MgO Cluster Models for Capture CO\textsubscript{2} Molecule: A Computational Study

Zinab Ibrahim Alhony and Fathi Hassan Bawa

Abstract—The density functional theory (DFT) method was used to study the adsorption of acidic CO\textsubscript{2} molecule on the oxide clusters (MgO)\textsubscript{n}, (n = 2, 4, 6, 8, 9 and 12). Basis sets, 6–311G, 6–311G (d) and 6–311G (2d) were employed in order to test the effect on adsorption structures and binding energies. Both Mg\textsuperscript{2+} and O\textsuperscript{2−}-adsorption sites have been considered. Our previous calculation DFT energies have been achieved for the (MgO)\textsubscript{n}, (CaO)\textsubscript{n}, (n = 1–4, 6, 8, 9, and 12 clusters), [WJERT, 2019, Vol.5, Issue 1, 328-341]. The present work investigates the adsorption properties (e.g., adsorption energies, geometries and HOMO and LUMO molecular orbitals) of a single CO\textsubscript{2} molecule. The results show that the CO\textsubscript{2} molecule / (MgO)\textsubscript{n} clusters prefer to adsorb as [Mg\textsubscript{surf} − CO\textsubscript{2}]\textsuperscript{2−} with one acidic Mg\textsuperscript{2+} sites, while the interaction with surface basic O\textsuperscript{2−} sites, carbonate species consequently may occur. The HOMO and LUMO interaction between CO\textsubscript{2} and MgO cluster models were also studied. Furthermore, such nanostructures systems can be potential candidates for practical applications of capturing CO\textsubscript{2} from hot exhaust gases.

Index Terms—CO\textsubscript{2} Capture, MgO Clusters, Adsorption Energy, DFT, HOMO, LUMO.

I. INTRODUCTION

Considering as one of the world’s consumable carbon sources, fossil fuels, including oil, coal and natural gas, are still the main resources consumed today. Statistical data shows that, in 2018, CO\textsubscript{2} emissions from the consumption of these resources grew by 2.0%, producing again the fastest expansion for many years, with an increase in emissions of around 0.6 gigatonnes over the previous year [1]. However, CO\textsubscript{2} emissions from the combustion of these fossil fuels are causing serious environmental issues. In fact, the massive emissions of CO\textsubscript{2} have resulted in a significant increase in the average temperature of the Earth over the last 200 years, a trend that still continues today [2]. Consequently, various abnormal changes in the climate are an indication that the world is facing a global warming issue [3, 4]. It is important to mention that, even though the demand for all fuels increased in 2019, the growth of demand was particularly strong for renewable energy sources. After “Paris agreement 2016”, the use of renewable energy increased by 14% in 2018, indicating that the energy production sector focus on renewable energy technologies [5].

Nano-chemistry, a branch of nano-science, is focused on building nanoscale systems (1–100 nm) mainly using atom or molecule as building block. Nano-chemistry brings together multiple disciplines using physical methods and chemical theories and experiments to investigate properties of materials at the nano-scale. Of the latter, the nan-clusters continue to attract much interest due to a manifold of potential industrial applications.

What are atomic clusters? A cluster is first defined as a finite group of atoms that are held together mainly or at least to a significant extent, by chemical interactions directly between the atoms. Clusters NM are thus aggregates of a finite number N of atoms or molecules M, thus, bridging the gap between the isolated atom/molecule and the macroscopic solid state of matter. The development of the societies with increase in population and standard of living has led to an explosive growth in the use of energy from fossil fuels [6]. Advanced technologies, new methods and materials have been developed to diminish the human / industrial need for fossil fuels, but it is estimated that more than 85% of the energy used worldwide still remains derivate from nonrenewable sources [7]. In addition, when carbon dioxide and other products of fossil fuel combustion build up in the atmosphere, they trap heat within the inner layers of the earth’s atmosphere, this additional heat will cause global climate change. To circumvent this problem, improved technologies for CO\textsubscript{2} capture are necessary to achieve low energy penalties. The fossil fuel combustion is responsible for high emissions of CO\textsubscript{2}, which is the main greenhouse gas produced by human activity [6]. Since the industrial revolution, the concentration of this gas in the atmospheric of the earth increased more than 30% and is the main cause of climate change and planetary temperature increase [6, 8]. The global warming is considered a risk for future generations given the cumulative nature of CO\textsubscript{2}. Therefore, sustained reduction of emissions has been found necessary [6, 9].

