Adsorption of CO2 Molecule on the (MgO)9 and (CaO)9 Nanoclusters; A Theoretical Study

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Abstract :Binding configurations of CO_2 on $(MgO)_9$ and $(CaO)_9$ cluster models are investigated by means of density functional theory model calculations. The results show that CO_2 adsorbs as monodentate on MgO and CaO terrace site leads to formation of surface carbonates CO_3^{2-}. Marginal differences in the binding stabilities between the CO_2 molecule and surface O^{2-} site were found to be significantly similar. The estimated adsorption energies are 1.47 eV and 1.52 eV at the $(MgO)_9$ and $(CaO)_9$ clusters, respectively. The similarity in binding energies is discussed in terms of cluster electro-positivity. Adsorbed CO_2, to $(MgO)_9$ surface vibration frequencies are calculated and compared to the experiment.
Keywords: Density functional theory, Catalysis, $(MgO)_9$ and $(CaO)_9$, CO_2 molecule, Surface of carbonate, Vibrational frequency

1. Introduction

In our society, we consume a huge amount of energy, in which we use electrical and heat energy each day. For example, the fuel powers our cars and the natural gas that heats our buildings. Sources of energy include fossil fuels (e.g., coal, oil, kerosene and natural gas) and nuclear power. Furthermore, when burned, carbon dioxide CO_2, CO, and NO_x environmental pollutant emit into the atmospheric [1]. There is great concern that human activity has led to significant increases in the concentrations of certain gases in the atmosphere, such as CO_2 and CH_4 that can warm the planet further with the potential of serious damage to the biosphere. This problem is referred to as global warming. Particularly carbon dioxide in large amounts has been found to cause global climate, and cause additional problems such as acid rain. The European Union (EU) and the governments have put up goals regarding future energy consumption and production. Until 2020, following requirements should be met [2], i) Greenhouse emissions (i.e. emissions of carbon dioxide, nitrogen oxides, methane etc.) have to be reduced by 20 %. ii) 20 % of the energy production should come from renewable energy sources. 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_2 capture are necessary to achieve low energy penalties.
Numerous studies have addressed catalysis or use of exhaust filters, and improvements to the combustion system have been extensively studied the adsorption and reaction of CO_2 and NO_2 with alkaline earth oxides such as MgO and CaO [3-15], to mitigate the rising levels of carbon dioxide in the atmosphere,

and retarding global warming. The quest to reduce CO_2 emissions increasingly sees fuel economy and environmental considerations working hand in hand. This is so simply because reduction of the amount of carbon dioxide emitted per distance of transportation or amount of electricity produced implies reduced fuel consumption, in conjunction with CO_2 from fossil fuels being considered a major greenhouse gas, responsible for long-term global warming. Different strategies to control CO_2 emission are considered dependent of whether stationary power plants or automotive engines are at focus. The process is removing carbon from the atmospheric and depositing it in a reservoir.
Again the gas absorption properties of the metal oxides and also there reduced properties are considered crucial. It has been suggested that alkaline earth oxides such as MgO and CaO play an important role in chemisorptions and catalytic reactions on oxides. The reduction of the CO_2 emission is performed industrially using magnesium and calcium based sorbents, like MgO, CaO and BaO surfaces, that interacts with CO_2 to form monodentate and /or bidentate carbonate species as the final products[3-5]. In a previous paper [11], computational studies reveal that adsorption energies for NO_2 are calculated onto stable $(MgO)_9$ cluster at the face site 0.32 eV and edge site 0.36 eV, in contrast, NO_2 appears to be more reactive with the $(CaO)_4$ and $(CaO)_9$ clusters 1.37 eV and 1.66 eV respectively. Furthermore, 2.82 eV and 3.64 eV have been calculated previously [12] for a pair of NO_2 adsorption molecules for $(MgO)_9$ and $(CaO)_9$ respectively, can cause enhanced stability. Cluster models of MgO and BaO have been widely used to study adsorption of small molecules (mostly NO_x and CO_x, x=1, 2) on the surface. The published investigations employing CaO cluster is limited, but some publications have been made (16)
The aim of the present study is to address the reaction of CO_2 on MgO and CaO surfaces to form carbonate (CO_3^{2-}). In addition, an effort is made to characterise the proposed $CO_2/(MgO)_9$ adsorption by calculating its vibration frequency and compare with experiment. A subsequent study will address the adsorption of SO_2 onto $(MgO)_9$ and $(CaO)_9$ cluster models.

