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Effect of Electron Transfer at Metal Oxide Surfaces; NO_2Adsorption on$(CaO)_n$, *n*=2, 3, 4, 6, 8, 9, 12 Cluster ModelCalculations

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ABSTRACT: In our previous article, the geometrical optimizations have been performed for the $(CaO)_n$, n = 1-4, 6, 8, 9, and 12 cluster models, [WJERT, 2019, **5 (1),** 328-341]. In this study,we have investigated the adsorption of performance NO_2gas towards metal oxide clusters $(CaO)_n$, n = 2, 3, 4, 6, 8, 9, 12) cluster models, and focus on electron transfer between the CaO and NO_2 molecule by employing density functional theory (DFT), B3LYP method. Results show that the charge transferred goes from surface clusters to NO_2 anti-bonding orbitals which makes more reactive, and becomes stronger. Moreover, NO_2 adsorbs at the one, two Ca^{2+}sites forming a nitrite (NO_2^-). Meanwhile, the interaction of NO_2 with Lewis baseO^{2-},and consequently may form a nitrate (NO_3^{2-}) species, which is less adsorption favorable. The total adsorption energies revealed that NO_2 gas was strongly chemisorbed on the$(CaO)_n$, *n* = 2, 4, 6 and 8cluster models, whereas $(CaO)_n$, n=3, 9 and 12 results in a weak interactions. Further, the results of optimized structure showed that the total adsorption energies and charge transfer contributions indicated that CaO is a better acid-base than MgO, due to the increasing basicity and bigger cationic size of the CaO. The reason for these different basicities and reactivates can be ascribed to the different electrostatic (Madelung) potentials at the two surfaces.
Keywords*-Adsorption energy, CaO Cluster models, Density functional theory DFT, NO_2 Adsorption*

I. INTRODUCTION

The world energy consumption is increasing and the mean energy sources are finite. The fact that fossil fuels such as petroleum, coal, natural gas are dominating the energy supply, challenges the society in different ways.The use of fossil fuels usually results in emissions of harmful species of Nitrogen Oxides (NO_2, NO, N_2O)[1, 2]are formed in automotive engines and industrial by the combustion of nitrogen present in air, an example of the former is the "NO_x storage/reduction" concept for efficient fuel consumption, which has the engine working under excess oxygen conditions [3, 4].The increased interest in environmental issues such air pollution, there is a great demand for reduction of automotive exhaust gases. Furthermore, NO_x are harmful compounds responsible for acid rain, it reacts with hydrocarbons to produce ground level ozone, which is a major component of smog.Also nitrogen dioxide (NO_2) causes a number of serious health issues including acute bronchitis, cough and also increase the risk for respiratory allergies.

Calcium oxide is a large band gap material that is a candidate for some applications like thermal energy storage [5],ceramics[6] and catalysis [14].Studying the adsorption of NO_2onto $(CaO)_n$, *n*=2, 3, 4, 6, 8, 9, 12 cluster models is an important part of the investigation of the catalytic behavior of metal oxide surfaces. Nitrogen dioxide is a paramagnetic bent molecule with C_{2V} point group symmetry. It has been used as such a molecule with many theoretical studies by using DFT calculations. Furthermore, theoretical studies and experiments have been demonstrated that the alkaline earth oxides can useful materials for nitrogen dioxide capture and storage technologies with the access of the air. Bawa and Malliavin investigations of $(CaO)_n$ revealed that small clusters of $(CaO)_n$, *n*= 2, 3, 4, 6, 8, 9, 12 are quite stable in nature cage form, also, theoretical studies unveil that a MgO hexagonal ring shape is quite stable in nature[7-10].Moreover, alkali-earth oxide is an important class of metal oxides and the most of them crystallize in the cubic rock salt (NaCl) structure, due to thisthe urgent necessity to find candidate materials able to efficiently capture $NO_2$and storage technologies. Our previous studies have shown the effect of NO_2adsorption for a variety of alkaline earth oxides particularly MgO and CaO clusters [11-15].In recent years, density functional theory (DFT) calculations have been increasingly applied in studies of elementary reaction steps on the surfaces of MgO and CaO [16, 17]. They are able to adsorb strongly enough NO_2, CO_2 and various adsorbed species may exist. Along this line, the present work focuses only on NO_2 which is the main form of NO_x in exhaust gas, adsorbed on and reacted with CaO cluster models using