CO\textsubscript{2} capture and storage is a technological solution to reduce the atmospheric concentration of the greenhouse gas CO\textsubscript{2} to mitigate climate change, long this line, MgO is promising solid CO\textsubscript{2} sorbent. The present work focuses only on CO\textsubscript{2} which is the main form of CO\textsubscript{2} in exhaust gas, adsorbed on and reacted with MgO cluster models using density functional theory. It is generally, believed that CO\textsubscript{2} reacts on ionic metal oxides, Mg\textsuperscript{2+}/Ca\textsuperscript{2+}/Ba\textsuperscript{2+} or O\textsuperscript{2−} sites, which formed and then stored on MgO as carbonates and carbonates species [10], as well as forming carbonates species on CaO (001) [11]. Also, NO\textsubscript{2} interact with metal oxide surfaces, i.e., the BaO (100) surface formed nitrite/nitrate [12]. In this context, the basicity of an oxide is defined as the ability of the surface to donate electronic charge to the adsorbed molecule, which is important in a variety of industrial and environmental applications such as methanol.

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synthesis exhaust cleaning, and CO₂ capturing [13, 14]. Alkaline earth oxides [15] are basic and interest in materials for CO₂, NOₓ, and SOₓ capture technologies, for example a strong oxide CO₂ capture and storage is emitted from an industrial process. On the other hand, usefulness of the cluster calculations for interpreting IR spectra by Bawa [16], have been performed for active modes of the (MgO)ₙ, (n = 3, 4, 6, 8, 9, 12) cluster models. In addition, Fukuda and Tanabe [17] studied CO₂ adsorption on MgO and CaO powders by infrared (IR) spectroscopy. They observed the appearance of a bidentate carbonate on MgO. Karlsen et al., [18] studied the interaction between NOₓ, SOₓ and CO₂ with M-O (001), M= Mg, Ca, Sr, Ba). They found that CO₂ is horizontally physisorbed on the MgO terrace sites, while chemisorption, distortion of the C–O is observed on CaO.

The present work, we report density functional theory calculations (B3LYP) that probe the relationship between cluster size and the adsorption energies E(ads) of CO₂ molecule on the (MgO)ₙ, (n = 2, 4, 6, 8, 9, 12) cluster models, as well as devoted to HOMO and LUMO orbitals, while a subsequent study will address the effect of electron transfer at metal oxide surfaces; NO₂ adsorption on MgO and CaO clusters.

II. METHOD AND MODELS

The calculations are carried out by DFT method. Density functional simulations allow one to describe catalytic activity for a wide diversity of reactions in different materials. Computational simulations could provide a theoretical guideline for the choice of conditions and nanomaterials to improve a specific catalytic reaction. All calculations were performed with the Gaussian 09 program package [19]. Solid MgO has the rock-salt structure with its nearest Mg–O distance 2.104 Å [20]. In addition, our previous investigation [21] demonstrated how the stabilities of alkaline earth oxide clusters increase with increasing size, and the applicability of the B3LYP hybrid density functional for such cluster calculations was tested. These neutral cluster models are (MgO)ₙ, (MgO)ₙ, (MgO)ₙ, (MgO)ₙ, (MgO)ₙ, (MgO)ₙ and (MgO)ₙ (see Fig. 1) and reference [21]. Table 1 reports the calculated energies, bond lengths, bond angles of the free CO₂ gas extracted from the 6–311G, 6–311G(d) and 6–311G(2d) basis sets. Density functional theory calculations were carried out using the gradient-corrected Becke three parameters hybrid exchange functional [22-26] in combination with correlation functional of Lee, Yang, and Parr [27]. In case of Carbon, Oxygen atoms of adsorbates, the 6–311G set was employed and for some stability tests using 6–311G (d) and 6–311G (2d) in this calculation. The results indicated that the B3LYP functional led to good energetic for NO₂ [28], CO₂ [29] and SO₂ [30].

