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Study on Structures and Binding Energies of SO₂ Adsorption

Onto (MgO)₉ and (CaO)₉ Clusters

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Abstract —A comparative study of the basic character and of the chemical reactivity of SO_2 molecule to MgO and CaO clusters has been performed on the basis of Density Functional Theory calculations. We have investigated the adsorption structures and energies for SO_2 at various $(MgO)_9$ and $(CaO)_9$ sites surface anions. The formation of strongly chemisorbed sulfite, SO_3^{2-} species occurs when SO_2 interacts with the basic O^{2-} ions. Marginal differences are seen in binding energies for SO_2 adsorption to $(MgO)_9$ and $(CaO)_9$ were determined to 1.77 eV and 1.93 eV respectively by employing (DFT-B3LYP approximation). The reason for the difference in binding energies is discussed in terms of cluster electro-positivity and the nature of the highest occupied molecular orbital.

Keywords: DFT calculations, $(MgO)_9$ and $(CaO)_9$ clusters, Adsorption, SO_2, SO_3^{2-}.

INTRODUCTION

Capture of CO_2 is currently one of the most important, due to the associated risks to our way of life, capturing of waste silver such as SO_2 gas with a silver-based material has its attractions as well. According to the Intergovernmental Panel on Climate Change, use of fossil fuels is the largest source of the increase in atmospheric CO_2. Use of fossil fuels currently emits about 32 Gton carbon dioxide (CO_2) per year [1]. Biomass is a renewable energy source that can be used to replace fossil fuels in order to reduce greenhouse gas emissions. In addition, biomass contains stored energy, that's because plants absorb energy from the sun through the process of photosynthesis. When biomass is burned, this stored energy is released as heat. Further, a majority of the consumed energy is generated by fossil fuels which include oil, coal and natural gas and only a minor part is generated from renewable energy sources. In order to stop the worldwide increase in energy use and reach a sustainable society where everyone can have a high life standard, some parts of the world has to decrease their energy consumption to achieve this, the European Union (EU), as well as individual governments, has set goals regarding future energy production and consumption. Already today there is a working strategy to optimize fossil fuel consumption by the so-called lean-burn strategy. The idea is to burn the fuel under excess of oxygen, and to store the harmful NO_x emissions in an oxides such as MgO, CaO, and BaO, the NO_x being reduced to the harmless N_2 at particular engine cycles. While, calcination has since long been used extensively as absorbent of SO_x in e.g. fluidized bed combustion (FBC), concepts are also being developed for using oxides as intermediate sinks for CO_2. In this context, the use of alkaline earth oxide clusters to capture and store sulfur dioxide is intrinsically attractive. Reactions occurring on complex surfaces play a major role in various fields of chemistry and physics where a dominant example is heterogeneous catalysis. A catalyst is a substance which accelerates a chemical reaction without being consumed itself [2]. In addition, sulfation of the catalyst led to an increase of the surface acidity and an increase of adsorption strength and therefore improvement of the adsorption

coverage of the substrates. Over the last two decayed, great attention has been given to the chemistry of basic solids because of their remarkable adsorption and acid-base catalytic performances [3]. Rock salt alkali earth oxides such as MgO and CaO are amongst the most important sorbent materials currently under investigation for this purpose [4, 5]. Due to the simplicity of its rock salt geometry and high degree of ionicity, basic oxides such as MgO are popular catalyst support materials which have been shown to display interesting reactivity when dopants or defects are included, opening up the possibility for their use as catalysts in their own right. Different strategies to control SO_2 emissions are considered, dependent of whether stationary power plants or automotive engines are at focus. Again, the gas absorption properties of the metal oxides and also their redox properties are considered crucial. The relevant quantum chemical studies in this context have focused mainly on the oxide surface chemistry. The purpose of this ongoing study is to determine how the shapes of nanometer-size clusters affect the reversible SO_2 storage and whether the exclusive position of MgO and CaO hold also at this length scale. Several technologies have been proposed to minimize CO_2 [6-8] and SO_2 [9-11] emissions. Storage mechanisms of SO_2 in alkaline earth metal oxides have been the subjects of some investigations MgO(s) [12], CaO(s) [13] and BaO(s) [14]. Moreover, the stabilities of amino-silica adsorbent materials also used for CO_2 capture were studied in the presence of SO_2, NO, and NO_2 [15]. The distinction between cluster and bulk regarding structures and binding energies was elucidated previously for the $(MO)_n$ series, where M denotes Mg, Ca, Sr and Ba and $2 \leq n \leq 12$ [16].