density functional theory. Furthermore, electron transfer may involve donors and acceptors at the molecular level, but often one of the components is a solid metal, a semiconductor, or an insulator. The capture and storage technique normally involve molecular activation achievable *via* electron transfer from the oxide substrate to NO_2 leading to two adsorbed NO_2 species were characterized, one corresponding to a surface nitrite and second nitrate species with $sp^3$with elongated N–O bonds and bond angles O–N–O.AlsoNO_2 may reacts with a thick BaO layer to form surface nitrite-nitrate ion pairs at 300 K, while only nitrates form at 600 K [18].

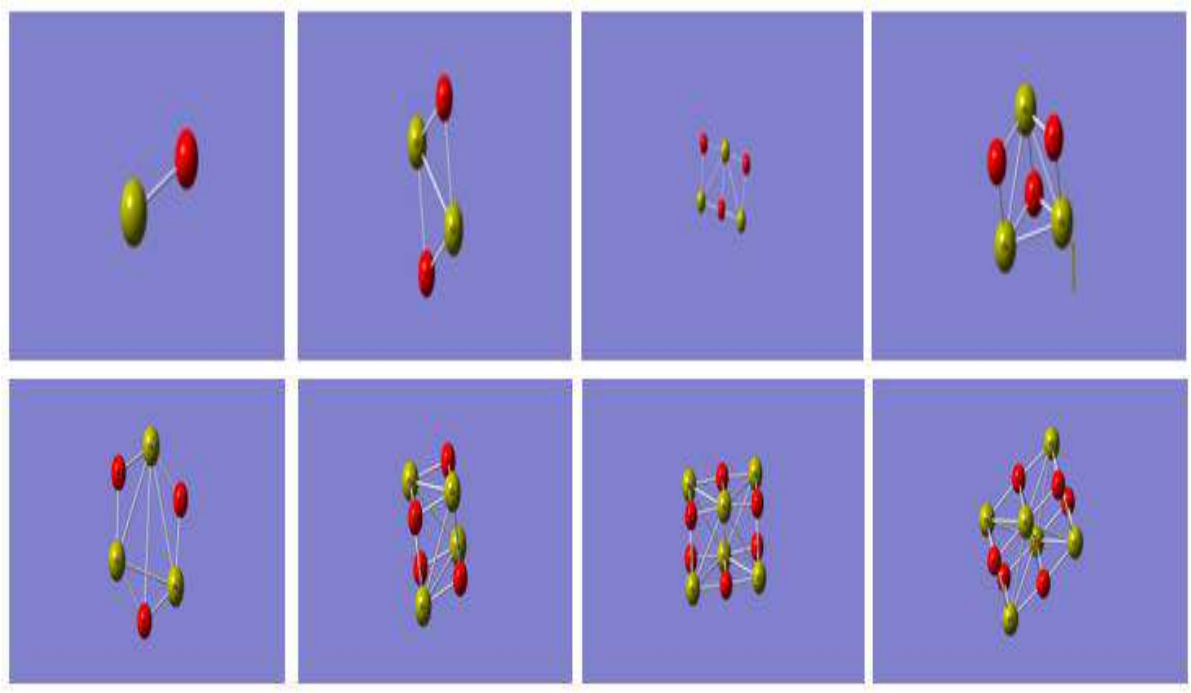
It is the goal of this paper to use density functional theory (DFT) calculations to explore the change in electronic and adsorption behavior of $(CaO)_n$, (n = 2, 3, 4, 6, 8, 9 and 12) upon NO_2 adsorption. It is a continuation of the work of Ref. [9], we wish to determine here structures and the adsorptions whether chemisorption or physisorption. A subsequent study will address a computational study of the vibrational frequencies and HOMO–LUMO adsorption of CO_2molecule on $(MO)_n$, M=Mg and Ca, (n = 3, 6, 9 and 12).

