

Competitive Adsorption of CO₂ and H₂O Molecules on the BaO (100) Surface: A First-Principle Study

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CO₂ adsorption on mineral sorbents has a potential to sequester CO₂. This study used a density functional theory (DFT) study of CO₂ adsorption on barium oxide (BaO) in the presence of H₂O to determine the role of H₂O on the CO₂ adsorption properties on the (2 × 2; 11.05 Å × 11.05 Å) BaO (100) surface because BaO shows a high reactivity for CO₂ adsorption and the gas mixture of power plants generally contains CO₂ and H₂O. We investigated the adsorption properties (e.g., adsorption energies and geometries) of a single CO₂ molecule, a single H₂O molecule on the surface to achieve molecular structures and molecular reaction mechanisms. In order to evaluate the coordinative effect of H₂O molecules, this study also carried out the adsorption of a pair of H₂O molecules, which was strongly bounded to neighboring (−1.91 eV) oxygen sites and distant sites (−1.86 eV), and two molecules (CO₂ and H₂O), which were also firmly bounded to neighboring sites (−2.32 eV) and distant sites (−2.23 eV). The quantum mechanical calculations show that H₂O molecule does not influence on the chemisorption of CO₂ on the BaO surface, producing a stable carbonate due to the strong interaction between the CO₂ molecule and the BaO surface, resulting from the high charge transfer (−0.76 e).

Key Words : Density functional theory, Adsorption, BaO, CO₂, H₂O

Introduction

Fossil fuels such as oil, gas, and coal are currently the most broadly employed energy sources, comprising more than 80% of global energy consumption.¹ Human activities, mainly the combustion of fossil fuels, have been the focus of attention because they primarily contribute to the increase in CO₂ emissions, regarded as the main origin of climate change. Of various sources of CO₂ emissions, the power generation is the largest source of CO₂ emissions, accounting for about 40% of the total.¹ For the reduction in CO₂ emissions from power plants, many separation technologies are available.

Among the various separation options, adsorption has become a promising candidate because of its simple operation, low corrosiveness, and overall low cost.^{2–5} Mineral carbonation (i.e., CO₂ adsorption on the mineral surface) shows the potential for CO₂ adsorption due to the formation of stable carbonates (i.e., CO₂ reacts with alkaline-earth metal oxides such as calcium oxide, magnesium oxide, and barium oxide to form a strongly bound carbonate on the mineral surface), minimizing the leakage of captured CO₂ into the atmosphere. Of alkaline-earth metal oxides, barium oxide (BaO) is selected for this study because the BaO surface provides a high reactivity that leads to the more active charge transfer from the surface sites to the CO₂ molecule, resulting from its high basicity.⁶

For CO₂ capture in the power plants, we have to consider the effect of water vapor because the flue gas mixture

generally contains 8–12% vol of CO₂ and 5% vol of H₂O after pretreatment with a wash tower.^{7,8} Due to the high affinity of H₂O instead of CO₂ to the typical sorbent surface, CO₂ capture capacity of the sorbents in the presence of water vapor should be discussed. In this study, quantum mechanical calculation is used to evaluate the adsorption properties of CO₂ on the mineral surface in the presence of water vapor.

The quantum calculation of CO₂ adsorption on BaO has been already investigated,^{9–13} but the effect of H₂O molecules on the CO₂ adsorption has not been discussed. Thus, we performed a density functional theory (DFT) study of CO₂ adsorption on the BaO surface in the presence of H₂O to understand the chemical activity of the oxygen site on BaO adsorbents and to establish the molecular structures and molecular reaction mechanisms of mineral carbonation because a DFT calculation yields high accuracy for adsorption energy and geometry with low cost.^{11,14} First, this study performs the adsorption energies and geometries of single CO₂ molecule and single H₂O molecule on the BaO (100) surface in the periodic-slab model. To determine the role of H₂O molecule, we represent the adsorption characteristics of a pair of H₂O molecules on the BaO (100) surface, and then that of one CO₂ molecule and one H₂O molecule, which are bound to distant and neighboring sites on the surface. For the electronic properties of CO₂ and H₂O adsorption, we investigate the charge transfer of the system using Mulliken population analysis to determine the molecular reaction mechanisms. Based on the optimized geometry and adsorp-

tion energy of the systems, we will discuss the effect of H₂O on CO₂ adsorption on BaO.

