

## Competitive Adsorption of CO<sub>2</sub> and H<sub>2</sub>O Molecules on the BaO (100) Surface: A First-Principle Study

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

**Key Words :** Density functional theory, Adsorption, BaO, CO<sub>2</sub>, H<sub>2</sub>O

### 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.<sup>1</sup> Human activities, mainly the combustion of fossil fuels, have been the focus of attention because they primarily contribute to the increase in CO<sub>2</sub> emissions, regarded as the main origin of climate change. Of various sources of CO<sub>2</sub> emissions, the power generation is the largest source of CO<sub>2</sub> emissions, accounting for about 40% of the total.<sup>1</sup> For the reduction in CO<sub>2</sub> 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.<sup>2-5</sup> Mineral carbonation (i.e., CO<sub>2</sub> adsorption on the mineral surface) shows the potential for CO<sub>2</sub> adsorption due to the formation of stable carbonates (i.e., CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> molecule, resulting from its high basicity.<sup>6</sup>

For CO<sub>2</sub> 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 CO<sub>2</sub> and 5% vol of H<sub>2</sub>O after pretreatment with a wash tower.<sup>7,8</sup> Due to the high affinity of H<sub>2</sub>O instead of CO<sub>2</sub> to the typical sorbent surface, CO<sub>2</sub> 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 CO<sub>2</sub> on the mineral surface in the presence of water vapor.

The quantum calculation of CO<sub>2</sub> adsorption on BaO has been already investigated,<sup>9-13</sup> but the effect of H<sub>2</sub>O molecules on the CO<sub>2</sub> adsorption has not been discussed. Thus, we performed a density functional theory (DFT) study of CO<sub>2</sub> adsorption on the BaO surface in the presence of H<sub>2</sub>O 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.<sup>11,14</sup> First, this study performs the adsorption energies and geometries of single CO<sub>2</sub> molecule and single H<sub>2</sub>O molecule on the BaO (100) surface in the periodic-slab model. To determine the role of H<sub>2</sub>O molecule, we represent the adsorption characteristics of a pair of H<sub>2</sub>O molecules on the BaO (100) surface, and then that of one CO<sub>2</sub> molecule and one H<sub>2</sub>O molecule, which are bound to distant and neighboring sites on the surface. For the electronic properties of CO<sub>2</sub> and H<sub>2</sub>O 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 H<sub>2</sub>O on CO<sub>2</sub> adsorption on BaO.

### Computation Details

We performed geometry optimizations using DMol<sup>3</sup> 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.<sup>9,15-17</sup>

For the quantum mechanical calculation, this study used three-dimensional periodic slab models.<sup>12,13</sup> 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 CO<sub>2</sub> and H<sub>2</sub>O and the BaO surface, Mulliken charge transfer was calculated.

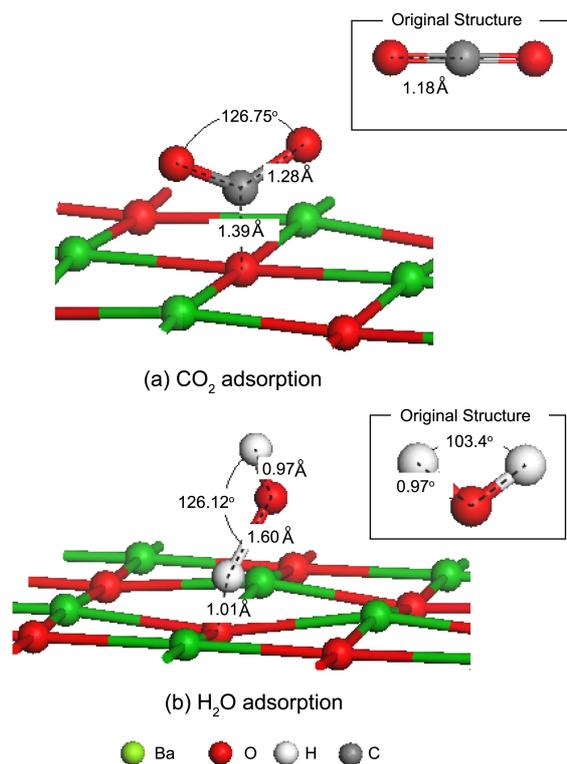
Adsorption energies  $E_{ads}$  between the adsorbate and the adsorbent surface were determined by three single total energy calculations: (i) the geometry optimization of adsorbates, CO<sub>2</sub> and H<sub>2</sub>O, (ii) the geometry optimization of the adsorbent surface slab without adsorbates, the (2 × 2) BaO surface, and (iii) the geometry optimization of the adsorbent surface slab along with adsorbates, CO<sub>2</sub> or H<sub>2</sub>O 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 CO<sub>2</sub> or H<sub>2</sub>O on the BaO surface;  $n_{CO_2}$  is the number of CO<sub>2</sub> molecules;  $n_{H_2O}$  is the number of H<sub>2</sub>O molecules;  $E_{BaO+CO_2+H_2O}$ ,  $E_{BaO}$ ,  $E_{CO_2}$ , and  $E_{H_2O}$  are the energy of the CO<sub>2</sub> or H<sub>2</sub>O adsorbed on BaO, the energy of BaO without CO<sub>2</sub> and H<sub>2</sub>O, and the energy of the single CO<sub>2</sub>, and the energy of the single H<sub>2</sub>O, respectively. The calculated adsorption energy will show the adsorption properties of CO<sub>2</sub> in the presence of H<sub>2</sub>O on the BaO surface.