II. CALCULATION METHOD

Calculations for open shell molecule NO_2 were done by using density functional theory at the B3LYP /6–311G. DFT 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.Here, we seek to contribute to the deepened understanding of this NO_2 storage mechanism by means of quantum chemistry. The calculations have been performed with the program package Gaussian-09 on a computing system[19], and visualization was done through Gauss–View 5.0 [20]. In our previous study we become interested to study the $(CaO)_2$, $(CaO)_3$, $(CaO)_4$, $(CaO)_6$, $(CaO)_8$, $(CaO)_9$ and $(CaO)_{12}$ cluster models for NO_2 adsorption[9],(see Figure 1).The Ca, O and N atoms were treated by6-311Gbasis set to optimized geometries and adsorption energies. In this work, we report density functional theory calculations (B3LYP) that probe the relationship between cluster size and the adsorption energies E_{ads}ofNO_2 molecule on the cluster surfaces. Density functional theory calculations were carried out using the gradient-corrected Becke three parameters hybrid exchange functional [21-25] in combination with correlation functional of Lee, Yang, and Parr [26]. B3LYP, appears to be the DFT method of choice for such kind of calculations on most molecules and the results indicated to good energetics for NO_2 [12], CO_2 [13] and SO_2 [11].The adsorption energy (E_{ads})of NO_2 gas adsorption process on the $(CaO)_n$, (n = 2, 3, 4, 6, 8, 9 and 12) was calculated by using Eq. (1),

$$\boldsymbol{E_{ads} = E_{cluster+NO2} - (E_{cluster}+E_{NO2})} \qquad \textbf{(1)}$$

Where,$E_{\text{cluster }+NO2}$ and $E_{\text{cluster}}$are the total energy of the systems with and without NO_2 adsorbed respectively, and E_{NO2} is the total energy of a NO_2 molecule in the gas phase.E_{ads}< 0 means that it is an exothermic process, while E_{ads}> 0 indicates that the adsorption process is an endothermicadsorption.



