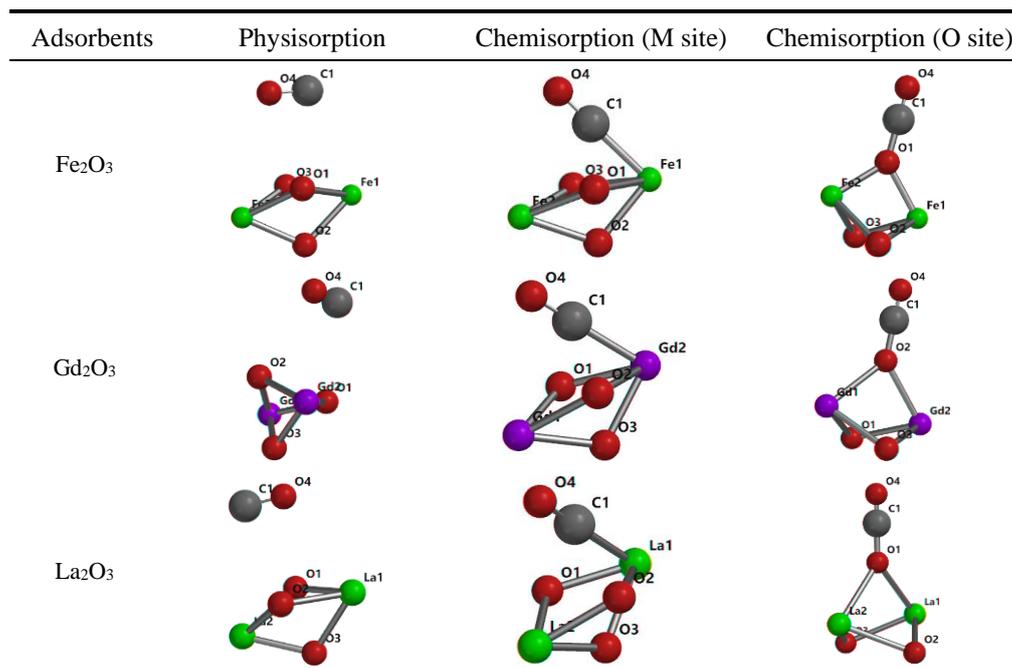
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6. Appendix

Table 7: Molecular Structures Used for the Simulations of Lewis Acidity of Site for Adsorbents

Sites	Fe ₂ O ₃	Gd ₂ O ₃	La ₂ O ₃
Metal			
Oxygen			

Table 8. CO adsorption across the different adsorbents



7. References

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