The adsorption energies (E_ads, eV) were defined as:

\[ E_{\text{ads}}(\text{CO}_2) = E_{\text{slab}+\text{CO}_2} - E_{\text{slab}} - E_{\text{CO}_2} \]  

where \( E_{\text{slab}+\text{CO}_2} \) and \( E_{\text{slab}} \) are the total energy of the systems with and without CO₂ adsorbed, respectively, and \( E_{\text{CO}_2} \) is the total energy of a CO₂ molecule in the gas phase. The minus sign in adsorption energy means it is an exothermic adsorption, while positive adsorption energies denote an endothermic adsorption.
III. RESULTS AND DISCUSSION

A. Adsorption of CO$_2$ on MgO cluster models

On a metal oxide clusters, CO$_2$ adsorption can occur in two different modes, either the metal cations (Mg$^{2+}$) or the oxygen anions (O$^{2-}$). Two binding situations were investigated for CO$_2$ adsorption corresponding to surface \([\text{Mg}^{\text{surf}}-\text{CO}_2]^{2-}\) and \((\text{CO}_2)^{2-}\) species. When CO$_2$ interacts with a metal oxide surface, a charge transfer from a surface anion, O$^{2-}$ to the CO$_2$ forming energetically surface carbonate species, therefore the interaction is HOMO and LUMO energy gap [31]. The adsorption energies (see equation (1)) of the CO$_2$ on (MgO)$_6$, (MgO)$_8$, (MgO)$_9$, and (MgO)$_{12}$ cluster models are plotted in Figures 2, 3, 4, 5, and given in Tables 1, 2, 3.

![Fig. 2. Monodentate adsorption on (MgO)$_6$ cluster model, (a) corner site, (b) The structure is generally described as monodentate parallel to the Mg-O surface.](image)

![Fig. 3. Adsorption structures identified for CO$_2$ parallel on (MgO)$_8$ cluster models, (a) with Mg atoms, (b) the oxygen atoms of the adsorbate are almost coordinated to O atoms.](image)

![Fig. 4. Physisorption structures identified for CO$_2$ parallel on (MgO)$_9$ cluster models, (a) with Mg oxygen atoms of the adsorbate are almost coordinated to surface O atoms.](image)
We found that the structures shown in Figs 2, 3, 4, 5 are called monodentate by Mg$^{2+}$ or O$^{2-}$. Initially, each promoter was placed on MgO clusters at a distances, 2, 2.5, 3, 4, 4.5, 5 Å as displayed in tables 2, 3, 4. Energetics and structural information has been acquired regarding CO adsorption. Here, connection or reality are sought by comparing computed and measured vibration spectra. Thus, the characteristic vibration frequencies are displayed in conjunction with those of the bare clusters. This becomes particularly important with the fact that CO$_2$(MgO)$_n$ carbocation displays characteristic absorption at $\omega_1$(Sym) [1322(C$_\alpha$), 993(C$_3$)], $\omega_2$(bend) [837(C$_3$), 746(C$_\alpha$), 695(C$_2$)] and $\omega_3$(asym) [1709] [29]. For more details, see the experimental and theory study the adsorption of SO$_2$ on MgO by Schneider et al [32]. These stabilization were attributed to an additional cluster binding energy between the CO$_2$ on (MgO)$_n$ and (CaO)$_n$ cluster models, as described by previous work [29], that a carbonate species forms, and $E_{ads}$ (CO$_2$) on the (MgO)$_n$ site was calculated 1.50 eV, similar to this work 1.41 eV. Further, the physisorption energy for the CO$_2$/MgO$_n$ was calculated 0.080 eV versus 0.075 eV have been calculated by [33]. We note for MgO clusters that stronger CO$_2$ adsorption is seen for (MgO)$_2$, which can be correlated with the shorter MgO-Bond of 2.0 Å. For (MgO)$_n$, the adsorption was found at longer bond of 4.0 Å, while for (MgO)$_6$, (MgO)$_8$ the adsorption was correlated with longer bond of 5.0 Å and longer bond 4.5 Å respectively. The (MgO)$_9$, (MgO)$_{12}$, the adsorption was stronger with the longer bond of 4.0 Å for both clusters, see Tables 2, 3, 4.

