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Interactive CO_2 Adsorption on the BaO (100) Surface: A Density Functional Theory (DFT) Study

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A density functional theory (DFT) study of CO_2 adsorption on barium oxide (BaO) adsorbents is conducted to understand the chemical activity of the oxygen site on the BaO (100) surface. This study evaluated the adsorption energies and geometries of a single CO_2 molecule and a pair of CO_2 molecules on the BaO (100) surface. A quantum calculation was performed to obtain information on the molecular structures and molecular reaction mechanisms; the results of the calculation indicated that CO_2 was adsorbed on BaO to form a stable surface carbonate with strong chemisorption. To study the interactive CO_2 adsorption on the BaO (100) surface, a pair of CO_2 molecules was bound to neighboring and distant oxygen sites. The interactive CO_2 adsorption on the BaO surface was found to slightly weaken the adsorption energy, owing to the interaction between CO_2 molecules.

Key Words: Density functional theory, Adsorption, BaO, CO_2

Introduction

Carbon dioxide is a major contributor to the greenhouse effect. Over 80% of CO_2 emissions by human beings are a result of energy production.[1] Therefore, reducing CO_2 emissions from energy sources is absolutely necessary to mitigate climate change. Among the numerous sources of CO_2 emissions, power plants are the largest point source, comprising approximately 41% of the total emissions; therefore, CO_2 must be separated from the released flue gas mixture.[2] For highly efficient CO_2 separation processes, CO_2 adsorption on a solid sorbent can be a method with a good potential because of its low operating costs and low energy demands.[3-6] Among various adsorption methods that use different adsorbents, mineral carbonation has the potential for CO_2 separation because it leads to the formation of stable carbonates, minimizing the leakage of CO_2 into the atmosphere after capture. Because mineral carbonation is the reaction between CO_2 and metal oxides to form carbonates, quantum chemical calculations can be performed to evaluate the adsorption mechanism of CO_2 on the surface of a solid sorbent.

This study investigates CO_2 adsorption on barium oxide (BaO) because the BaO surface provides a simple cubic structure as well as a simple surface product layer ($BaCO_3$).[7] In addition, the BaO surface has a high reactivity that enables it to donate charge to the adsorbed CO_2 molecule; the high reactivity can be attributed to the fact that it has a high basicity resulting from the low Madelung potential energy.[8] The quantum chemical calculation of CO_2 adsorption on BaO has been already studied,[7,9-12] but the previous studies did not examine the interactive adsorption of CO_2 molecules on O sites on the BaO surface; this study investigates the interaction effect of CO_2 molecules.

To explore CO_2 molecular adsorption, a density functional theory (DFT) study is performed to evaluate the adsorption properties of CO_2 on surface materials. DFT calculation was chosen as it yields high accuracy for adsorption energy and geometry.[11,13] To determine adsorption properties, this study examines the adsorption geometry and the adsorption energy of CO_2 on BaO (100) using a periodic-slab calculation. For the minimized geometry configuration, the adsorption energy of surface coverage is discussed. The structure optimization and energy information enable us to determine the basis of the reaction mechanism of CO_2 adsorption on the BaO surface.

Calculation Details

This study utilized DFT calculations to evaluate the CO_2 adsorption on O sites on the BaO surface in the periodic slab model. Geometry optimizations were performed using $Dmol^3$ under the following conditions: (i) The general gradient approximation (GGA) was at the PBE level for functional option and (ii) the DND basis to predict the properties of adsorbents and adsorbates was employed because PBE shows good performance for relevant adsorbates and DND provides a good agreement with the experimental data.[9,14-16]

For the quantum calculation, three-dimensional periodic slab models were employed.[7,12] In the supercell, the sorbent surface was exposed as a slab, providing three layers. For the development of the surface structure, three atomic layers were cleaved at the (100) plane. Vacuum thickness (size of unit cell perpendicular to slab-slab thickness) was set to 10 Å. All three layers were geometry-optimized without constraint.

Coverage study determines the minimized adsorption energy between adsorbate molecules and adsorbents. It also evaluates the effect of the self-interaction of CO_2 molecules in the supercell. Adsorption coverage θ as a function of the different lattice size of the supercell is prepared from the coverage ($\theta = 0.5$, 0.125, 0.056, and 0.032) of an adsorbed CO_2 molecule on the center atom of a (1 × 1), (2 × 2), (3 × 3), and (4 × 4) unit cell, respectively. For the interactive adsorption, a pair of CO_2 molecules was bound to both neighboring sites and distant sites on the BaO (100) surface.