### Results and Discussion

**Molecular CO<sub>2</sub> and H<sub>2</sub>O Adsorption on BaO.** Due to the presence of water vapor in a flue gas mixture, CO<sub>2</sub> adsorption with water vapor remains a relevant topic for CO<sub>2</sub> separation because the surface of oxidic matrix is likely to be readily saturated with H<sup>+</sup> and OH<sup>-</sup> molecules due to the



**Figure 1.** Optimized geometries of CO<sub>2</sub> adsorption (a) and H<sub>2</sub>O 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 Ba<sup>2+</sup>, respectively.<sup>11</sup>

For competitive CO<sub>2</sub> and H<sub>2</sub>O adsorption on the BaO surface, Figure 1 firstly represents the geometry optimization of molecular CO<sub>2</sub> adsorption and H<sub>2</sub>O adsorption on the (2 × 2) BaO (100). CO<sub>2</sub> and H<sub>2</sub>O 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 CO<sub>2</sub> and hydrogen of H<sub>2</sub>O. Previous studies also represent the properties of molecular CO<sub>2</sub> and H<sub>2</sub>O 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.<sup>11,18</sup> Figure 1a shows the optimized geometry of CO<sub>2</sub> adsorption on the BaO surface. In the interaction between the BaO surface and the CO<sub>2</sub> molecule, a charge rearrangement results in linking between the CO<sub>2</sub> molecule and the O site. The charged site on the surface provides the strong bond (bond length = 1.39 Å) of O<sub>surface</sub>-CO<sub>2</sub> because the adsorbed CO<sub>2</sub> at the charged O site forms charged molecules.

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

**Table 1.** Adsorption properties of molecular CO<sub>2</sub> and H<sub>2</sub>O on the (2 × 2) BaO (100) surface

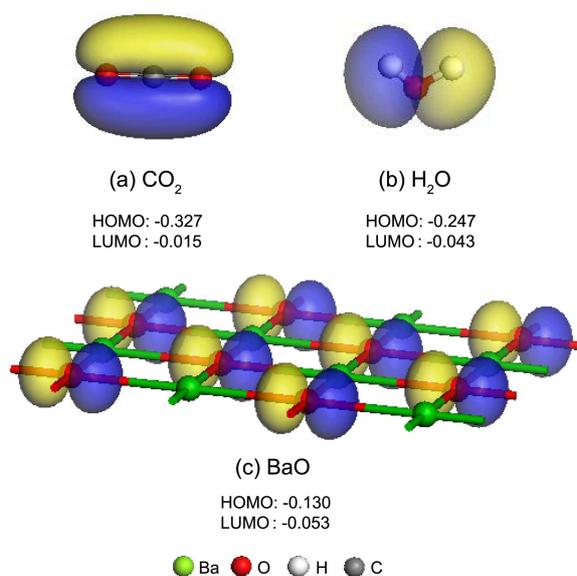
Adsorbates		Bond length (O <sub>surface</sub> -CO <sub>2</sub> ) <sup>a</sup> (Å)	Bond length of adsorbate (Å)	Bond angle (°)	Adsorption energy (eV)	Net charge transfer (e)
Theory <sup>11</sup>	CO <sub>2</sub>	1.41	1.26(O-C) <sup>b</sup>	127.5	-1.7	-0.8
	H <sub>2</sub> O	1.01	1.46(O-H) <sup>c</sup>	126.8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

<sup>a</sup>Distance between O<sub>surface</sub> (O site on the BaO surface) and C atom of CO<sub>2</sub>. <sup>b</sup>Distance between O atom and C atom within CO<sub>2</sub>. <sup>c</sup>Distance between O atom and lower H atom within H<sub>2</sub>O.

duct layer with surface sites.