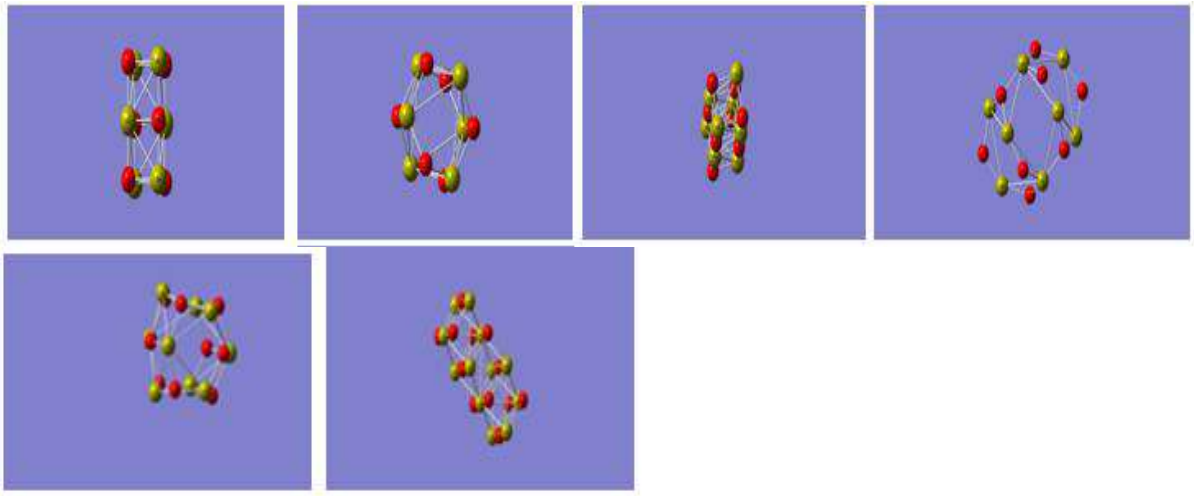


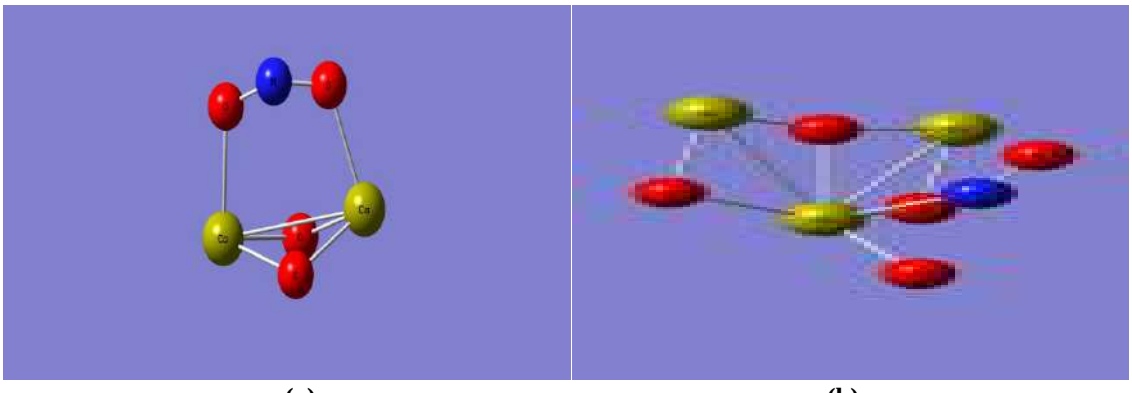
Fig.1:Optimized geometries of $(CaO)_n$, *n* = 1, 2, 3, 4, 6, 8 ,9 ,12, cluster models used in the presnt work,(see Reference 10) for details**.**

III. RESULTS AND DISCUSSION

3.Adsorption of NO_2on the $(CaO)_n$, n = 2, 3, 4, 6, 8, 9 and 12cluster models

3.1.Adsorption of NO_2 on the $(CaO)_n$, n = 2, 3 cluster models

As we know, NO_2 possesses one more electron than CO_2, which gives it a bent structure in the gas phase with an experimental N–O bond length of 1.197 Å and O – N – O bond angle of 134.3°. To obtain the stable adsorption clusters, we optimized two different sites of the $(CaO)_n$, *n*= 2, 3, 4, 6 clusters. Two binding situations were investigated for NO_2 adsorption corresponding to surface NO_2^-nitrite, and NO_3^{2-}nitrate species. Furthermore, in general binding as Ca^{2+}–[O–N–O]–Ca^{2+}, nitrite can be interpreted as producing an electron vacancy in the O^{2-} ions, while the interaction of the O^{2-}– NO_2forming of nitrate NO_3^{2-}species. The twocluster modelsand the corresponding structural parameter, adsorption energy, total energy and bond length are exhibited in Fig. 2 and Table 1.Our calculations predict that the NO_2 can binds to the CaO cluster sites in two different modes, the O_2bridgingdownapproaching to the cluster model with the twoCa^{2+}cation sites, with O–Ca distance of 2.5 Å.As shown in Fig. 2 (a) the adsorption energy of $(CaO)_2$is calculated to be 3.68 eV. The stronger adsorbed interactions between acidic Ca– Ca surface sites and NO_2 molecule is due to the electrostatic interactions and shorter $(CaO)_2$ – NO_2distance of 2.5 Å. Fig. 2(b)shows the NO_2 adsorption on $(CaO)_3$, the preferred mode to bonding is when the molecule approaches to the cluster model with N down which reveals the molecule is weakly bound with small adsorption energy$E_{ads}$of 0.09 eV.



(a) **(b)**

Fig.2: Adsorption structures (a and b) of NO_2on the $(CaO)_2$and $(CaO)_3$cluster models.

Table 1: Equilibrium Distance (Z), Total Energies and Adsorption Energies of NO_2on $(CaO)_2$, $(CaO)_3$, Cluster Models at the B3LYP / 6–311G Basis set of DFT