2. Computational Method

This investigation concerns the adsorption of CO_2 on $(MgO)_9$ and $(CaO)_9$ clusters by utilising the B3LYP hybrid density functional [17-19] as implemented in the Gaussian 98 program suite [20]. The 6−31+G(d) and/or 6−311G(d) basis sets were used, since they are big enough for the study of large molecules, and our previous work [11,12] has shown that they yields an accurate description of the geometries, and predict the energies

as well as infrared spectra [21-22]. In case of C and O atoms, the 6−31+G(d) set was used except for some stability tests using the 6−311G(d) set, where 6−311G basis set was used for Mg and Ca. For Ca this acronym implies the inclusion one d-function. Geometries of neutral cluster models of $(MgO)_9$, $(CaO)_9$ and CO_2 were fully optimized with the 6−31+G(d) and the 6−311G(d) basis sets, followed by vibrational analyses. As an example of adsorption of a molecule, we choosing CO_2 adsorbs as monodentate on terrace site O^{2-} on $(MgO)_9$ and $(CaO)_9$ cluster models. The stoichiometric MO (M = Ca/Mg, O = oxygen) clusters used are $(MgO)_9$ and $(CaO)_9$ for terrace, see Figure 1. Table 1 presents the calculated energies, bond lengths, bond angles and vibrational frequencies of the isolated CO_2, CO_3, CO_3^{2-} gases extracted from the 6−311G(d) and 6-31+G(d) basis sets. The DFT calculated vibrational frequencies is investigated the basic properties of adsorption of $(MgO)_9/CO_2$.
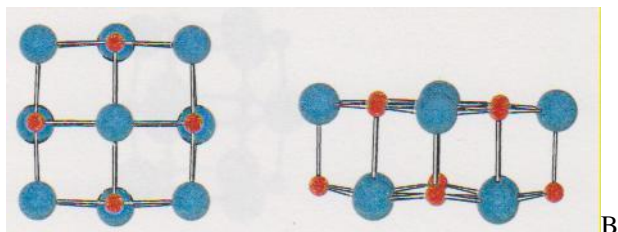
Adsorption energies of CO_2 onto the $(MgO)_9$ and $(CaO)_9$ cluster models were calculated for cylinder and slab shapes using the expression

$$\Delta E(\text{ads}) = E(CO_2) + E(\text{cylinder surface}) - E(CO_2 + \text{cylinder surface}) \quad (1)$$

$$\Delta E(\text{ads}) = E(CO_2) + E(\text{slab surface}) - E(CO_2 + \text{slab surface}) \quad (2)$$
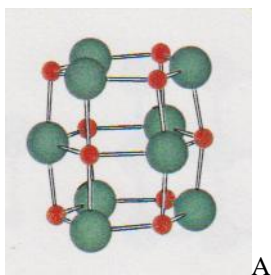
A

B

Figure 1. The optimized geometries of the bare $(MgO)_9$ (A) and the bare $(CaO)_9$ (B). Green and blue balls are represented the Mg and Ca ions respectively, while the red balls represented the oxygen ions, these clusters are considered in the present study and taken from previous study [23].

where $E(CO_2)$ is the total energy of free molecule, E(slab, cylinder surface) is the total energy of the optimized $(MgO)_9$ and $(CaO)_9$ clean slab and cylinder and $E(CO_2$ adsorbed surface) is the total energy of adsorbed system.