To determine adsorption energies E_{ads} between the adsorbate and the adsorbent surface, three single total energy calculations are used for: (i) geometry optimization of the adsorbate, (ii) geometry optimization of the adsorbent surface slab without the adsorbate, and (iii) geometry optimization of the adsorbent surface slab with the adsorbate. The adsorption energies were determined in the following way:

$$E_{ads} = E_{(adsorbent+adsorbate)} - (E_{adsorbent} + E_{adsorbate}) \qquad (1)$$

where E_{ads} is the adsorption energy of the adsorbate on the adsorbent, $E_{(adsorbent+adsorbate)}$ the total energy of the adsorbate with the adsorbent, $E_{adsorbent}$ the total energy of the adsorbent, and $E_{adsorbate}$ the total energy of the adsorbate. Using the calculation of adsorption energy, the adsorption properties of adsorbates on BaO are discussed.

Results and Discussion

Geometry optimization of bulk adsorbent and CO_2 molecules. After the geometry optimization of the 1 × 1 BaO (100) surface (unit cell), the surface was not relaxed, as shown in Table 1. After the interaction of CO_2 with 1 × 1 BaO (100), the surface relaxation of both O and Ba sites was observed. The O site where CO_2 was bonded was considerably relaxed and the Ba site surrounding the O-CO_2 site was also symmetrically relaxed compared to the origin of the BaO surface. Table 2 presents the geometry properties of bulk BaO and CO_2 molecules. The calculated bond length and bond angles are in a good agreement (within 1.7%) with the experimental data and another DFT calculation.[11,17,18]

CO_2 adsorption on BaO. Figure 1 shows the optimized geometries for the CO_2 adsorption on the 2 × 2 BaO (100) surface, forming a single carbonate layer ($BaCO_3$). During the interaction between BaO and CO_2, a charge rearrangement results in the linking between the CO_2 molecule and the O site. The charged site on the surface provided the strong bond (bond length = 1.389 Å) of $O_{surface}$-CO_2 because the adsorbed CO_2 at the charged O site formed charged molecules, resulting from charge transfers from the BaO surface to CO_2; this weakened the O-C bond for CO_2 and the CO_2 molecule bended. The electrostatic stabilization of the CO_2 molecule on the BaO surface relied on the affinity of CO_2 to the O site for the high interaction with the charge distribution in the lattice. The larger lattice parameter provides the smaller internal Madelung stabilization, leading to the larger charge transfer.[10] Because the cubic lattice parameter of BaO (5.5 Å) is larger than that of MgO (4.21 Å) reported by experiment, the charge transfer from the BaO surface is larger than that from MgO, evidencing the relatively strong interaction of CO_2 with BaO compared to other metal oxides.[19] Therefore, the DFT calculation can support the strong formation of a surface carbonate.

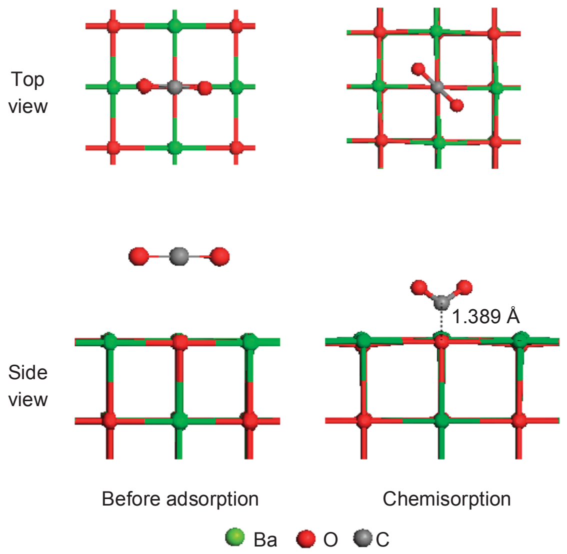


Figure 1. Geometries before/after CO_2 adsorption on the 2 × 2 BaO (100) surface.

