To realize CO₂ capture and storage, many methods for CO₂ sequestration should be investigated from a long-term viewpoint. The development of novel CO₂ absorbent material is considered to be a candidate for the effective CO₂ sequestration. Investigation of CO₂ absorbent material is usually based on the experiment with following thermodynamic analysis of obtained data. Recently, the introduction of large-scale simulation based on modern computational chemistry methods is found to be a powerful approach in order to explain and understand the experimental data. In the present study, the experimental measurements and ab-initio calculations were employed for studying the adsorption process of CO₂ on both clean and doped CaO (001) surface. The effect of addition of other alkaline earth metal oxide to CaO on adsorption energy of CO₂ was analyzed in detail. The relationship between the standard free energy change of carbonation of added alkaline earth metal oxide and extent of variation in the adsorption energy was not clear. However, the structural deformation of CaO surface caused by formation of compound or solid solution would vary the adsorption energy and in the case of CaO/BeO, it leads to significantly improve the capture of carbon dioxide during the first step of adsorption process. Reactivity of CaO with CO₂ was investigated by experimental. The experimental results agree with calculation result. Atomistic level description of adsorption process of CO₂ on the doped alkaline earth oxides was successfully carried out by ab-initio calculations.

KEY WORDS: global warming; CO₂ sequestration; solid absorption material; adsorption; ab-initio calculation; CaO; double oxide system.

1. Introduction

The reduction of CO₂ emissions is an essential subject for the prevention of global warming and a common issue in every industry. In order to drastically mitigate CO₂ emissions, the CO₂ capture and storage (CCS) is a key technology from a long-term viewpoint even in steel industry, where a large amount of CO₂ is discharged. Several process such as amine liquid absorption and PSA (Pressure Swing Adsorption) are under development. To effectively operate CO₂ sequestration process, CO₂ absorbent material is required to absorb CO₂ selectively from gas emission containing CO₂ of low concentration, and emit gas containing high concentration of CO₂. Then absorption rate of CO₂ at lower temperatures and calorific value for desorption of CO₂ would an important issue.

In steel works, CO₂ gas is included in the exit gas from many processes such as sintering machine, hot stove, coke oven and blast furnace, thus the concentration of CO₂ and temperature of emission gas are different from each other by the process condition. The favorable CO₂ absorbent materials are desired for the efficiency in the reaction rate and covering large extent of gas composition and temperature. In order to reduce the CO₂ emissions from new technological aspect, the novel solid absorbent material was proposed by the authors. The alkaline earth metal oxides easily form carbonates. Therefore, MgO and CaO have been proposed as the appropriate absorbent for the chemical absorption of CO₂. The carbonation reaction of alkaline earth metal oxides is represented as MO + CO₂ = MCO₃ (M: alkaline earth metal). BaO and BaCO₃ are equilibrated with 1 atm of CO₂ at 1557°C, thus CO₂ desorption would progress at higher temperature region than 1557°C. The desorption behavior of CO₂ will be important for BaO. CaO and CaCO₃ are equilibrated with 1 atm of CO₂ at 886°C, thus decreasing desorption temperature will be the point at issue. The reactivity and reaction temperature might be controlled by formation of compound or add impurity.

The total process of absorption of CO₂ can be separated to two steps. In the 1st step, CO₂ is chemically adsorbed on the surface of the absorbent. In the 2nd step, CO₂ diffuses into the absorbent. Ab-initio calculations can provide the detailed information especially about the first step of CO₂ adsorption on the surface of alkaline earth metal oxide. The calculated value of adsorption energy could be used to estimate carbonation reaction rate and reaction behavior in parallel to experimental measurements.
Recently the adsorption of typical combustion gases on alkaline earth metal oxides was studied using ab-initio calculations. Thus, density functional cluster calculations of the CO2, NO and CO2 adsorption on the CaO (100) surface were performed. The periodic density functional calculations were also applied in order to study the adsorption chemistry of CO2, SOx (x=1,2) and NOx (x=1,2,3) on the (001) surfaces of alkaline earth metal oxides ranging from MgO to BaO. These studies have focused on both the determination of the stable adsorption sites and the difference between adsorption of various gases for a variety of metal oxides.