The present study aims at acquiring a fundamental insight into the nature of the interactions of SO_2 with various types of MgO and CaO surfaces [17]. To deal with surface stability and adsorption calculations, we modeled two surface geometries as three dimensional 3-hexagonal ring stack $(MgO)_9$ and $(CaO)_9$ slab system, see Figure 1.
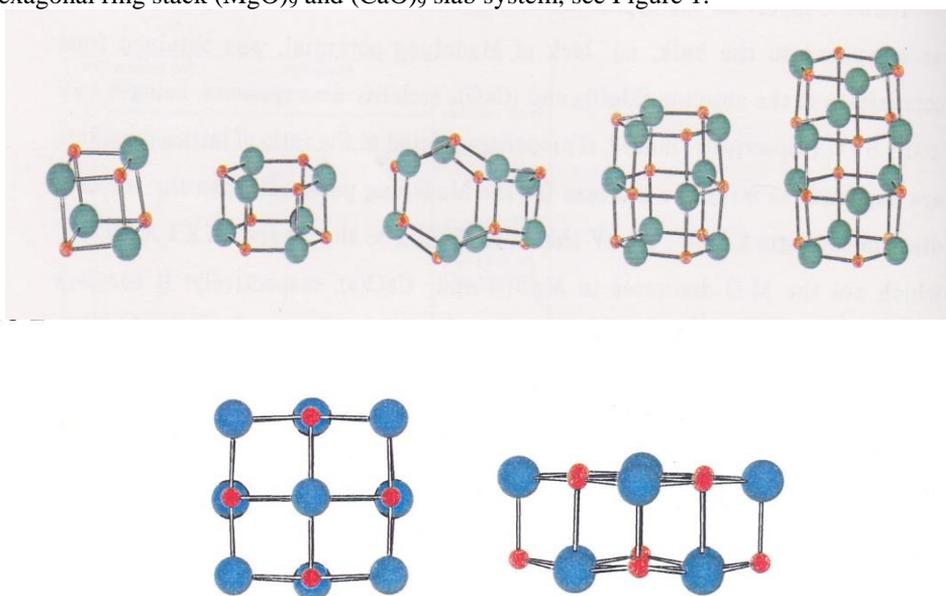

Figure 1. The optimized geometries of different cluster models of $(MgO)_4$, $(MgO)_6$, $(MgO)_8$, the bare $(MgO)_9$ and $(MgO)_{12}$ (upper) and the bare $(CaO)_9$ (lower). Green and blue

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 [16].

METHOD

Throughout this paper, DFT calculations using the Gaussian 98 suite of programs [18] were performed to investigate the electronic structure of $(MgO)_9$ and $(CaO)_9$ clusters by employing the B3LYP [19-21] hybrid density functional. In addition, the Becke 3LYP gives accurate ground state properties for neutral and charged clusters. Theoretical results about the equilibrium geometries and binding energies of MgO and CaO clusters show strong variations, depending on calculation methods and types of basis sets [22]. In case of S and O, the split valence 6-31+G(d) set was used except for some stability tests using the 6-311G(d) set. For the atoms, Mg and Ca, the 6-311G basis set was used throughout. In case of Ca, this acronym implies the inclusion one d function. While, the more extensive 6-311G(2d) basis splits, the valence into three functions, represented by three, one and one PGTOs (primitive Gaussian type orbitals) respectively was selected for S in order to ensure proper description of the well known hybridization effects involving the sulfur 3d orbitals. Hybrid functional B3LYP has been widely used to compute inorganic molecules successfully. Furthermore, it takes account of some dynamic correlations by mixing in the exact exchange from Hartree-Fock, which is important in order to describe long-range interactions like conjugation well [23]. To study heterogeneous reactions, cluster approaches were used in this work to obtain binding energies, which is defined as the difference in energy between the complex (adsorbent-adsorbate system) and its component parts both (adsorbent and adsorbate). Adsorption energies of SO_2 onto the $(MgO)_9$ and $(CaO)_9$ cluster models were calculated for global sulfation reactions (so called adsorption energy $\Delta E(ads)$ as

$$E_{(Tinitial)} = E_T (SO_2) + E_T \text{ (clean surface)} \qquad (1)$$

$$E_{(Tfinal)} = E_T (SO_2 + \text{clean surface}) \qquad (2)$$

$$\Delta E_{(ads)} = \Delta E_T = E_{(Tfinal)} - E_{(Tinitial)} \qquad (3)$$

where $E_{(Tinitial)}$ and $E_{(Tfinal)}$ are the total energies of the system before and after the adsorption respectively.

RESULTS AND DISCUSSION

Adsorption of SO_2 on $(MgO)_9$ and $(CaO)_9$ clusters

The B3LYP technique is employed to examine the thermodynamic stability of the SO_2 adsorption on the nano magnesium and calcium oxide clusters. As mentioned above, alkaline earth oxides clusters are particularly attractive, in this context as they are already relatively cheap with highly reactive towards the NO_2 [24], CO_2 [25] and SO_2 [26].