Computation Details

We performed geometry optimizations using DMol³ under the following conditions: (i) the general gradient approximation (GGA) with the Perdew-Burke-Ernzerhof correlation (PBE) level for the functional option, and (ii) the double numerical basis plus *p*-polarization functions (DNP) basis set to obtain the adsorption properties.^{9,15-17}

For the quantum mechanical calculation, this study used three-dimensional periodic slab models.^{12,13} The BaO surface was exposed as a slab with four layers. Four atomic layers of optimized slab were cleaved at the (100) plane for the exposure of the surface structure. During a DFT calculation, this study chose the surface cell dimension of (2 × 2; 11.05 Å × 11.05 Å) in *a*- and *b*-axis, and the thickness of the vacuum (i.e., size of the unit cell perpendicular to the slab-slab thickness) was set to 20 Å in *c*-axis to avoid the effect of self-image interaction between original structure and its self-image through the periodic boundary. All layers were geometry-optimized with the constraint of the fourth layer. The calculated model of (2 × 2) BaO surface provides total 64 atoms, including 32 barium atoms (Ba) and 32 oxygen atoms (O). To determine the electronic interaction between the adsorbed molecules such as CO₂ and H₂O and the BaO surface, Mulliken charge transfer was calculated.

Adsorption energies E_{ads} between the adsorbate and the adsorbent surface were determined by three single total energy calculations: (i) the geometry optimization of adsorbates, CO₂ and H₂O, (ii) the geometry optimization of the adsorbent surface slab without adsorbates, the (2 × 2) BaO surface, and (iii) the geometry optimization of the adsorbent surface slab along with adsorbates, CO₂ or H₂O on the BaO surface. The adsorption energies were determined as follows:

$$\Delta E_{adsorption} = \frac{E_{BaO+CO_2+H_2O} - (E_{BaO} + n_{CO_2} \times E_{CO_2} + n_{H_2O} \times E_{H_2O})}{n_{CO_2} + n_{H_2O}} \quad (1)$$

where $\Delta E_{adsorption}$ denotes the adsorption energy of CO₂ or H₂O on the BaO surface; n_{CO_2} is the number of CO₂ molecules; n_{H_2O} is the number of H₂O molecules; $E_{BaO+CO_2+H_2O}$, E_{BaO} , E_{CO_2} , and E_{H_2O} are the energy of the CO₂ or H₂O adsorbed on BaO, the energy of BaO without CO₂ and H₂O, and the energy of the single CO₂, and the energy of the single H₂O, respectively. The calculated adsorption energy will show the adsorption properties of CO₂ in the presence of H₂O on the BaO surface.

Results and Discussion

Molecular CO₂ and H₂O Adsorption on BaO. Due to the presence of water vapor in a flue gas mixture, CO₂ adsorption with water vapor remains a relevant topic for CO₂ separation because the surface of oxidic matrix is likely to be readily saturated with H⁺ and OH⁻ molecules due to the

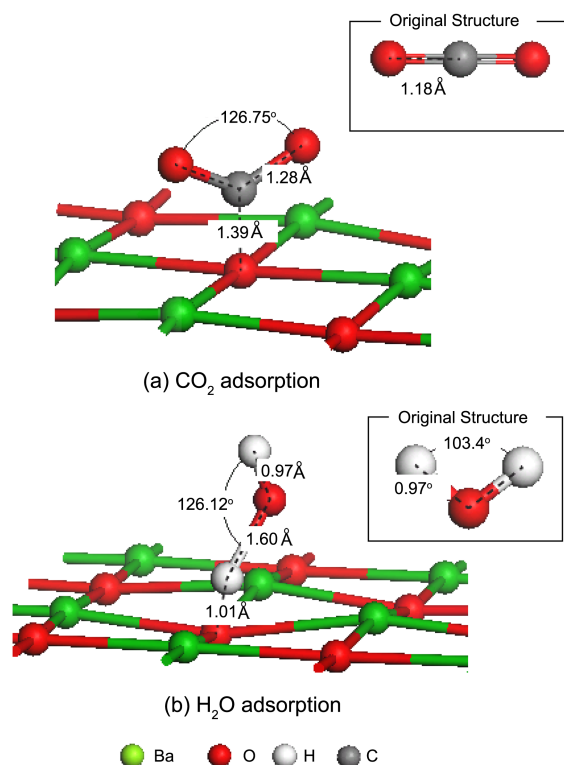


Figure 1. Optimized geometries of CO₂ adsorption (a) and H₂O adsorption (b) on the (2 × 2) BaO (100) surface.