Table 1. Calculated DFT Geometries (Å), Bond angles (Deg.), Energies (au) for free CO_2, CO_3, CO_3^{2-}, and Calculated Vibrational Frequencies (cm^{-1}) of Asymmetric stretching (ω_1), Bending (ω_2), and Symmetric stretching (ω_3) Modes of CO_2.

Species	R(C−O)	$\angle$ O−C−O	ω (asym)	ω (sym)	ω (bend)	Bind.Energy
Free CO_2						
6-31+G(d)	1.169	180˙	-	-	-	-188.597850
6-311 G(d)	1.160	180	1706	1399	766	-188.641138
Free CO_3						
6-31+G(d)	1.255	120˙	-	-	-	-263.640708
6-311 G(d)	1.248	120	1303	1364	803	-263.706197
Free CO_3^{2-}						
6-31+G(d)	1.312	120˙	-	-	-	-263.698670
6-311 G(d)	1.309	120	1431	1068	716	-263.687552

3. Results and discussions

3.1. Structure and Energetics-CO_2 on $(MgO)_9$ and $(CaO)_9$ clusters

The most stable structures were determined from the relaxed stable structures of $(MgO)_9$ and $(CaO)_9$ clusters [23]. It becomes interesting to compare the stability of the surface CO_3^{2-} species on $(MgO)_9$ with that on $(CaO)_9$ are comparatively shown in Figure 2 and listed in Table 2. The calculated binding energies are 1.47 eV and 1.52 eV, respectively. In addition, CO_2 interacts with the defects, step, sites of MgO [24], and interacts strongly with the surface O^{2-} sites of CaO [25] forming stable surface carbonates. Adsorption of CO_2 molecule causes elongation of the surface bound C–O bond to 1.262 and (1.262) Å for MgO and (CaO) as compared to the bond length of 1.17 Å of the free unperturbed C–O and an O−C−O angle of 132˚ and 128˚ respectively (see Table 2). The geometrical properties and adsorption energies of CO_2 on O^{2-} terrace site are collected in Table 2 for one, two and three CO_2 molecules to
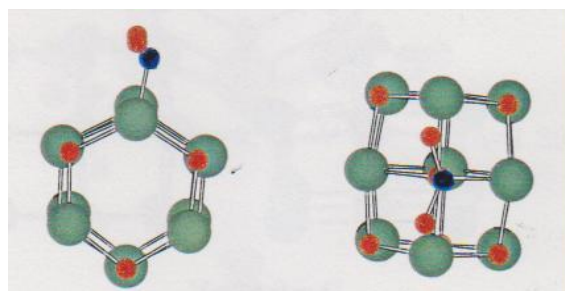
A
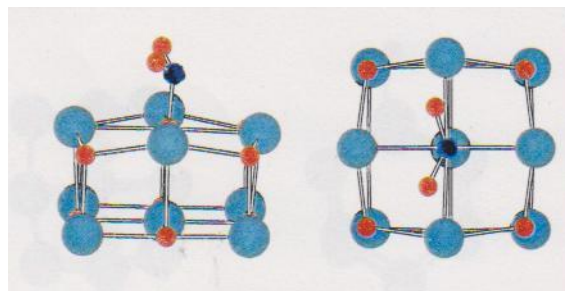
B

Figure 2. Monodentate-model geometries for adsorption CO_2 on $(MgO)_9$, $[O_{surf}\text{-}CO_2]^{2-}$ (A) and adsorption CO_2 on $(CaO)_9$, $[O_{surf}\text{-}$

$CO_2]^{2-}$ (B) display a 1.47 eV and 1.52 eV stabilities, respectively.