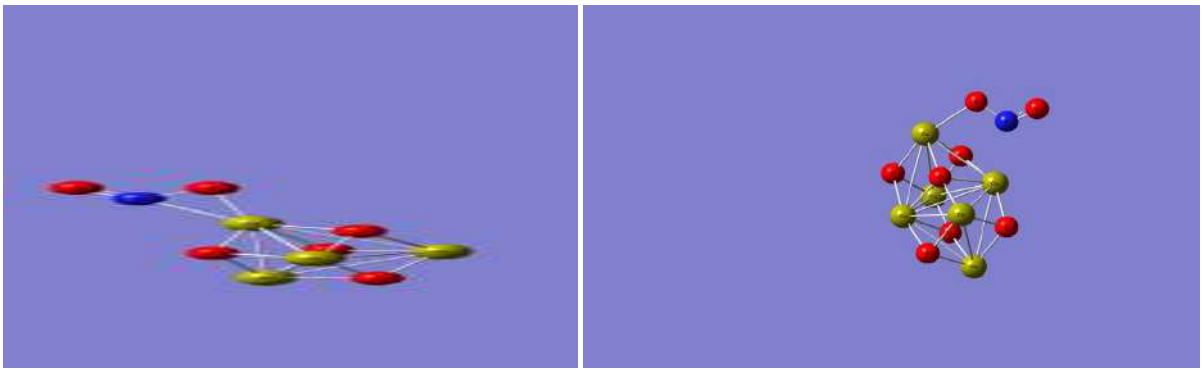
Systems	Z(Ca-NO_2) (Å)	Tot. Energy (au)	Ads. Energy (eV)[(a)]
$NO_2/(CaO)_2$	2.5	–1710.777795	3.68
$NO_2/(CaO)_3$	2.5	–2463.569094	0.09

[(a)] Adsorption energy is calculated by Eq. (1).

3.2. Adsorption of NO_2 on the $(CaO)_n$, n= 4, 6 cluster models

For $(CaO)_4$, as can be seen in Fig.3 (a), the NO_2 molecule is attached to the $(CaO)_4$ cluster model, where the N atom in the NO_2 is oriented to the $(CaO)_4$ cluster, and the corresponding parameter are listed in Table 2.In this context, we have performed cluster model calculations on the adsorption of NO_2 with cationic Ca^{2+} sites with strong chemisorbed interactions. During the adsorption process, distortion appears on the $(CaO)_4$cluster.The calculated E_{ads} for NO_2 adsorption is 3.66 eV with distance of 2.5 Å.

Regarding to $(CaO)_6$ cluster model, Fig. 3 (b) showsNO_2 adsorbed on cluster oxygen atom, the unpaired electron was found to remain and localized at the adsorption site resulting surface species NO_3^{2-}may occur as it comes out sp^3 hybridized three oxygen O fragments bound to the central nitrogen N. The stability of the NO_3^{2-}surface species increased to 3.79 eV, (see Table 2). The calculated adsorption energy of 3.66 eV and 3.79 eV are in good agreement with the previous work [12, 14].



(a) **(b)**

Fig. 3: Adsorption structures (a and b) of NO_2 on the $(CaO)_4$ and $(CaO)_6$ cluster models

Table 2: Equilibrium Distance (Z), Total Energies and Adsorption Energies of NO_2onto $(CaO)_4$ and $(CaO)_6$ cluster models at the B3LYP / 6–311G Basis set of DFT.

Systems	Z(Ca-NO_2) (Å)	Tot. Energy (au)	Ads. Energy (eV)[(a)]
$NO_2/(CaO)_4$	2.5	–3216.719453	3.66
$NO_2/(CaO)_6$	2.5	–4722.652415	3.79

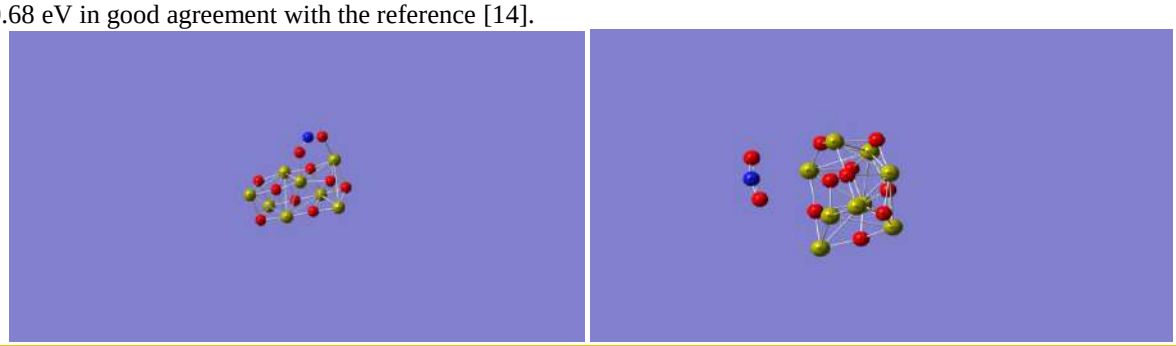
[(a)] Adsorption energy is calculated by Eq. (1).