highly Lewis-basic and -acidic property of the surface oxygen sites and metal ion sites such as Ba²⁺, respectively.¹¹

For competitive CO₂ and H₂O adsorption on the BaO surface, Figure 1 firstly represents the geometry optimization of molecular CO₂ adsorption and H₂O adsorption on the (2 × 2) BaO (100). CO₂ and H₂O molecules are adsorbed on the free oxygen sites of the BaO surface due to the Lewis-basic and -acidic characteristics between the oxygen sites of BaO, and carbon of CO₂ and hydrogen of H₂O. Previous studies also represent the properties of molecular CO₂ and H₂O adsorption on the BaO surface, as shown in Table 1. The adsorption energy and geometry information obtained in our study are in good agreement with another DFT calculation.^{11,18} Figure 1a shows the optimized geometry of CO₂ adsorption on the BaO surface. In the interaction between the BaO surface and the CO₂ molecule, a charge rearrangement results in linking between the CO₂ molecule and the O site. The charged site on the surface provides the strong bond (bond length = 1.39 Å) of O_{surface}-CO₂ because the adsorbed CO₂ at the charged O site forms charged molecules.

We calculated the adsorption geometry and energy of an adsorbed H₂O molecule on BaO for the formation of barium hydroxide (Ba(OH)₂) (Figure 1b). The optimized geometry provides a bond length of O_{surface}-HOH (1.01 Å), Ba_{surface}-HOH (2.90 Å), H-OH_{surface} (i.e., one short OH of single H₂O molecule) (0.97 Å), and HO-HO_{surface} (i.e., elongated OH bond) (1.60 Å). This optimized structure indicates a partial dissociation of H₂O molecule forming a stable pro-

Table 1. Adsorption properties of molecular CO₂ and H₂O on the (2 × 2) BaO (100) surface

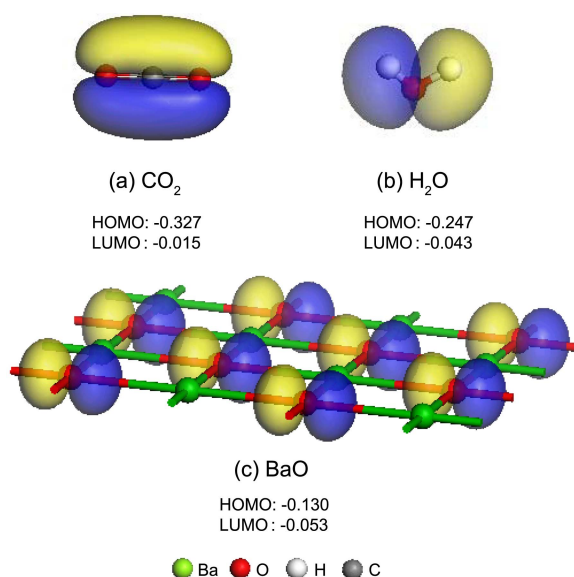
| Adsorbates | | Bond length (O _{surface} -CO ₂) ^a (Å) | Bond length of adsorbate (Å) | Bond angle (°) | Adsorption energy (eV) | Net charge transfer (e) |
|----------------------|------------------|--|---------------------------------|----------------|---------------------------|----------------------------|
| Theory ¹¹ | CO ₂ | 1.41 | 1.26(O-C) ^b | 127.5 | -1.7 | -0.8 |
| | H ₂ O | 1.01 | 1.46(O-H) ^c | 126.8 | -1.54 | -0.4 |
| This study | CO ₂ | 1.39 | 1.28(O-C) ^b | 126.8 | -2.72 | -0.76 |
| | H ₂ O | 1.01 | 1.60(O-H) ^c | 126.1 | -1.94 | -0.38 |

^aDistance between O_{surface} (O site on the BaO surface) and C atom of CO₂. ^bDistance between O atom and C atom within CO₂. ^cDistance between O atom and lower H atom within H₂O.

duct layer with surface sites.