Table 1. Geometry optimization of the 1 × 1 BaO (100) surface and CO_2 adsorption on the 1 × 1 BaO (100) surface

	BaO (100)		BaO (100)-CO_2			
	Bond length of $O_{surface}$ (Å)	Bond length of $Ba_{surface}$ (Å)	Bond length of $O_{surface}$ (Å)	Bond length of $O_{surface}$-CO_2 (Å)	Bond length of $Ba_{surface,1}$ (Å)[a]	Bond length of $Ba_{surface,2}$ (Å)[b]
1st to 2nd atomic layer	2.961	3.005	2.742	3.067	3.013	3.031
2nd to 3rd atomic layer	2.961	3.005	2.966	2.813	3.095	3.088

[a] Up and down Ba site located near the $O_{surface}$ site of BaO bound to CO_2. [b] Left and right Ba site located near the $O_{surface}$ site of BaO bound to CO_2.

Table 2. Geometry properties of bulk BaO and CO_2 molecules obtained by DFT calculation

	This study		Tutuianu *et al.*[11]		Experiment[17,18]	
	Bond length (Å)	Bond angle (°)	Bond length (Å)	Bond angle (°)	Bond length (Å)	Bond angle (°)
BaO (cubic bulk)	2.76		2.78		2.76	
CO_2	1.18	179.9	1.17	179.9	1.16	180

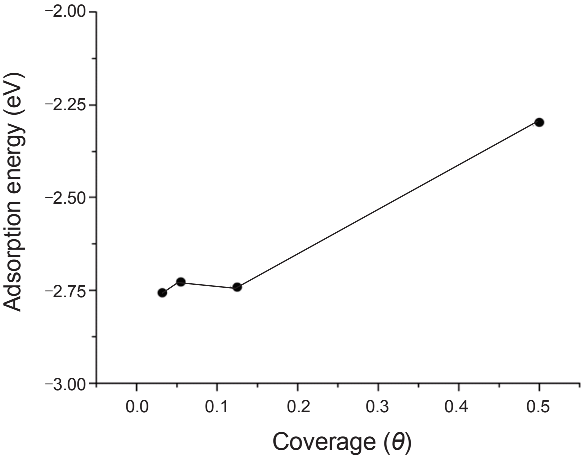


Figure 2. Effect of CO_2 adsorption energy as a function of coverage (θ).

For the evaluation of the lowest energy minimized (100) structures for adsorption, Figure 2 represents the CO_2 chemisorption with respect to coverage. The adsorption energy is described as a function of coverage ($\theta = 0.032$, 0.055, 0.125, and 0.5), resulting in the strong dependence of adsorption properties on coverage. As coverage decreases, the adsorption energy decreases, indicating that the chemisorbed CO_2 becomes significantly stable. The adsorption energy (−2.30 eV) at coverage $\theta = 0.5$ (in a (1 × 1) supercell) is higher than that at other coverages due to the self-interaction of the CO_2 molecule in a small cell (5.52 Å × 5.52 Å). Table 3 presents the adsorption properties of CO_2 on the BaO (100) surface, dependent on coverage. The bond length of $O_{surface}$-C at $\theta = 0.5$ is 1.414 Å while that at $\theta = 0.125$ is 1.389 Å. This result supports the effect of self-interaction of CO_2 molecules, resulting in a relatively weaker chemisorption. At less than 0.125 of coverage, the energy of adsorption is minimized, leading to the optimized geometry of CO_2 adsorption on the BaO (100) surface in a supercell greater than a (2 × 2) supercell. The adsorption energy of CO_2 is thus −2.74 eV, according to DFT calculation. This low value indicates that CO_2 adsorption is energetically more favorable to the BaO surface than CaO (−1.0 eV) and MgO (−1.2 eV).[20,21]

Compared to the DFT study by another group (bond length (O-C) = 1.23 Å, bond angle (OCO) = 131.6°), this study (bond length (O-C) = 1.27 Å, bond angle (OCO) = 128.1°) showed better agreement with the experimental data (bond length (O-C) = 1.30 Å, bond angle (OCO) = 120°) because they did not consider the self-interaction of CO_2 in the small size of the periodic cell.[11,18] The adsorption energy obtained in our study is in poor agreement with their results because a different tool and different calculation conditions were employed. Their adsorption energy (−0.8 eV) at $\theta = 0.5$ is higher than the CO_2 adsorption energy (−1.0 eV) on the CaO surface (as reported by the Pacchioni group).[11,20] This indicates that the interaction of BaO to CO_2 is smaller than that of CaO, but does not explain the correlation between surface activity and basicity because the base strength of BaO is higher than CaO, leading to the higher affinity of CO_2 adsorption.[8,20]