On a metal oxide cluster, SO_2 adsorption can occur on either the surface metal cations or the oxygen anions as in the case of MgO (Figure 2) as well as CaO model clusters (Figure 3). In addition, SO_2 can interact with the basic oxide anions of the MgO and CaO surfaces by accepting charge to form sulfite species, SO_3^{2-}. In our previous paper, NO_2 can perform nitrite and nitrate surfaces when adsorbed onto Mg^{2+}, Ca^{2+} and onto an O^{2-}_{surf} sites [24] and CO_2 forming surface carbonates [25]. After the adsorption process, surface cluster and molecule are stick together in one single body with a new total binding energy value Etot

(clean surface + molecule). In this study a three layer slab and 3-hexagonal ring stack were enough to guarantee the stability of the adsorption energy values. Two possible orientations where SO_2 acts as a mono with single surface Mg^{2+} cation or bidentate with double surface Mg^{2+} cations [11]. Table 1, represents the results of the adsorption of SO_2 molecule (on the O^{2-} sits) of MgO and CaO surface. It is therefore important to analyze if SO_2 molecule exhibits a higher reactivity towards surfaces of MgO and CaO at anions O^{2-}. It is now interesting to compare thermodynamic stabilities of sulfite on the surfaces of metal oxide $(MgO)_9$ and $(CaO)_9$ clusters on anionic sites located on various geometrical (flat surface and step edge). The results show that, the bond length (S-O) is elongated as well as increased of (O-S-O) angle compared to free SO_2 (1.45 Å) and S-O-S angle (119°) in good agreement with green wood et al. [27].
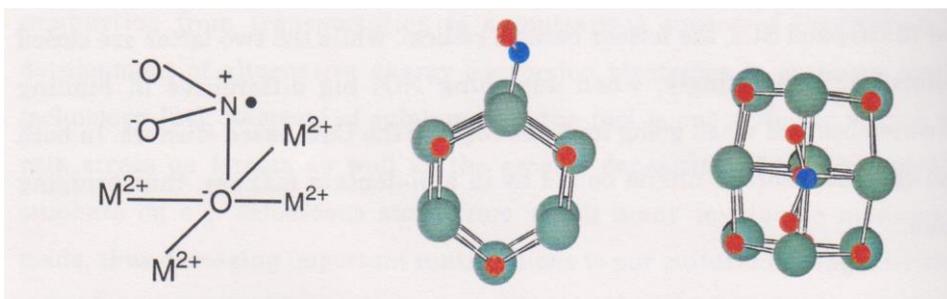

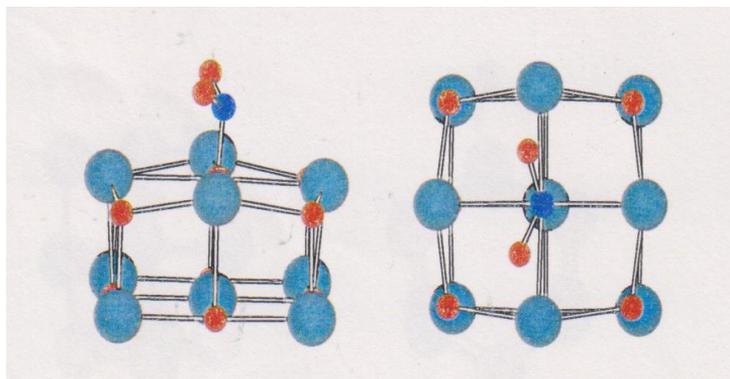**Figure 2.** Schematic representation of the surface SO_3^{2-} species and adsorption on $(MgO)_9$ cluster.

Figure 3. SO_2 Adsorption on $(CaO)_9$ cluster forming sulfite species SO_3^{2-}

Table 1. Optimal geometrical parameters and binding energies for SO_2 bound at surface, $(MgO)_9$ and $(CaO)_9$ clusters with formation of surface sulfite[c] SO_3^{2-}

System angle	R(S−O) D_e(eV)	R(S−O$_{surf}$)	∠ O-S-O	M-OSO	Tilt
Free SO$_2$					
Calc.	1.45		119°		
Exp.	1.43		119°		
SO$_2$/ (MgO)$_9$					
	1.52	1.64	109°	2.11	1.77
	1.53			2.01	
SO$_2$/ MgO(s)					
Flat surface [a]	1.50	1.76		2.11	1.10
Step edge [a]	1.50	1.66		2.16	1.97
	1.54			2.13	
OMg$_4$/SO$_2$					
Step[b]	1.466	1.684	118°		1.80
SO$_2$/ (CaO)$_9$					
	1.51	1.71	111°	2.41	1.93
OCaO$_5$/SO$_2$					
Surface[b]	1.800	1.447	115°		1.30

[a] See Ref. [9]
[b] From Ref. [6].
[c] See figures 2 and 3 for structure identification.