![Fig. 5. Parallel orientations of linear CO$_2$ on (MgO)$_2$ cluster model, (a) Parallel coordinated with the two O$^{2-}$ surface, (b) parallel with the Mg-O surface, (c) and (d), the two structures are generally described as monodentate with the Mg$^{2+}$ atom. Mg atom is green, O atom is red, carbon is gray.](image)

**TABLE I: CALCULATED BOND LENGTHS, BOND ANGLES, AND TOTAL ENERGIES FOR FREE CO$_2$ MOLECULE**

<table>
<thead>
<tr>
<th>System</th>
<th>O-C (Å)</th>
<th>O-C-O (°)</th>
<th>Tot. Energy (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free CO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-3G</td>
<td>1.22</td>
<td>180</td>
<td>−185.93946</td>
</tr>
<tr>
<td>6-31G</td>
<td>1.18</td>
<td>180</td>
<td>−188.57232</td>
</tr>
<tr>
<td>6-31G(d)</td>
<td>1.16</td>
<td>180</td>
<td>−188.59846</td>
</tr>
<tr>
<td>Exp.</td>
<td>1.17</td>
<td>180</td>
<td>−188.66056</td>
</tr>
</tbody>
</table>

**TABLE II: CALCULATED CO$_2$ STRUCTURE AND ADSORPTION ENERGIES OF CO$_2$(MgO)$_2$ AND (MgO)$_n$ CLUSTER MODELS**

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Mg-CO$_2$ (Å)</th>
<th>Total energy (au)</th>
<th>Adsorption energy (eV)$^{(a)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$(MgO)$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-31G</td>
<td>2.5</td>
<td>−739.174607</td>
<td>0.59</td>
</tr>
<tr>
<td>6-31G(d)</td>
<td>2.0</td>
<td>−739.116766</td>
<td>2.16</td>
</tr>
<tr>
<td>Exp.</td>
<td>1.18</td>
<td>−739.281533</td>
<td>3.67</td>
</tr>
</tbody>
</table>

$^{(a)}$ Adsorption energy is calculated by (1)

**TABLE III: ADSORPTION PROPERTIES OF A SINGLE CO$_2$ ON THE STRUCTURE AND ADSORPTION ENERGIES OF CO$_2$ ON (MgO)$_n$ AND (MgO)$_{12}$ CLUSTER MODELS**

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Mg-CO$_2$ (Å)</th>
<th>Total energy (au)</th>
<th>Adsorption energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$(MgO)$_n$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-31G</td>
<td>3.0</td>
<td>−1841.101801</td>
<td>0.08</td>
</tr>
<tr>
<td>6-31G(d)</td>
<td>3.0</td>
<td>−1841.097288</td>
<td>0.04</td>
</tr>
<tr>
<td>Exp.</td>
<td>1.83</td>
<td>−1884.79238</td>
<td>7.04</td>
</tr>
</tbody>
</table>

**TABLE IV: CALCULATED CO$_2$ STRUCTURES AND ADSORPTION ENERGIES, ADSORPTION OF CO$_2$ ON (MgO)$_n$ AND (MgO)$_{12}$ CLUSTER MODELS**

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Mg-CO$_2$ (Å)</th>
<th>Total energy (au)</th>
<th>Adsorption energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$<em>2$(MgO)$</em>{12}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-31G</td>
<td>4.0</td>
<td>−3494.124111</td>
<td>2.80</td>
</tr>
<tr>
<td>6-31G(d)</td>
<td>4.0</td>
<td>−3494.106874</td>
<td>0.10</td>
</tr>
</tbody>
</table>