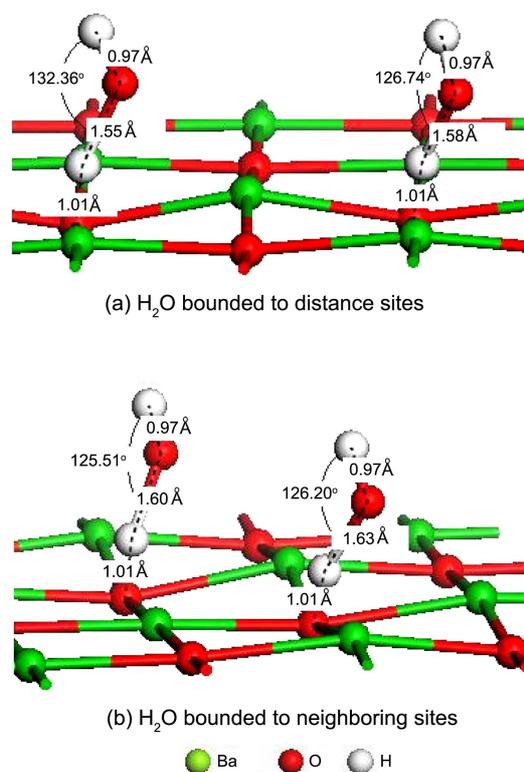
In comparison of two adsorption energies of CO<sub>2</sub> and H<sub>2</sub>O molecules, CO<sub>2</sub> adsorption (-2.72 eV) is energetically more favorable to BaO than H<sub>2</sub>O adsorption (-1.94 eV) because the stronger interaction of CO<sub>2</sub>-BaO system is driven by more distributed charge transfer from the surface to the adsorbate. To determine the electronic properties of CO<sub>2</sub> and H<sub>2</sub>O 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 (CO<sub>2</sub> and H<sub>2</sub>O) initiates and the charge of the adsorbed CO<sub>2</sub> and H<sub>2</sub>O is -0.76 e and -0.36 e, respectively, indicating that a net electron donation of CO<sub>2</sub> molecule is higher than that of H<sub>2</sub>O molecule. These results indicate that CO<sub>2</sub> adsorption tends to take place rather than H<sub>2</sub>O adsorption on the surface. A charge transfer from the BaO surface to the CO<sub>2</sub> molecule weakened the O-C bond within CO<sub>2</sub>, and the CO<sub>2</sub> molecule was bent due to the hybridization. These results support that CO<sub>2</sub>-BaO system provides the strong electron interaction. It is concluded that CO<sub>2</sub> and H<sub>2</sub>O are chemisorbed on the BaO (100) surface.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of CO<sub>2</sub>, H<sub>2</sub>O, and clean (2 × 2) BaO surface were calculated

**Figure 2.** The HOMO energy configuration and the HOMO and LUMO energy levels of CO<sub>2</sub> (a), H<sub>2</sub>O (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 CO<sub>2</sub> shows a higher energy state than that of H<sub>2</sub>O, indicating that CO<sub>2</sub> can be adsorbed more actively than H<sub>2</sub>O. This result also supports that CO<sub>2</sub> adsorption on BaO is stronger than H<sub>2</sub>O adsorption.

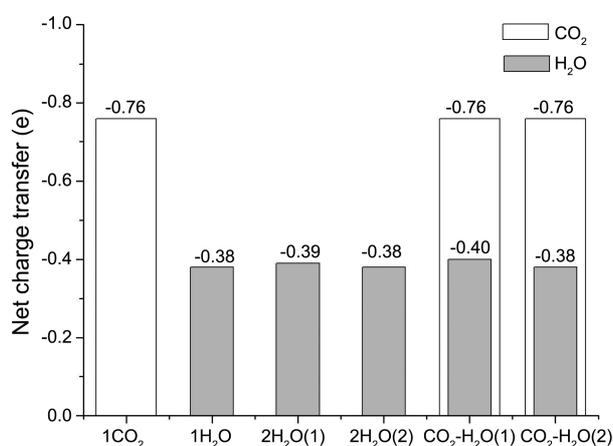
**A Pair of H<sub>2</sub>O Adsorption on BaO.** In order to evaluate CO<sub>2</sub> adsorption in the presence of H<sub>2</sub>O, this study investigated a pair of H<sub>2</sub>O adsorption on distant surface sites (distance between O atoms of H<sub>2</sub>O molecules: 5.53 Å) and neighboring sites (distance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

**Figure 3.** Optimized geometry structures of H<sub>2</sub>O adsorbed to distant sites (a) and neighboring sites (b) on the 2 × 2 BaO (100) surface.