In comparison of two adsorption energies of CO₂ and H₂O molecules, CO₂ adsorption (-2.72 eV) is energetically more favorable to BaO than H₂O adsorption (-1.94 eV) because the stronger interaction of CO₂-BaO system is driven by more distributed charge transfer from the surface to the adsorbate. To determine the electronic properties of CO₂ and H₂O adsorption, we investigate the charge distribution of the system using Mulliken population analysis, as shown in Table 1. During the adsorption, the charge transfer from the surface to the adsorbed molecules (CO₂ and H₂O) initiates and the charge of the adsorbed CO₂ and H₂O is -0.76 e and -0.36 e, respectively, indicating that a net electron donation of CO₂ molecule is higher than that of H₂O molecule. These results indicate that CO₂ adsorption tends to take place rather than H₂O adsorption on the surface. A charge transfer from the BaO surface to the CO₂ molecule weakened the O-C bond within CO₂, and the CO₂ molecule was bent due to the hybridization. These results support that CO₂-BaO system provides the strong electron interaction. It is concluded that CO₂ and H₂O are chemisorbed on the BaO (100) surface.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of CO₂, H₂O, and clean (2 × 2) BaO surface were calculated

**Figure 2.** The HOMO energy configuration and the HOMO and LUMO energy levels of CO₂ (a), H₂O (b), and clean (2 × 2) BaO surface (c).

(Figure 2). In the BaO surface, oxygen atoms have a high energy state and π^* molecular orbitals which are formed from 6s(Ba) and 2p(O) atomic orbitals. The HOMO energy level of CO₂ shows a higher energy state than that of H₂O, indicating that CO₂ can be adsorbed more actively than H₂O. This result also supports that CO₂ adsorption on BaO is stronger than H₂O adsorption.

A Pair of H₂O Adsorption on BaO. In order to evaluate CO₂ adsorption in the presence of H₂O, this study investigated a pair of H₂O adsorption on distant surface sites (distance between O atoms of H₂O molecules: 5.53 Å) and neighboring sites (distance between O atoms of H₂O molecules: 4.99 Å) on the BaO surface to determine the adsorption characteristic of H₂O molecules, as shown in Figure 3 and Table 2. The adsorption geometry and the adsorption properties of H₂O molecules presents the strong chemisorption between the oxygen site on the surface and the hydrogen molecule within water (bond length of O_{surf}-H₂O=1.01

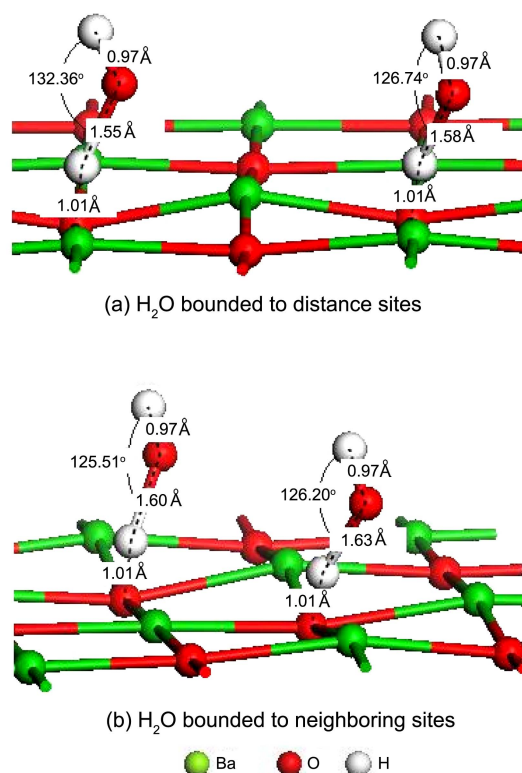
**Figure 3.** Optimized geometry structures of H₂O adsorbed to distant sites (a) and neighboring sites (b) on the 2 × 2 BaO (100) surface.

Table 2. Adsorption properties of a single CO₂ and H₂O, two H₂O, and CO₂ with H₂O on the (2 × 2) BaO (100) surface

| Adsorption | | Adsorption energy (eV) ^a | Bond length (O _{surface} -CO ₂) (Å) | Bond length (O _{surface} -H ₂ O) (Å) |
|---------------------------------------|------------------------------------|-------------------------------------|--|--|
| Single CO ₂ | | -2.72 | 1.39 | — |
| Single H ₂ O | | -1.94 | — | 1.01 |
| Two H ₂ O | Distant sites | -1.86 | — | 1.01 |
| | Neighboring sites | -1.91 | — | 1.01 |
| CO ₂ with H ₂ O | Distant sites (1) ^b | -2.23 | 1.39 | 1.01 |
| | Distant sites (2) ^c | -2.23 | 1.39 | 1.02 |
| | Neighboring sites (1) ^b | -2.32 | 1.38 | 1.02 |
| | Neighboring sites (2) ^c | -2.20 | 1.40 | 1.01 |

^aAdsorption energy is calculated by Eq. (1). ^bSimultaneous CO₂ and H₂O adsorption on the BaO surface. ^cCO₂ adsorption after H₂O adsorption on the BaO surface.