form the corresponding carbonates CO_3^{2-}. Significantly, smaller differential effects were observed for these electron pair accepting adsorbates. Thus, as we mentioned above the carbonate ion stability increases from 1.47 eV to 1.52 eV, when switching the Mg^{2+} cation for Ca^{2+}. These limited variations in stability are consistent with what was found for the NO_3^{2-} species [12], and make the nitrite stability change upon switching cations stand out. Thus, a chemical aspect on the asymmetry of adding a hole or an electron to an oxide cluster has emerged. It is suggested that the electro-positive property is more sensitive to cation radius for adsorption at the cation positions than at the oxygen anion sites. This in turn implies that it is the locality and flexibility of the polar covalent bonds $O_{surf} -CO_2^{2-}$ and $O_{surf} - NO_2^{2-}$, which render these ions their comparable insensitivities to the choice of cation. In contrast, the energetics associated with the accommodation of a delocalized hole in an oxide cluster is found to be significantly more sensitive to the particular cation.

Table 2 Structure and Stability of the CO_3^{2-} surface Species on $(MgO)_9$ and $(CaO)_9$ at $6-31+G(d)$ basis set. See Figs. 2 and 3.

System	C–O	O_{surf}–C	∠O–C–O	∠O_{surf}–C–O	Tilt Angl	D_e (eV)
Free CO_2						
Calc.	1.17		$180^‡$			
Exp.	1.16		$180^‡$			
$CO_2/(MgO)_9$	1.262	1.384	$132^‡$	$114^‡$	$180^‡$	1.47
$CO_2/(CaO)_9$	1.260	1.403	$128^‡$	$116^‡$	$180^‡$	1.52
$C_2O_4/(MgO)_9$						2.76
$CO_2/(MgO)_9$	1.261	1.388	$133^‡$	$113^‡$	–	–
$CO_2/(MgO)_9$	1.261	1.388	$133^‡$	$113^‡$	–	–
$C_3O_6/(MgO)_9$						3.83
$CO_2/(MgO)_9$	1.259	1.394	$134^‡$	$113^‡$	–	–
$CO_2/(MgO)_9$	1.258	1.392	$134^‡$	$113^‡$	–	–
$CO_2/(MgO)_9$	1.258	1.392	$134^‡$	$113^‡$	–	–

The coverage dependence of chemisorption energy was investigated in order to test the generality of this feature. Thus, the evolution of adsorbate stability upon adding one, two and three CO_2 molecules to form the corresponding carbonates was monitored (Figure 3) and Table 2. Decrease in average chemisorption energy with increased coverage was found (Δ in Figure 3).
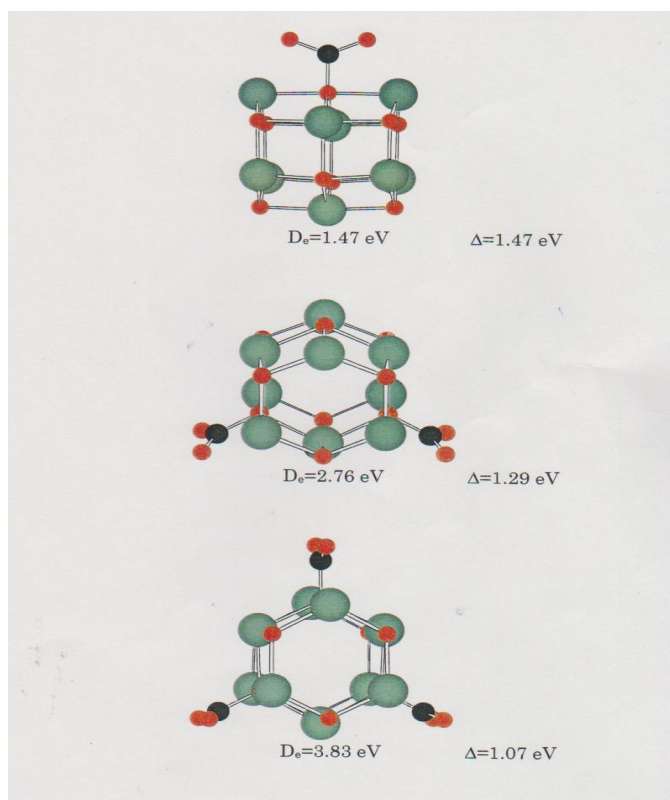

$D_e=1.47$ eV $\Delta=1.47$ eV

$D_e=2.76$ eV $\Delta=1.29$ eV

$D_e=3.83$ eV $\Delta=1.07$ eV

Figure 3. Optimized structures corresponding to the adsorptions of one, two and three CO_2 molecules, to form the corresponding carbonates. Stabilities and incremental stabilizations are included.