**Table 2.** Adsorption properties of a single CO<sub>2</sub> and H<sub>2</sub>O, two H<sub>2</sub>O, and CO<sub>2</sub> with H<sub>2</sub>O on the (2 × 2) BaO (100) surface

Adsorption		Adsorption energy (eV) <sup>a</sup>	Bond length (O <sub>surface</sub> -CO <sub>2</sub> ) (Å)	Bond length (O <sub>surface</sub> -H <sub>2</sub> O) (Å)
Single CO <sub>2</sub>		-2.72	1.39	–
Single H <sub>2</sub> O		-1.94	–	1.01
Two H <sub>2</sub> O	Distant sites	-1.86	–	1.01
	Neighboring sites	-1.91	–	1.01
CO <sub>2</sub> with H <sub>2</sub> O	Distant sites (1) <sup>b</sup>	-2.23	1.39	1.01
	Distant sites (2) <sup>c</sup>	-2.23	1.39	1.02
	Neighboring sites (1) <sup>b</sup>	-2.32	1.38	1.02
	Neighboring sites (2) <sup>c</sup>	-2.20	1.40	1.01

<sup>a</sup>Adsorption energy is calculated by Eq. (1). <sup>b</sup>Simultaneous CO<sub>2</sub> and H<sub>2</sub>O adsorption on the BaO surface. <sup>c</sup>CO<sub>2</sub> adsorption after H<sub>2</sub>O adsorption on the BaO surface.

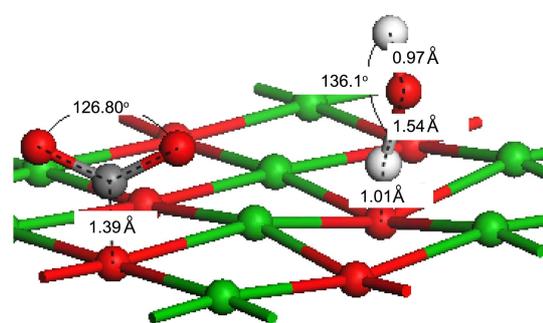


**Figure 4.** The net charge transfer of CO<sub>2</sub> and H<sub>2</sub>O adsorption. Note that 1CO<sub>2</sub> is the adsorption of a single CO<sub>2</sub> molecule; 1H<sub>2</sub>O is the adsorption of a single H<sub>2</sub>O molecule; 2H<sub>2</sub>O(1) is the adsorption of two H<sub>2</sub>O molecules on neighboring surface sites; 2H<sub>2</sub>O(2) is the adsorption of two H<sub>2</sub>O molecules on distant surface sites; CO<sub>2</sub>-H<sub>2</sub>O(1) is simultaneous CO<sub>2</sub> and H<sub>2</sub>O adsorption on neighboring surface sites; CO<sub>2</sub>-H<sub>2</sub>O(2) is simultaneous CO<sub>2</sub> and H<sub>2</sub>O adsorption on distant surface sites.

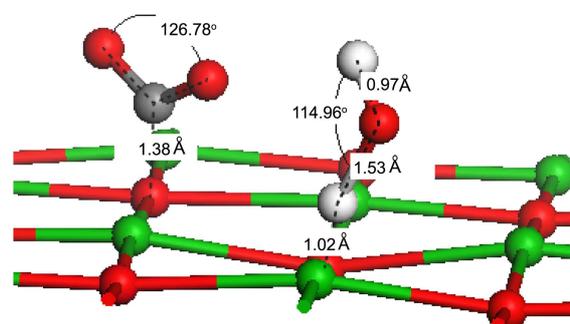
Å, which is shorter than that of hydrogen bond). In addition, the bond length of OH bond for both H<sub>2</sub>O molecules on the surface is 0.97 Å and that of elongated OH bond (OH-HO<sub>surf</sub>) is above 1.60 Å, indicating that the optimized geometry shows a partially dissociated water molecules forming a stable matrix with the BaO surface, which provides the same pattern of a single H<sub>2</sub>O adsorption on the surface.<sup>11</sup>

In the most stable configuration, the partial dissociative H<sub>2</sub>O 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<sub>surf</sub>-H<sub>2</sub>O=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 H<sub>2</sub>O molecules.