**B. Molecular orbital, HOMO and LUMO**

The Frontier orbitals HOMO and LUMO, determine the way, the molecule interacts with other species and the gap between them helps in characterizing the chemical reactivity as well as kinetic stability of the molecule. The HOMO illustrated the ability to donate an electron, LUMO is an electron acceptor represents the ability to obtain an electron. Moreover, energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability
for structures. In order to understand the electronic properties of the clusters, the HOMO and LUMO, electronic densities and the Mulliken charges for adsorption CO$_2$ on MgO are represented in Figs. 6-9. According to the molecular orbital theory, High occupied molecular orbital (HOMO) and Low occupied orbital (LUMO) are two crucial factors influencing the activity of MgO clusters. HOMO is usually prone to provide electrons, while LUMO accepts electrons. Further, based on such a concept, the study on the frontier orbital energy can provide useful information for the active structures. The HOMO and LUMO of CO$_2$ were mainly reflected in O atom and C atom, and the HOMO-LUMO of MgO were reflected in O and Mg as well. Thus, MgO (HOMO) donates electrons to CO$_2$ (LOMO) rather than CO$_2$ (HOMO) to MgO (LUMO) resulting the formation of new bond C-O bond. Our results show the HOMO and the LUMO population of CO$_2$/MgO cluster models, (Figs. 6-9).

Fig. 6. Molecular orbitals for the HOMO (a) and LUMO (b) for (MgO)$_8$. The red and green parts represent the cloud density of orbitals at HOMO or LUMO states.

Fig. 7. Milliken Population (charge density of atoms in adsorption structure of (MgO)$_{12}$ (a and b), (red ball: O atom, grey ball: C atom and green ball: Mg atom)

Fig. 8. The HOMO molecule orbital density distribution of CO$_2$ @ (a) (MgO)$_{12}$ (b) (MgO)$_9$ cluster models
IV. CONCLUSIONS

We have investigated the adsorption of CO$_2$ molecule at (MgO)$_n$, n = 2, 4, 6, 8, 9, 12 cluster models by DFT/B3LYP at the 6-311G, 6-311G (d) and 6-311G (2d). We are able to draw the following conclusions:

(a) Rock-salt earth oxides such as MgO is promising material for capturing CO$_2$ from hot exhaust gases.

(b) The adsorption energies show a marked dependence on the cluster size and basis sets.

(c) There are little studies regarding to carbonate CO$_3^{2−}$, in contrast to carbonate $CO_2^{2−}$, NO$_2^−$, NO$_3^−$, SO$_2^{2−}$, SO$_3^{2−}$ [34].

(d) Adsorption energies of CO$_2$ to MgO cluster models with adsorption energies of 0.59, 1.92, 0.08, 0.67, 1.41 and 2.80 eV for n = 2, 4, 6, 8, 9 and 12 respectively. The experimental value for Mg$^+ – CO_2$, 0.64 eV [35].

(e) Adsorption energies of CO$_2$ and SO$_2$ to alkaline earth oxide clusters are fairly insensitive to choice of cation, as carbonates and sulphonates are formed via local bonding, 1.41 eV(this work) for CO$_2$ and 1.77 eV [30] for SO$_2$ on (MgO)$_n$ respectively.

(f) Due to charge transfer to CO$_2$ molecule, the CO$_2$/MgO cluster models prefer to adsorb as [Mg$_{m+n}$CO$_2$]$^{2−}$ with one acidic Mg$^{2+}$sites as charge transfer to CO$_2$ molecule, while it is apparent that in the presence of CO$_2$, CO$_3^{2−}$ species may occur on Lewis base O$^{2−}$ sites.

(g) The formation of the carbonate CO$_3^{2−}$ can described as two orbitals HOMO and LUMO interaction involving charge transfer from a filled orbital of O$^{2−}$ to the empty molecular orbitals of CO$_2$.

(h) DFT is a useful tool to investigate the HOMO and LUMO orbital energies, (donating electrons from filled orbitals of MgO into the vacant of CO$_2$ molecule). The location of HOMO and LUMO suggest that Lewis acids bonding with CO$_2$ and Lewis base bonding to CO$_2$.

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REFERENCES


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