

# First-principles study adsorption properties of CO<sub>2</sub> molecule on CaO(100) surfaces

Xiaodong Li<sup>1, a</sup>, Meimei An<sup>2, b</sup>, Yuancheng Zhu<sup>1, a</sup> and Haiyan Ma<sup>3</sup>

<sup>1</sup> School of Chemical Engineering and Technology, Tianshui Normal University, Tianshui, China

<sup>2</sup> School of literature and history, Tianshui Normal University, Tianshui, China

<sup>3</sup> School of Chemical Engineering, Northwest University

<sup>a</sup>lixxd@163.com, <sup>b</sup>anmm9999@163.com

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**Abstract.** The process of stable adsorption of CO<sub>2</sub> molecules on CaO (100) surfaces were studied using a periodic slab model by PW91 of generalized gradient approximation (GGA) within the framework of density functional theory (DFT). The results indicated that the surface oxygen atoms (O<sub>surf</sub>) are the most active adsorbed sites for adsorb CO<sub>2</sub> on the CaO (100) surfaces.

## 1. Introduction

It is a truth universally acknowledged that the emission of carbon dioxide (CO<sub>2</sub>) leads to global warming which results in a change in the climatic conditions. Despite this, CO<sub>2</sub> or synthetic discharge gas is produced during the burning or gasifying process of the carbon-based fuels, in particular, from the burning of fossil fuel in fossil fuel heat-engine plant which causes more than 30% of the total CO<sub>2</sub> emissions [1]. The heat-engine plants become the largest source of CO<sub>2</sub> emission, and this has attracted significant world-wide attention. However, CO<sub>2</sub> is also an effective carbon resource, which can meet the ever increasing demand for energy; thus, providing solution for the environmental problems. Therefore, the economical capture, transport, storage, and transformation of CO<sub>2</sub> are highly desirable for the gradual reduction and control of anthropogenic greenhouse gas emissions.

In recent years, capture and storage of CO<sub>2</sub> by the cyclic reaction involving adsorption, carbonation, and calcination of calcium-based sorbents have attracted significant attention of the researchers world-wide [2-3]. Utilizing this technology, CO<sub>2</sub> was captured in order to shift the steam reforming equilibrium for the production of hydrogen [4], and the CO<sub>2</sub> in dual curing coal combustion system could be attached directly to the bed [5]. According to the study of the calcium-based sorbent, the absorptivity of calcium oxide (CaO) and calcium hydroxide (Ca(OH)<sub>2</sub>) (with higher theoretical absorbance) is better than other sorbents. Theoretically, 0.786 g of CO<sub>2</sub> could be adsorbed by 1 g of CaO. CaO is commercially and readily available as it is easy to prepare [6-7] and it is cost effective. However, reports based on the theoretical research on the CO<sub>2</sub> adsorption by CaO are limited [6, 8], and studies on its decomposition kinetics have not been reported.

In this study, the process of stable adsorption of CO<sub>2</sub> molecules on CaO surfaces was investigated by using density functional theory. The CO<sub>2</sub> adsorption behavior on the surface of CaO was simulated by Materials studio. The adsorption was configured; and the charge, frequency, and density of the states were analyzed. Moreover, the temperature and pressure dependence reaction kinetics on the adsorption behavior were investigated to provide theoretical support for further research on CaO as adsorbent for CO<sub>2</sub>.

## 2. Surface model and calculation method

CaO is known to have the same crystal structure as sodium chloride, with a lattice parameter of 4.8105 nm. It is an ionic crystal. The atoms are connected mainly through electrostatic interaction, with the space group of 225, Fm3m. In this study, CaO (100) surface was selected to investigate the adsorption behavior because it is the most stable surface of the CaO crystal. The thickness of vacuum

layer between two adjacent layer planes was 1 nm, in order to ensure that the interaction force between the planes is small enough. The super cells with size of  $1 \times 1 \times 1$  and  $2 \times 2 \times 1$  were used to study the adsorption properties of CO<sub>2</sub> molecules and the repulsive interaction between CO<sub>2</sub> molecules under different coverages of the adsorption space.