3.3. Adsorption of NO_2 on the $(CaO)_n$, n= 8 and 9 cluster models

The optimized geometries and adsorbed energies for NO_2 on the $(CaO)_8$, and $(CaO)_9$ clusters models are presented in Fig. 4 (a), (b)and Table 3at the B3LYP/6–311G basis set of DFT. According to the computational results, NO_2 chemisorbs strongly on $(CaO)_8$cluster surfacewith the two Ca^{2+} cation sites forming nitrite species. The distance and adsorption energies play a vital role for obtaining the stability and seeking for the resultant designed geometries for adsorption.

In the case of $(CaO)_8$, the calculated bond distances of Ca^{2+}–NO_2 is 4 Å with the oxygen atom bridging two Ca^{2+} along the cluster model and after optimization we obtained the adsorption energy NO_2–$(CaO)_8$ is 4.15 eV. Further, the adsorption energy of NO_2 on two Ca cations of the CaO surface is strong, which might be due to the charge transfer results from cluster surface to NO_2 molecule.

The optimized geometry and adsorption energy of NO_2 –$(CaO)_9$ atB3LYP /6–311G are depicted in Fig. 4 (b)and Table 3. Adsorption of NO_2 on $(CaO)_9$ predict physisorbed with the two-O down orientations, it shows a small value of adsorption energy (E_{ads}= 0.46 eV). The small adsorption energy may due to the distortion of the inside the cluster structure. We observed that the adsorption energy comes out fairly similar, i.e. 0.46 eV *versus* 0.68 eV in good agreement with the reference [14].



(a) (b)

Fig. 4: Adsorption structures (a and b) of NO_2 on the $(CaO)_8$ and $(CaO)_9$ cluster models.

Table 3: Equilibrium Distance (Z), Total Energies and Adsorption Energies of NO_2 on $(CaO)_8$, $(CaO)_9$, and Cluster Models at the B3LYP / 6–311G Basis set of DFT.

Systems	Z(Ca-NO_2) (Å)	Tot. Energy (au)	Ads. Energy (eV)[(a)]
$NO_2/(CaO)_8$	4.0	–6228.597469	4.15
$NO_2/(CaO)_9$	3.0	–6981.419596	0.46

[(a)] Adsorption energy is calculated by Eq. (1).

The unpaired spin density is almost localized on the adsorbed NO_2, and during the adsorption process, the partial charge is transferred from the surface cations (Ca $_{surf}$) to the anti-bonding π^* orbital of NO_2, resulting in an elongation of the N–O bond length in the gas phase on the surfaces. In addition, the adsorption of NO_2 on the Ca sites can be formally as nitrite species. It is interesting to note that, the stronger interactions are reflected in the shorter NO_2 distances on the Ca^{2+} and O^{2-} sites.

3.4. Adsorption of NO_2 on the $(CaO)_n$, *n*= 12 cluster model

The last cluster isthe adsorption of NO_2 on $(CaO)_{12}$ cluster model is studied, and results are presented in Fig. 5 and Table 4.The adsorption process between NO_2 molecule and the $(CaO)_{12}$can be reduced the average Ca–Obond lenghtand bond angleinsidethe cluster and an extension of the N–O bond inside NO_2.

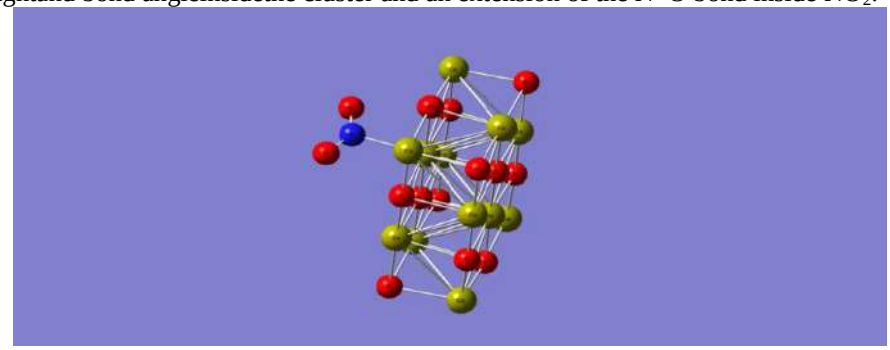


Fig. 5: Adsorption structures (a and b) of NO_2 on the $(CaO)_{12}$ cluster model

Table 4: Equilibrium Distance (Z), Total Energies and Adsorption Energies of NO_2 on $(CaO)_{12}$ Cluster Models at the B3LYP / 6–311G Basis set of DFT.