An important aspect of an atomistic level calculation is that the influence of compound and impurity on the adsorption properties of adsorbent can be also derived. In the present study, the experimental measurements and ab-initio calculations have been employed for studying the CO2 adsorption process on (001) surface of CaO and BaO. The preset calculations have not limited to estimation of adsorption energies alone but also extend to the analysis of electronic properties of carbon dioxide during adsorption process through the examinations of local density of states and Bader charge analysis. Moreover, the effects of addition of other alkaline earth metal oxides to CaO on adsorption energy of CO2 were also investigated both experimentally and theoretically.

2. Computational Methods

All calculations were performed in the framework of the density functional theory using the Venna Ab Initio Simulation Package (VASP). The projector augmented wave (PAW) method has been employed to describe the electron-ion interaction. The electrons exchange–correlation has been treated by generalized gradient approximation (GGA) based on Perdew and Wang (PW91) functional. The plane wave basis sets with cut-off energy of 400 eV is used for all calculations. The conjugate gradient method was used for the geometry optimization has been performed and structural parameters were considered as converged when the atomic forces were less than 0.04 eV/Å.

The CaO and BaO have the rock salt (NaCl) structure. The (001) surface is represented by a slab model arranged in six layers of sixteen ions each with vacuum space of 17 Å. The in-plane repeat distances are derived from the calculated bulk lattice constants. The calculated lattice constants exceed the experimental values by approximately 1%. This tetragonal supercell contains 48 MO formula units and it is shown in Fig. 1(a). The four topmost layers of the slab surface are allowed to relax while the remaining two layers are fixed to their bulk positions to represent the semi-infinite bulk crystal beneath the surface. The selected slab model is more accurate represent the (001) surface as comparable with 3 layer model including 1 fixed layer which used in previous calculations. A 6 × 6 × 2 Monkhorst-Pack mesh is used to sample the first Brillouin zone.

CO2 might be adsorbed vertically and horizontally. Figure 1(b) shows the 14 configurations considered here. The first four correspond to vertical adsorption configurations in which carbon dioxide is located directly over oxygen and alkali metal atoms and also the bridge and hollow sites. Other ten initial structures correspond to horizontal adsorption configurations directly on top of the atoms, and the bridge and hollow sites with varying rotation angles around axis perpendicular to the surface. Adsorption energies of CO2 molecule are obtained for each configuration using the following expression:

\[
E_{ads} = E_{CO2+surface} - (E_{surface} + E_{CO2}), \quad \cdots\cdots\cdots \quad (1)
\]

where \( E_{surface} \) and \( E_{CO2} \) represent the binding energies of the alkali metal surface, free CO2 molecules and the total adsorption system, respectively. The negative value of \( E_{ads} \) means that the corresponding adsorption state is thermodynamically favorable.

After finding the most stable adsorption configuration, the effect of the second alkali metals (M = Be, Mg, Sr, and Ba) of CO2 adsorption on CaO surface has been investigated by substitution of one Ca atoms in supercell on the selected element.