In Figure 4, H<sub>2</sub>O 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



(a) CO<sub>2</sub> & H<sub>2</sub>O bounded to distant sites



(b) CO<sub>2</sub> & H<sub>2</sub>O bounded to neighboring sites



**Figure 5.** Geometries of simultaneous CO<sub>2</sub> and H<sub>2</sub>O 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 H<sub>2</sub>O molecules is observed as -0.4 e. This result indicates that the strong adsorption of two H<sub>2</sub>O molecules on distant and neighboring surface sites was favorable.

The strong adsorption of H<sub>2</sub>O molecules on the surface may result in a decrease in CO<sub>2</sub> adsorption on the mineral surface because the adsorption of a number of H<sub>2</sub>O molecules may cause water aggregation on the surface.<sup>19</sup> Thus, we should investigate the effect of H<sub>2</sub>O on the CO<sub>2</sub> adsorption on the BaO surface.

**Competitive CO<sub>2</sub> and H<sub>2</sub>O Adsorption on BaO.** Since H<sub>2</sub>O can be adsorbed strongly on the BaO surface and, to the

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

When they are close, their interaction on the surface increases slightly, but the bond length of O<sub>surface</sub>-CO<sub>2</sub> does not significantly depend on the interaction between CO<sub>2</sub> and H<sub>2</sub>O due to the high interaction between the CO<sub>2</sub> molecule and the surface, resulting from the high charge transfer of CO<sub>2</sub> adsorption (-0.76 e) compared to that of H<sub>2</sub>O 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 CO<sub>2</sub> and H<sub>2</sub>O (-2.33 eV). (i.e., the adsorbed CO<sub>2</sub> is still stable in spite of the presence of H<sub>2</sub>O), indicating that H<sub>2</sub>O does not affect CO<sub>2</sub> adsorption for the formation of carbonates because a charge transfer from the surface O site and H<sub>2</sub>O molecule to the CO<sub>2</sub> molecule still leads to an energetically favorable formation of surface carbonates. In addition, the charge transfer of H<sub>2</sub>O even slightly increases whereas that of CO<sub>2</sub> does not change during competitive CO<sub>2</sub> and H<sub>2</sub>O 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 H<sub>2</sub>O adsorption on the BaO surface is strong, we investigated CO<sub>2</sub> adsorption after H<sub>2</sub>O adsorption on the BaO surface (Table 2). The energy of CO<sub>2</sub> adsorption after H<sub>2</sub>O adsorption process is not quite different from that of simultaneous CO<sub>2</sub> and H<sub>2</sub>O adsorption, indicating that H<sub>2</sub>O does not affect CO<sub>2</sub> adsorption although H<sub>2</sub>O is strongly adsorbed on the surface initially.

An analysis of surface interaction energies and charge transfer can ensure the energetic feasibility of CO<sub>2</sub> adsorption in the presence of H<sub>2</sub>O on the BaO surface. Compared to our previous study of interactive CO<sub>2</sub> adsorption, which shows that the interaction of CO<sub>2</sub> molecules for the surface adsorption affects CO<sub>2</sub> adsorption on the BaO surface, H<sub>2</sub>O does not significantly affect on the CO<sub>2</sub> adsorption.<sup>18</sup>

In conclusion, we investigated the competitive adsorption of CO<sub>2</sub> and H<sub>2</sub>O molecules on the BaO surface to determine the role of H<sub>2</sub>O on CO<sub>2</sub> adsorption. A DFT study using Dmol<sup>3</sup> represented molecular structures and energies of CO<sub>2</sub> adsorption in the presence of H<sub>2</sub>O on the BaO (100) surface. Electronic stabilization of the CO<sub>2</sub> molecule on the BaO

surface relies on the affinity of CO<sub>2</sub> for the O site because of their high interaction driven by the strong charge distribution. The results of the DFT calculation indicate that CO<sub>2</sub> molecule and H<sub>2</sub>O molecule are strongly adsorbed on the BaO surface, which forms a stable surface carbonate and a barium hydroxide, respectively. The chemisorption of two H<sub>2</sub>O molecules on distant and neighboring surface sites was also favorable on the adsorption on the surface. This study showed that the adsorption of CO<sub>2</sub> does not depend on the presence of H<sub>2</sub>O in spite of the strong adsorption of H<sub>2</sub>O on the BaO surface. These DFT computations provide the basic adsorption mechanism of CO<sub>2</sub> on BaO minerals in the presence of H<sub>2</sub>O for CO<sub>2</sub> sequestration, forming barium carbonate which can be permanent storage species under realistic gas-solid phase reaction.

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