Interactive CO_2 adsorption on BaO. Because many CO_2 molecules can be adsorbed on the O sites of metal oxides, and the DFT calculation of interactive (bound to neighboring sites and distant sites) CO_2 adsorption on the BaO surface has not yet been studied, we investigate the geometry and energy of the interactive CO_2 adsorption. Interaction energy was calculated as follows:

$$E_{Int} = 2 \times E_{ads,1CO_2} - E_{ads,2CO_2} \tag{2}$$

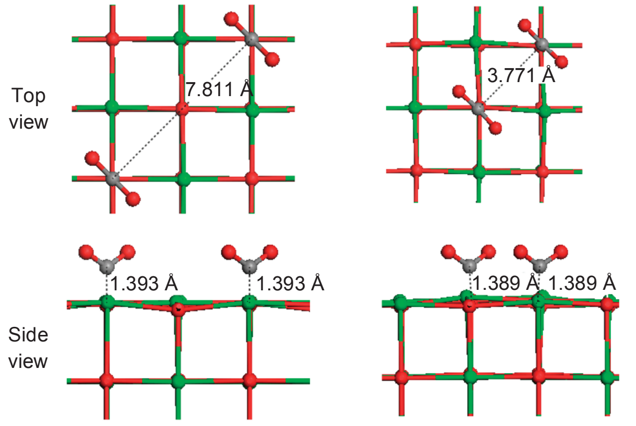
where E_{Int} denotes the interaction energy of a pair of CO_2 molecules (eV); $E_{ads,1CO_2}$, a single CO_2 adsorption energy molecule (eV); and $E_{ads,2CO_2}$ a pair of CO_2 adsorption molecules (eV). A pair of CO_2 adsorption molecules on the surface is slightly less favorable than molecular CO_2 adsorption on both neighboring and distant surface sites, as illustrated in Figure 3 and Table 4. Compared to the energy of the purely isolated molecular adsorption of CO_2 ($2 \times E_{ads,1CO_2}$), the energy of interactive adsorption is slightly higher, indicating the slightly less stable formation of carbonate due to the interaction of CO_2 molecules on the

Table 3. Adsorption properties of single molecular CO_2 on the BaO (100) surface

Coverage (θ)	Bond length ($O_{surface}$-CO_2) (Å)	Bond length (O-C, CO_2) (Å)	Bond angle (°)	Adsorption energy (eV)	Adsorption energy of reference (eV)[11]
Experiment[18]		1.30	120		
0.5	1.414	1.269	128.1	−2.30	−0.8
0.125	1.389	1.278	126.7	−2.74	−1.7
0.055	1.387	1.278	126.4	−2.73	
0.032	1.386	1.277	126.3	−2.76	

Table 4. Adsorption properties of a pair of CO_2 molecules on the 2 × 2 BaO (100) surface

	Adsorption energy (eV)	Bond length (CO_2-CO_2) (Å)	Bond length ($O_{surface}$-CO_2) (Å)	Interaction energy of CO_2-CO_2 (eV)
Single	−2.742		1.389	
Distant sites	−5.326	7.811	1.393	−0.158
Neighboring sites	−5.321	3.771	1.389	−0.163



(a) CO_2 bounded to distance sites (b) CO_2 bounded to neighboring sites

● Ba ● O ● C

Figure 3. Geometries of CO_2 adsorbed to distant (a) and neighboring sites (b) on the 2 × 2 BaO (100) surface.

surface. Because CO_2 molecules are close, their interaction on the surface increases slightly. However, the bond length of $O_{surface}$-CO_2 does not significantly depend on the interaction of CO_2 although CO_2 molecules are close. An analysis of surface interaction energies can ensure the energetic feasibility of a number of CO_2 adsorption molecules on the adsorbent surface.

In conclusion, the quantum chemical study by DFT calculation using Dmol^3 represents geometric parameters and adsorption energies of CO_2 on the BaO (100) surface. A pair of CO_2 interaction molecules on the BaO surface is investigated to evaluate the interaction effect between CO_2 molecules for the surface adsorption. This result indicates that CO_2 interaction weakens the adsorption energy. This DFT study can predict the adsorption properties of CO_2 on the BaO surface and can identify the basic quantum adsorption mechanism of the BaO carbonation for CO_2 capture.

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