3. Results and Discussions

3.1. CO2 Adsorption on the CaO and BaO (001) Surfaces

First, we investigated of CO2 adsorption on the clean CaO (001) surface. In this case the most stable adsorption configurations (11 and 12 in Fig. 1(b)) were observed when CO2 molecules initially located parallel to the surface. In other configurations, CO2 does not adsorb via the O atom due to repulsion with surface oxygen or on Ca sites. The configuration 12 with angle of 45° between the CO2 plane and Ca–O–Ca plane of the surface is the most stable one. In
this configuration the CO$_2$ molecule is placed above the CaO surface oriented with the O atoms up, such that the C atom lies closest to the oxygen site as shown in Fig. 2(a). This configuration allows the C atom to interact directly with the surface O atom, which results in adsorption energy of $-36.32$ kcal/mol. This is in consistent with results of previous slab calculations$^5$ and in agreement with enthalpy of carbonation reaction as will be shown below. It is known that the energy derived by the cluster model is depending on cluster size. The previous reported value of adsorption energy of $-23.9$ kcal/mol calculated for the same adsorption site using the cluster model$^5$ was significantly lower than obtained here. The distance between CO$_2$ molecule and surface is equal to 1.385 Å, the C–O bonds are elongated by 0.095 Å as compared to that of an isolated CO$_2$ molecule and the O–C–O angle of adsorbed molecule amounts to 129.2$^\circ$ (see Table 1). Such local structural changes clearly indicate the formation of carbonates in agreement with experimental data. The Bader charge analysis indicates the electron transfer (0.0816 e) to carbon dioxide from calcium oxide surface. Figure 2(b) shows the increasing of the electron density on oxygen atoms of CO$_2$ as well as on the surface oxygen interacted directly with carbon atom of adsorbed molecule. The depletion of the electronic density is observed on the carbon atom of carbon dioxide as well as on the Ca atoms from the first and second layers (see Fig. 2(c)).

### Table 1.

| Distance (Å)         | C–O1(CO$_2$) | C–O2(CO$_2$) | C–O2II |
|----------------------|--------------|--------------|--------|
| C–O1(CO$_2$)         | 1.271 (+0.095)| 1.271 (+0.095)| 1.385  |
| C–O2(CO$_2$)         | 1.271 (+0.095)| 1.271 (+0.095)| 1.385  |
| C–O2II               | 1.385        | 1.385        |        |
| Angle (°)            | O1–C–O2(CO$_2$) | 129.2 (–50.8) |        |
| C(CO$_2$)            | 4.0000 (+0.0003) |         |        |
| O1(CO$_2$)           | −1.9777 (–0.0562) |        |        |
| O2(CO$_2$)           | −2.1039 (–0.0257) |        |        |
| Ca$_1$II             | 1.9501 (+0.0184)  |         |        |
| Ca$_1$IV             | 1.9341 (+0.0024)  |         |        |
| Ca$_2$I              | 1.9501 (+0.0184)  |         |        |
| Ca$_2$III            | 1.9501 (+0.0184)  |         |        |
| Ca$_3$I              | 1.9501 (+0.0184)  |         |        |
| Ca$_3$IV             | 1.9501 (+0.0184)  |         |        |
| Ca$_4$I              | 1.9341 (+0.0024)  |         |        |
| Ca$_4$III            | 1.9341 (+0.0024)  |         |        |
| O$_1$I               | −1.9290 (+0.0183) |        |        |
| O$_1$III             | −1.9755 (–0.0214) |        |        |
| O$_2$I               | −2.0836 (–0.1577) |        |        |
| O$_2$IV              | −1.9328 (+0.0272) |        |        |
| O$_3$I               | −1.9755 (–0.0529) |        |        |
| O$_3$III             | −1.9289 (+0.0209) |        |        |
| O$_4$I               | −1.9328 (–0.0240) |        |        |
| O$_4$IV              | −1.9495 (–0.0269) |        |        |

Fig. 2. The most stable configuration of CO$_2$ on the CaO(001) surface: (a) adsorption geometry; (b) the top view of excess (green) charges; (c) the side view of excess (orange) and depletion (blue) charges.