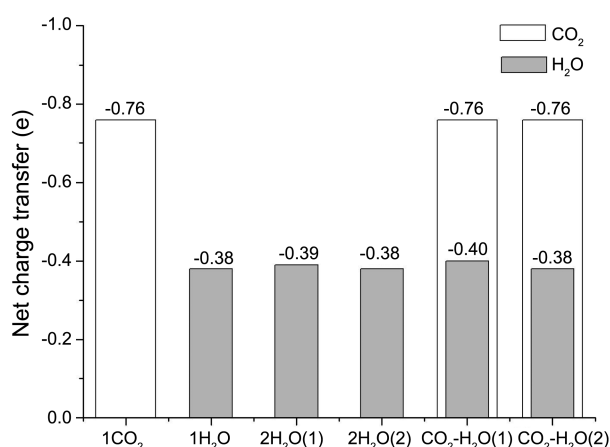


Figure 4. The net charge transfer of CO₂ and H₂O adsorption. Note that 1CO₂ is the adsorption of a single CO₂ molecule; 1H₂O is the adsorption of a single H₂O molecule; 2H₂O(1) is the adsorption of two H₂O molecules on neighboring surface sites; 2H₂O(2) is the adsorption of two H₂O molecules on distant surface sites; CO₂-H₂O(1) is simultaneous CO₂ and H₂O adsorption on neighboring surface sites; CO₂-H₂O(2) is simultaneous CO₂ and H₂O adsorption on distant surface sites.

Å, which is shorter than that of hydrogen bond). In addition, the bond length of OH bond for both H₂O molecules on the surface is 0.97 Å and that of elongated OH bond (OH-HO_{surf}) is above 1.60 Å, indicating that the optimized geometry shows a partially dissociated water molecules forming a stable matrix with the BaO surface, which provides the same pattern of a single H₂O adsorption on the surface.¹¹

In the most stable configuration, the partial dissociative H₂O molecule adsorbs to the surface oxygen through strong chemisorption since the strong chemical interaction (adsorption energy: > -1.86 eV) made by charge donation from the surface causes the chemisorption. In addition, bond length of O_{surf}-H₂O=1.01 is short and net charge transfer takes place due to the high basicity of BaO surface, leading to the well-distributed enough charge transfer from the surface to the two H₂O molecules.

In Figure 4, H₂O interaction with the BaO surface is also verified by the analysis of Mulliken charge transfer that supports a net transfer of electron charge from the surface to

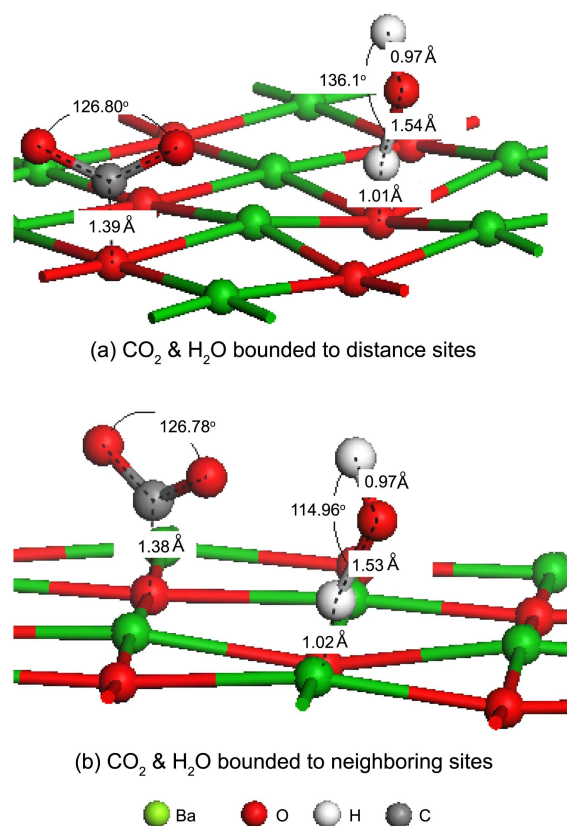


Figure 5. Geometries of simultaneous CO₂ and H₂O adsorbed to distant sites (a) and neighboring sites (b) on the 2 × 2 BaO (100) surface.

the adsorbates. During adsorption, the charge transfer from the surface to the H₂O molecules is observed as -0.4 e. This result indicates that the strong adsorption of two H₂O molecules on distant and neighboring surface sites was favorable.