Systems	Z(Ca-NO_2) (Å)	Tot. Energy (au)	Ads. Energy (eV)[(a)]
$NO_2/(CaO)_{12}$	2.5	–9240.290102	2.03

[(a)] Adsorption energy is calculated by Eq. (1).

The adsorption energy reaches 2.03 eV in this NO_2 @ $(CaO)_{12}$. It is interesting to notice that the functional B3LYP describes the cluster well, which predicts adsorption energy 2.03 eV with a distance of 2.50 (Å). NO_2 binding to CaO cluster models is characterized by a charge transfer and presents a strong dependency on cluster size. Moreover, the results of the charge transfer from HOMO sorbent to the radicals LUMO adsorbate [27], as well as the electron transfer behavior between the $NO_2$and the adsorbent surface, hence bind them to the slab cluster. In addition, the lowest value of adsorption energy is might be due to low charge transfer from HOMO substrate to LUMO adsorbate and a small distance from nitrogen atom to (Ca $_{surf}$). We should note that the surface chemistry of the alkaline earth oxides (MgO, CaO, SrO and BaO) is dominated by the Lewis basicity of surface oxide anions[28]. This basicity increases along with the alkaline earth family as the metal ions become larger and more electropositive, and become gradually increased for adsorption.

IV. CONCLUDING REMARKS

Molecular clusters have long been understood to comprise conceptual bridges between the atoms and the solid. As cluster models become increasingly more relevant due to technological applications, interest in the clusters and their chemistry *per se* is increasing. In a serious of studies, Bawa et al, has focused on the alkaline earth oxides, e.g. it has inferred that substrate electropositivity [12] would be critical property for nitrite formation at the MgO and CaOion sites. In this paper, quantum chemical techniques have been used for exploring the adsorption behavior of NO_2 onto $(CaO)_n$, *n*= 2, 3, 4, 6, 8, 9, 12 cluster models.It is important to predict the acidic-basic character of various surface sites of different metal oxides. Further to that, the structures and adsorption energies of NO_2 on Ca^{2+} andO^{2-}siteswere investigated by means of the B3LYP hybrid density functional theory (DFT) calculations. The results of B3LYP have been shown to predict the major products of NO_2 adsorption on CaO cluster models with adsorbing energies of physisorption and chemisorption.

In the case of nitrite the molecule acts as an electron acceptor and the bonding mode can be classified as acidic, and it is stable but is located 2.5 Å away from the surface, whereas, nitrate species, the O atoms of NO_2 formally act as electron donors and the interaction can be classified as basic.

Interestingly, the surface nitrite stability is found significantly similar for $(CaO)_n$ (n=2, 4, 6)as 3.68 good candidates for NO_2 adsorption, particularly, n= 2, 4, 6, and 8 due to high adsorption energy valeus.eV, 3.66 eV and 3.79 eV were computed respectively. In contrast, adsorption of NO_2 on $(CaO)_n$ (n= 8, 9, 12) takes place with an adsorption energies of 4.15 eV, 0.46 eV and 2.03 eV. The consistency was tested by computing the corresponding properties for CO_2 and SO_2 when adsorbed to $(MgO)_9$ and $(CaO)_9$ [11, 13]. These results provide a comprehensive understanding of the NO_2 adsorption onto CaO surface regarding the mentioned species.

From the above discussion, it is concluded that $(CaO)_n$ (n= 2, 3, 4, 6, 8, 9, 12) cluster models aregood candidates for NO_2 adsorption, particularly, n= 2, 4, 6, and 8 due to high adsorption energy valeus.

VI. ACKNOWLEDGMENTS

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