Fig. 3. The total and partial density of states of the most stable configuration of CO$_2$ on the CaO(001) surface. The Fermi level has been chosen as zero energy.
In order to describe the interaction between CO$_2$ molecule and CaO surface it is important to review an electronic density of states (DOS). For the CO$_2$/CaO system, the calculated total and partial density of states projected on the $s$ and $p$ states of O atoms, on the $s$, $p$ and $d$ states of Ca atoms as well as on molecular states of carbon dioxide are shown in Fig. 3. The total DOS consists from several peaks and their origin can be characterized by analyzing a partial density of states (PDOS). Thus the conductance band is mostly consisted from calcium unoccupied $3d$ states. The highest valence band is formed by hybridization between O $2p$ and Ca $3p$ and $3s$ states. The second largest valence band is mostly characterized by $2s$ states of surface oxygen. The DOS also has the several small peaks related to occupied molecular orbitals of adsorbed CO$_2$ molecule. Due to the charge transfer to carbon dioxide, the two unoccupied $\pi^*$ orbitals of isolated molecules are shifted to low energy region below Fermi level and strongly hybridized with highest valence band of CaO surface. The large overlapping in this energy region indicates a strong interaction of adsorbed molecule with CaO surface.

In the case of the BaO(001) surface, the CO$_2$ molecule stably adsorbed on top of the oxygen sites for three initial configurations, 10, 11 and 12 (see Fig. 1(b)). The adsorption energies for these configurations are lower than $-40$ kcal/mol and hence the adsorption of CO$_2$ on the BaO (001) surface is more stable than that on the CaO one. As in the case of CaO surface, the highest adsorption energy of $-55.9$ kcal/mol was observed for configuration 12. The difference in adsorption energy can be explained by the fact that BaO surface more basic that resulted in more significantly structural changes of adsorbed species. Thus, the surface-molecule distance is equal to 1.359 Å which is shorter than that in the case of adsorption of CO$_2$ on the CaO(100) one. Moreover, the C–O bonds are elongated as compared to that of CO$_2$ molecule adsorbed on the CaO(001) surface. As a result, the larger charge transfer from surface to carbon dioxide molecule is found and hence the stronger interaction between surface and carbon dioxide molecule is observed.

3.2. CO$_2$ Adsorption on the Ca$_{1-x}$M$_x$O (001) Surface (M = Be, Mg, Sr, and Ba; at x=0.02)

As a continuation, the adsorption CO$_2$ on the doped CaO(001) surface has been studied. The doped surface has been selected as Ca$_{1-x}$M$_x$O (001) surface (M = Be, Mg, Sr, and Ba). Since the selected additional atoms are also alkali earth elements, the doped system can be considered as double oxide compounds and the possibility to experimentally formed that structures will be discussed in the last sections. Three different positions (A, B and C) for substitution of single Ca atoms have been considered as shown in Fig. 4(a). The most stable configuration 12 has been selected as the initial configuration of adsorbed molecule. The substitution position A is a metal atom near oxygen adsorption site in first layer, the position B is the second nearest metal atom positions and the C position is located below oxygen site in Fig. 4. Adsorption of CO$_2$ on the Ca$_{1-x}$M$_x$O (001) surface ($x=0.02$): (a) selected 3 different position (named A, B and C) of M element (M = Be, Mg, Sr, and Ba). The most stable configuration of CO$_2$ on the Ca$_{1-x}$Be$_x$O (001) surface (at x=0.02) in the: (b) A; (c) B; and (d) C cases, respectively.

![Fig. 4. Adsorption of CO$_2$ on the Ca$_{1-x}$M$_x$O (001) surface ($x=0.02$): (a) selected 3 different position (named A, B and C) of M element (M = Be, Mg, Sr, and Ba). The most stable configuration of CO$_2$ on the Ca$_{1-x}$Be$_x$O (001) surface (at x=0.02) in the: (b) A; (c) B; and (d) C cases, respectively.](image)