The strong adsorption of H₂O molecules on the surface may result in a decrease in CO₂ adsorption on the mineral surface because the adsorption of a number of H₂O molecules may cause water aggregation on the surface.¹⁹ Thus, we should investigate the effect of H₂O on the CO₂ adsorption on the BaO surface.

Competitive CO₂ and H₂O Adsorption on BaO. Since H₂O can be adsorbed strongly on the BaO surface and, to the

best of our knowledge, quantum calculation of CO₂ adsorption in the presence of H₂O on the BaO surface has not been investigated, we performed a DFT calculation for the geometry and energy of the competitive CO₂ and H₂O adsorption on the (2 × 2) BaO (100) surface (i.e., simultaneous loading of CO₂ and H₂O molecules on the surface, which are bound to neighboring sites (distance between C atom of CO₂ and O atom of H₂O: 4.96 Å) and distant sites (distance between C atom of CO₂ and O atom of H₂O: 5.55 Å)) to determine the role of H₂O molecule in CO₂ adsorption (Figure 5). Table 2 also represents the adsorption properties of CO₂ and H₂O adsorption on BaO.

When they are close, their interaction on the surface increases slightly, but the bond length of O_{surface}-CO₂ does not significantly depend on the interaction between CO₂ and H₂O due to the high interaction between the CO₂ molecule and the surface, resulting from the high charge transfer of CO₂ adsorption (−0.76 e) compared to that of H₂O adsorption (−0.40 e) (Figure 4). The value of the competitive adsorption energy (−2.32 eV) is almost close to that of the average adsorption energies of the isolated molecular adsorption of CO₂ and H₂O (−2.33 eV). (i.e., the adsorbed CO₂ is still stable in spite of the presence of H₂O), indicating that H₂O does not affect CO₂ adsorption for the formation of carbonates because a charge transfer from the surface O site and H₂O molecule to the CO₂ molecule still leads to an energetically favorable formation of surface carbonates. In addition, the charge transfer of H₂O even slightly increases whereas that of CO₂ does not change during competitive CO₂ and H₂O adsorption, supporting that the presence of a water layer does not disturb the chemical reactivity of the surface of BaO to form a carbonate.

Since H₂O adsorption on the BaO surface is strong, we investigated CO₂ adsorption after H₂O adsorption on the BaO surface (Table 2). The energy of CO₂ adsorption after H₂O adsorption process is not quite different from that of simultaneous CO₂ and H₂O adsorption, indicating that H₂O does not affect CO₂ adsorption although H₂O is strongly adsorbed on the surface initially.

An analysis of surface interaction energies and charge transfer can ensure the energetic feasibility of CO₂ adsorption in the presence of H₂O on the BaO surface. Compared to our previous study of interactive CO₂ adsorption, which shows that the interaction of CO₂ molecules for the surface adsorption affects CO₂ adsorption on the BaO surface, H₂O does not significantly affect on the CO₂ adsorption.¹⁸

In conclusion, we investigated the competitive adsorption of CO₂ and H₂O molecules on the BaO surface to determine the role of H₂O on CO₂ adsorption. A DFT study using Dmol³ represented molecular structures and energies of CO₂ adsorption in the presence of H₂O on the BaO (100) surface. Electronic stabilization of the CO₂ molecule on the BaO

surface relies on the affinity of CO₂ for the O site because of their high interaction driven by the strong charge distribution. The results of the DFT calculation indicate that CO₂ molecule and H₂O molecule are strongly adsorbed on the BaO surface, which forms a stable surface carbonate and a barium hydroxide, respectively. The chemisorption of two H₂O molecules on distant and neighboring surface sites was also favorable on the adsorption on the surface. This study showed that the adsorption of CO₂ does not depend on the presence of H₂O in spite of the strong adsorption of H₂O on the BaO surface. These DFT computations provide the basic adsorption mechanism of CO₂ on BaO minerals in the presence of H₂O for CO₂ sequestration, forming barium carbonate which can be permanent storage species under realistic gas-solid phase reaction.

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