3.2. Vibrational frequencies characteristic of single absorbed CO_2 on $(MgO)_9$ cluster

The magnitude of the forces which hold the magnesium oxide clusters together with the carbon dioxide gas may be obtained from the results of the analysis of the band spectra of the adsorption of CO_2 on MgO surface. Here, connection between theoretical predictions and reality are sought by comparing computed and measured vibration spectra for investigating the basic properties of oxide clusters. The vibration frequency of CO_2 at $(MgO)_9$ may help us to understand the surface structure of the oxides, and thus a good characteristic in stretching regions may be quite useful [26].

Table 3. Calculated Vibrational Frequencies (in cm^{-1}) of Symmetric Stretching (ω_1), Bending (ω_2), and Asymmetric Stretching (ω_3) Modes of CO_2 on $(MgO)_9$ cluster.

Species	ω_1 Symmetry	ω_2 Bending	ω_3 Asymmetry
CO_2 @ $(MgO)_9$			
CO_3^{2-}	1322 (C_{2v})	837 (C_{3v})	1709
	933 (C_{3v})	746 (C_s)	695
			(C_{2v})

In addition, CO_2 adsorption and storage on catalysts has been studied by infrared absorption. Thus, Table 3 shows our calculated estimates of the vibration frequencies, they have

spectral features absorption of carbonate at symmetric $1322(C_{2v})$, $993(C_{3v})$, asymmetric 1709 cm^{-1} and at bend $837(C_{3v})$, $746(C_s)$ and $695(C_{2v})$ on the $(MgO)_9$ cluster. In this context Fukuda and Tanabe [27], identified the formation of carbonates formed on powder MgO and CaO by IR spectroscopy. Y. Yanagisawa et al. was also performed and computed IR of CO_2 adsorbed at $(MgO)_6$ and $(MgO)_8$ model clusters. Usefulness of cluster calculations for interpreting vibration spectra is supported by a combined experimental and theory study on the adsorption of CO_2 on MgO by Morten B. Jensen et al. [28].

4. Conclusions

Molecular clusters have long been understood to comprise conceptual bridges between the atom and the solid. As clusters become increasingly more relevant due to technological applications, interest in the clusters and their chemistry *per se* is increasing. In a series of studies, we have focused on the alkaline earth oxides, and discussed boundary conditions related differences between cluster and bulk, e.g. it has been inferred above that substrate electro positivity would be a critical property for carbonate formation at the anion sites.

We have presented the results of DFT cluster model calculations on the interaction of CO_2 with the oxide sites of surfaces of MgO and CaO, which indicated that the bulk intuition is applicable also for clusters as the chemisorption energies increase when switching the Mg^{2+} cation for the Ca^{2+} in $(MO)_9$, c.f. 1.47 eV *versus* 1.52 eV for CO_2 adsorptions to $(MgO)_9$ and $(CaO)_9$ respectively, towards formation of surface CO_3^{2-}. The limited differential effects seen, which suggest it is the locality aspect of the polar covalent bonding to O^{2-}_{surf}, which significantly reduces the sensitivity to choice of cation. This is in contrast to the nitrite formation route, corresponding to NO2 adsorption at cation sites [11].

Based on the observations here, it is concluded that in the absence of Madelung potential, as the case for clusters, the local Lewis basicities at the O^{2-}_{surf} sites display similar strengths irrespective of the different alkaline earth cations. On the other hand, it is possible that carbonate species could exists as a monodentate model adsorption, that in general the higher frequencies corresponding to a strong interaction between CO_2 and MgO surfaces.

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