![Fig. 5. Adsorption energies of CO$_2$ adsorbed on the Ca$_{1-x}$M$_x$O (001) surface (M = Be, Mg, Ca, Sr and Ba, at x=0.02) for M substitution in A, B and C positions. Solid line indicate the value of adsorption energy of CO$_2$ on the CaO(001) surface.](image)
the 2nd surface layer. Here we have considered only single substitution which corresponds in our model Ca_{1-x}M_xO (x=0.02) compositions. Figures 4(b), 4(c) and 4(d) show the final configurations of CO_2 molecules on Ca_{0.98}Be_{0.02}O(001) surface after the full structural optimization for three cases considered in the present study. Dark gray circle denotes Be. It is clearly seen that the Be substitution leads to a significant surface reconstruction due to the large difference in the atomic radius between Be and Ca ions. As a result, the CO_2 adsorption energies on Ca_{0.98}Be_{0.02}O are lower than that of the CO_2/CaO system. Figure 5 shows the values of adsorption energy of CO_2 on the Ca_{0.98}M_{0.02}O (001) surface at three different substitution sites. The solid lines show the reference state corresponded to value of carbon dioxide adsorption energy on the clean CaO(001) surface. In all cases of the alkaline earth metal substitution on the position A, all second elements improve the CO_2 absorption energy and the order of variation of adsorption energies is Be > Mg > Ba > Sr (see Fig. 5). In the case of the position B, the Be and Mg atoms improve the adsorption ability of CaO surface, however, the substitution of Sr or Ba atom for Ca one does not affect on carbon dioxide adsorption. The substitution of Be and Mg at the position C leads to almost the adsorption energy as in case of a clean CaO surface. The Ba substitution in second layer improves the properties of the CaO(001) surface toward carbon dioxide adsorption and Sr atom has the opposite effect but adsorption is still thermodynamically favorable. It has been found that the most significant improvement in catalytic activity of doped CaO surface was observed for Be substitutions. Table 2 shows the geometric parameters and charge distribution of CO_2/Ca_{0.98}Be_{0.02}O system for three different substitution positions. As mentioned before, the significant surface reconstruction was observed in the both first and second surface layers. This leads to more complicated charge redistribution in first surface layer as shown in Table 2. As in the case of clean CaO surface, the Bader charge analysis shows charge transfer to CO_2 from the calcium oxide surface (see Fig. 6). The amounts of the electron transfer are equal to 0.096 e, 0.077 e and 0.0458 e for A, B and C positions, respectively. Only in the case of atom substitution in the position A, the value of the charge transfer is larger than that in the case of clean CaO surface. However, the largest change in the adsorption energy is found for atom replacement in B site. In this case, the largest electron charge is accumulated on the surface oxygen atom located below carbon of CO_2 molecule as shown in Table 2 by bold type. This results in the shortening and strengthening of C–O bond between