Binding energies-SO$_2$ on (MgO)$_9$ and (CaO)$_9$ clusters

Physical and chemical adsorption can numerically distinguished from adsorption energy (positive value of binding energies). If the adsorption is in the range of 10-30 KJ/mole indicating that the attractive force between the adsorbent and adsorbate is weak, the adsorption is a physical process. If the adsorption is in the range of 50-960 KJ/mole, indicating that there is a strong attractive force between the adsorbent and adsorbate, the adsorption is a chemical process. Structural characteristics and binding energies of SO$_2$ adsorbed on (MgO)$_9$ and (CaO)$_9$ are depicted in Figure 2 and Figure 3, respectively.

Characteristic structural aspects of the sulfite SO_3^{-2} surface species are collected in Table 1. It becomes interesting to compare the stability of the surface SO_3^{-2} species on $(MgO)_9$ with that on $(CaO)_9$, (see Fig. 2 and 3). With the information on SO_2 and O^{2-} interactions, we are able to complete the image of SO_3^{-2} formation following the global reaction equation 3. In addition, the optical distances between adsorbed sites both of M (Mg, Ca) ions and each one of the nearest O ions are also reported as shown in Table 1. The adsorption energies (E_{ads}) are collected by using equation 3. We found no significant difference of both structural parameters and adsorption energies, i.e. 1.77 eV and 1.93 eV respectively. Significantly, smaller differential effects were observed for these electron pair accepting adsorbates (see Fig. 2 and 3 and Table 1). Thus, the sulfite ion stability enhancement becomes slightly greater, 1.77 eV on $(MgO)_9$ as compared to 1.93 eV on $(CaO)_9$ cluster. It is suggested that the electro-positivity 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 in O_{surf}-NO_2^{2-} [22], O_{surf}-CO_2^{2-} [23], and this paper O_{surf}-SO_2^{2-}, which render these ions their comparable insensitivities to the choice of cations.

For reference, it is interesting to compare the flat surface, and step edge GGA adsorption energies obtained by Schneider et al [8] for SO_2 to what is found for the clusters. Indeed, the step edge site adsorption properties come out similar to those of the $(MgO)_9$ cluster (Table 1).

CONCLUDING REMARKS

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 nitrite formation at the metal ion sites. As cluster grow, polarization forces increase and the Madelung potential of the increasingly more ionic lattice makes the substrate less reactive to electron accepting adsorbates, i.e. the bulk surface becomes a weaker Lewis base than the cluster. Given that the Madelung potential decreases with increasing cation radius, and taking the O^{2-} ion radius to be constant, the capability of electron pair donation increases in the series MgO(s) <CaO(s) < SrO(s) < BaO(s).

Results were presented in the present study, which indicate 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 $(MO)_9$, M=Mg and Ca, 1.77 eV versus 1.93 eV for SO_2. In previous work, similar analysis was performed for NO_2, 0.36 eV versus 0.68 eV, and 1.48 eV versus 1.52 eV for CO_2 adsorptions to $(MgO)_9$ and $(CaO)_9$ respectively, towards formation of surface SO_3^{2-}, NO_3^{2-} and CO_3^{2-}. Still, the limited differential effects seen, suggest that 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 NO_2 adsorption at cation sites. Whereas the cluster oxygens are again the providers of the electron. Based on the observations here, it is concluded that in the absence of Madelung potential, as in the case for clusters, the local Lewis basicities at the O^{2-}_{surf} sites display similar strengths irrespective of the different alkaline earth cations. This is in contrast to the Lewis acidity property of the M^{2+} sites, where significant differences were observed for NO_2 adsorption as a nitrite, i.e. adsorption involving electron transfer in conjunction to binding to cation sites.

NO_2 chemisorption to a closed shell $(MO)_x$ cluster involves the issue of where to accommodate the odd electron. When this oxidizing agent forms a nitrite at the M^{2+} sites, the odd electron becomes a delocalized electron vacancy (hole) among cluster oxygen's and adsorbate. In contrast, when NO_2 attacks at an O^{2-}_{surf} site, two possibilities can be envisaged, in that either NO_3^- is formed in conjunction with a delocalized electron, or the unpaired electron remains on the adsorbate, resulting in a formal NO_3^{2-} surface species, the latter was found.

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