| Position of Be | A         | B         | C         |
|---------------|-----------|-----------|-----------|
| Distance (Å)  |           |           |           |
| C–O1(CO_2)    | 1.268 (+0.092) | 1.281 (+0.105) | 1.285 (+0.109) |
| C–O2(CO_2)    | 1.268 (+0.092) | 1.273 (+0.097) | 1.270 (+0.094) |
| C–O2II        | 1.401      | 1.365     | 1.400     |
| Angle (°)     |           |           |           |
| O1–C–O2(CO_2) | 127.5 (–52.5) | 128.0 (–52.0) | 128.6 (–51.4) |
| C(CO_2)       | 3.9999 (+0.0002) | 4.0000 (+0.0003) | 4.0000 (+0.0003) |
| O1(CO_2)      | –2.0006 (–0.0791) | –1.9959 (–0.0744) | –1.9650 (–0.0435) |
| O2(CO_2)      | –2.0950 (–0.0168) | –2.0808 (–0.0026) | –2.0810 (–0.0023) |
| Ca_2layer     | 1.9989 (+0.0001) | 1.9979 (–0.0001) | /         |
| Ca_1II        | 2.0000 (+0.0665) | 1.9052 (+0.0204) | 1.9456 (+0.0083) |
| Ca_1IV        | 1.9352 (+0.0111) | /         | 1.9344 (+0.0003) |
| Ca_2I         | /         | /         | 2.0000 (+0.0659) |
| Ca_2II        | 1.9290 (+0.0442) | 2.0000 (+0.0665) | 1.9693 (+0.0102) |
| Ca_3II        | 2.0000 (+0.0667) | 1.9538 (+0.0184) | 1.9576 (+0.0021) |
| Ca_3IV        | 1.9345 (+0.0009) | 1.9995 (+0.1143) | 1.9347 (+0.0011) |
| Ca_4I         | 1.8953 (+0.0101) | 1.9337 (+0.0001) | 1.9341 (+0.0004) |
| Ca_4II        | 1.9352 (–0.0002) | 1.9341 (+0.0008) | 1.9344 (+0.0017) |
| Ca_4III       | 2.0000 (+0.0003) | 1.9997 (+0.0000) | 2.0000 (+0.0000) |
| Be            | –2.0427 (–0.0423) | –1.9912 (+0.0447) | –1.9318 (+0.0235) |
| O_1I          | –1.9507 (–0.0036) | –1.8306 (+0.0112) | –1.9637 (+0.0113) |
| O_1II         | –1.9853 (–0.1165) | –2.0212 (+0.2541) | –2.0300 (+0.1404) |
| O_2I          | –2.0064 (+0.0295) | –1.8195 (+0.1809) | –1.9529 (+0.0137) |
| O_3I          | –1.8158 (+0.0288) | –1.9520 (–0.0183) | –1.9628 (+0.0142) |
| O_3II         | –1.9742 (–0.0302) | –1.9025 (+0.0540) | –1.9140 (+0.0496) |
| O_4I          | –1.9474 (+0.0266) | –1.9183 (+0.0527) | –1.9378 (+0.0274) |
| O_4II         | –1.9181 (+0.0156) | –2.1106 (–0.2660) | –1.9490 (+0.0265) |
adsorbed molecule and Ca$_{0.98}$Be$_{0.02}$O surface. In the A substitution case, the adsorbed CO$_2$ molecule is slightly tilted away from the surface normal and the angle between the CO$_2$ plane and Ca–O–Ca plane of the surface is changed from 45° to 0° as can be seen in Fig. 6(a). This adsorption geometry corresponds to configuration 11 (see Fig. 1(b)) in which carbon dioxide found to be less stable as comparable to the most stable configuration 12. It is interesting to note that after the Be substitution the surface structure is changed not only in the first but also in second and third layers (see Fig. 6). Accordingly, the changes in electron density are found even in 3rd layer. This indicates that the application of slab model with three layers used previously$^6$) may not enough to represent the doped CaO surface and hence the larger slab model with four relaxed layers used in the present study is more reliable.

Figure 7 shows both DOS and PDOS of the CO$_2$/Ca$_{0.98}$Be$_{0.02}$O system. From the PDOS analysis it can be seen that Be atom only formed the weak bonds with nearest O atoms of surface via s-p hybridization and does not form any bond with adsorbed carbon dioxide molecule. As in the case of the clean CaO(001) surface, the DOS also has the several small peaks related to occupied molecular orbitals of CO$_2$ and the interaction between adsorbed molecule and surface is also associated with charge transfer to CO$_2$ and the two unoccupied $\pi^*$ orbitals of isolated molecules are shifted to low energy region below Fermi level and hybridized with highest valence band of Ca$_{0.98}$Be$_{0.02}$O surface.

Thus, the alkali earth metal substitutions for Ca atom result in surface reconstruction followed by increasing the carbon dioxide adsorption due to the strong C–O bond between adsorbed molecule and surface.

3.3. Comparison of Adsorption Energy and Carbonation Energy

Carbonation reaction of alkaline earth metal oxide is represented as Eq. (2).

$$\text{MO} + \text{CO}_2 = \text{MCO}_3 \quad \text{.......................... (2)}$$

Enthalpy changes of reaction for Ca and Ba$^{16}$) those can be found in literature, are shown in Fig. 8. The enthalpy slightly changes with a changing in temperature. It can been seen that the values of the enthalpy changes are well correlated with the calculated values of adsorption energies of −36.3 and −55.9 kcal/mol for the most stable CO$_2$ configurations on CaO and BaO, respectively. The adsorption energy consist of energy change of adhesion of CO$_2$ on the surface of MO supercell, however thermodynamic data include total energy change generating MCO$_3$. In 3.2, effect of alkali earth ion impurities in the CaO(001) surface on the adsorption energy of CO$_2$ was derived. A minimal addition (2%) of BeO into CaO improves the adsorption energy of CO$_2$, however, those of MgO, SrO and BaO varied slightly.
The partial pressure of CO$_2$ at the equilibrium between MO and MCO$_3$ can be calculated from Eq. (3) using the standard free energy change$^{16}$ of Eq. (2).

$$\log P_{CO_2} = \frac{\Delta G^\circ_2}{RT}. \quad (3)$$

where $P_{CO_2}$, $\Delta G^\circ_2$, $R$, and $T$ denote the partial pressure of CO$_2$, the standard free energy change of Eq. (2), the gas constant, and absolute temperature, respectively. The standard free energies of Eq. (2) are shown in Fig. 9. Thermodynamic stability of carbonate decreases in the order of Ba, Sr, Ca, Mg, and Be. Decreasing in adsorption energy is unrelated to stability of carbonate of additive. Phase diagrams for the CaO–BeO$^{17}$, CaO–MgO$^{18}$, and CaO–SrO$^{19}$ systems were reported and the CaO–BaO$^{20}$ system was calculated. Solid solution of CaO including 2% SrO would be formed. Meanwhile, there is almost no solubility of BeO, MgO, and BaO in CaO phase.

Double oxide compound, namely Be$_2$Ca$_2$O$_5$ exists for the CaO–BeO system, and no compound is reported for the other systems. The standard free energy change of formation of Be$_2$Ca$_2$O$_5$ is not reported, however formation of compound decreases activity of BeO and CaO. That means BaO and CaO have interaction between them, and that caused distortion of CaO structure, then the adsorption energy of CO$_2$ decreased for some specific site. On the other hand, MgO, SrO, and BaO does not form double oxide compounds. Therefore the interactions between them and CaO and hence the influence on the CaO structure should be smaller than that between BeO and CaO. Addition of SrO slightly decrease the adsorption energy of CO$_2$. Since a small amount of SrO can be dissolved into CaO and solid solution of CaO with 2% of SrO would be formed. Therefore as shown in Fig. 5, the influence of addition of SrO into CaO expected to be smallest as compared with other alkaline earth metal oxide.

4. Experimental Study on CO$_2$ Absorption Behavior of BeO Doped CaO

As shown in Fig. 5, the calculation results show that the CO$_2$ adsorption energy of CaO has been increased with addition of BeO. Meanwhile, no experimental study about that was reported. Here, the CO$_2$ absorption on BeO added CaO compound was measure experimentally and compared with the result of ab-initio calculations.

Reagent grade of CaO and BeO was well mixed. About 1.0 gram of the mixture was pressed in a 10-mm die at 9.8 MPa to form a tablet of the sample, and then heated at 1573 K for 24 hours in air atmosphere. The pellet was ground and the pelletizing and heating processes were conducted again. CaO was prepared by the decomposition of CaCO$_3$ at 1673 K. Concentration of BeO was set to 1, 2, and 5 mass%. TG-DTA was employed to measure CO$_2$ absorption and desorption. A continuous flow of CO$_2$ gas at 100 ml/min was used to control atmosphere in the reaction chamber.

Weight change ratios of sample are shown in Fig. 10. The sample was heated from room temperature to 1373 K; the temperature was increased at a rate of 5 K/min. Diameter of particle was within ranges of 53–100 $\mu$m. The experimental result shows that addition of BeO enhanced absorption of
CO₂ and decreased temperature at which sample start to increase the weight. Since extent of enthalpy change is almost independent of variation of temperature, the calculation result can be applied for the experimental temperature. Absorption of CO₂ would be enhanced with an increasing in affinity between the oxide and CO₂ molecule. This experimental result agrees well with ab-initio calculation results that showed an increasing affinity between CaO and CO₂. Relationship between concentration of BeO in CaO and maximum weight change ratio was not observed. The calculation result shows that Be affects on the shape of CaO crystalline structure. Meanwhile, according to phase diagram for the CaO–BeO system, the solubility of BeO in Be₃Ca₂O₅ was a little. Therefore, a small addition of BeO to CaO would improve the reactivity with CO₂, and compound of CaO–BeO was formed excess BeO. The obtained experimental results show the potential of ab-initio calculations for understanding the properties of complex alkali earth metal oxides and for supporting the experimental exploration of novel CO₂ capture and storage materials.

5. Conclusions

In order to develop CO₂ absorbent material, the large scale ab-initio calculations were performed for an accurate estimation of adsorption energy of CO₂ on the CaO and BaO (001) surfaces. In the first time the effects of addition of other alkaline earth metal oxides to CaO on the CO₂ adsorption energy were also investigated both theoretically and experimentally.

The following conclusions can be obtained:

(1) Results of ab-initio calculations of CO₂ adsorption are comparable to the enthalpy change of carbonation of alkaline earth metal oxides in thermodynamic data.

(2) It is confirmed both theoretically and experimentally that addition of BeO into CaO substrate significantly improves adsorption properties of adsorbent toward CO₂ capture and storage.

(3) Variation of CO₂ adsorption energy is unrelated to stability of carbonate of added alkaline earth metal oxide.

The obtained results suggest that the selected model is more reliable than one previously used and can be applied for study the carbon dioxide adsorption process on multi-component oxide surfaces.

REFERENCES

1) M. Onoda: J. Jpn. Inst. Energy, 88 (2009), 278.
2) R. Inoue, S. Ueda, K. Wakuta, K. Sasaki and T. Ariyama: CAMP-ISIJ, 23 (2010), 90, CD-ROM.
3) S. C. Lee, H. J. Chae, S. J. Lee, B. Y. Choi, C. K. Yi, J. B. Lee, C. K. Ryu and J. C. Kim: Environ. Sci. Technol., 42 (2008), 2736.
4) Y. Li, C. Zhao, H. Chen, L. Duan and X. Chen: Fuel, 89 (2010), 642.
5) E. Kadossov and U. Burghaus: J. Phys. Chem. C, 112 (2008), 7390.
6) W. F. Schneider: J. Phys. Chem. B, 108 (2004), 273.
7) W. Tang, E. Sanville and G. Henkelman: J. Phys. Condens. Matter., 21 (2009), 084204.
8) G. Kresse and J. Furthmüller: Phys. Rev. B, 54 (1996), 11169.
9) G. Kresse and J. Furthmüller: Comput. Mater. Sci., 6 (1996), 15.
10) P. E. Blöchl: Phys. Rev. B, 50 (1994), 17953.
11) G. Kresse and D. Joubert: Phys. Rev. B, 59 (1999), 1758.
12) J. P. Perdew and Y. Wang: Phys. Rev. B, 45 (1992), 12344.
13) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais: Phys. Rev. B, 46 (1992), 6671.
14) R. W. G. Wyckoff: Crystal Structures, Willey, New York, (1963).
15) H. J. Monkhorst and J. D. Pack: Phys. Rev. B, 13 (1976), 5188.
16) JANAF Thermochemical Tables, ed. by D. R. Stull and H. Prophet, U.S. Department of Commerce, Washington, (1985). Cp Fitted by CRCT, Montreal.
17) Phase Diagrams for Ceramist, ed. by M. K. Reser, The American Ceramic Soc., OH, (1964), 99.
18) R. C. Donnan, J. B. Barr, R. N. McNally and A. M. Alper: J. Am. Ceram. Soc., 46 (1963), 313.
19) Phase Equilibria Diagrams CD-ROM Database v.3.2, Acers-NIST, OH, (2008), s-188.
20) W. J. M. Van der Kemp, J. G. Blok, P. R. Van der Linde, H. A. J. Oonk, A. Schuijff and M. L. Verdonk: Calphad, 18 (1994), 255.