In this study, the local density approximation (LDA) and generalized gradient approximation (GGA) were used. The adsorption behavior of CO<sub>2</sub> molecules and exchange correlation energy stimulated by periodic CaO (100) mode were described by the exchange correlation function LA-PZ, Perdew–Burke–Ernzerhof (PBE), and Perdew and Wang (PW91). All the calculations were performed by Castep software package. The inner electrons of Ca atom were expanded by the effective core potential (ECP), and the full electronic base cluster were used for non-metal atoms C and O. The Mibkhorst–Pack grid parameter of Brillouin zone integration was set to be  $4 \times 4 \times 2$ . During optimization, the nether 9 layers were fixed, and the 3 layers and above on the surface were released.

### 3. The optimization of adsorption model

In order to obtain more accurate data during the calculation process, the LDA correlation function (LDA-LA-PZ), GGA-PBE correlation function, and GGA-PW91 correlation function were used independently to optimize the CaO structure cell to determine the best method for computation. The corresponding values are listed in Table 1 which reveal that the calculated result for the CaO structure cell parameter using GGA-PW91 is the closest to the experimental data. Therefore, GGA-PW91 method was selected as the optimized method to calculate the parameters of the CaO surface and to investigate the behavior of CO<sub>2</sub> adsorption.

Table 1 The effect of different calculated methods for CaO cell parameters (in nm)

Computational methods	Lattice constants	
	Computational results	Expt <sup>[14, 18]</sup>
LDA-LA-PZ	0.471517	0.48105
GGA-PBE	0.483724	
GGA-PW91	0.482829	

Previous research indicated that there are two modes of the CO<sub>2</sub> adsorption on the surface of CaO (100). The first approach demonstrates that after the CO<sub>2</sub> molecules are adsorbed on CaO (100) surface, the angle between the CO<sub>2</sub> molecular plane and the CaO (100) cutting edge is 45° (see Figure 1 (a)). It is the most stable adsorption structure according to the previous studies. The second mode is that the CO<sub>2</sub> molecular plane and the CaO (100) cutting edge are parallel to each other. The repulsion between oxygen atoms increases due to the smaller space between CO<sub>2</sub> molecules, resulting in the unstable state of the CO<sub>2</sub> adsorption on CaO surface. In the structural optimization process, the structure gradually transforms into the first adsorption form. Therefore, only the first type of adsorption structure was analyzed and discussed concretely in this study.

In this study, three different scenarios for CO<sub>2</sub> adsorption process were considered. First, CO<sub>2</sub> molecules were adsorbed on the  $1 \times 1 \times 1$  CaO (100) super crystal cell surface. It was a relatively simple adsorption model because the influence of surrounding atoms on CO<sub>2</sub> molecules was neglected. Second, CO<sub>2</sub> molecule was adsorbed on the  $2 \times 2 \times 1$  CaO (100) super crystal cell surface assuming that only one CO<sub>2</sub> molecule was adsorbed on a relatively large surface. Therefore this model was an ideal adsorption model, and the structure is shown in Figure 1 (b). In the third model, four CO<sub>2</sub> molecules were adsorbed on the  $2 \times 2 \times 1$  CaO (100) super crystal cell surface. The intermolecular repulsive interaction was taken into account to study the repulsive energy during the adsorption of CO<sub>2</sub> molecules. This adsorption model is shown in Figure 1 (c).

The geometric parameters of CO<sub>2</sub> molecule absorption on different CaO (100) surfaces are listed in Table 2. Adsorption of one CO<sub>2</sub> molecule on the  $1 \times 1 \times 1$  CaO (100) super crystal cell surface

leads to an increase in the space between surface and subsurface layer, as well as between subsurface and third layer. This was attributed to the fact that the molecular  $\text{CO}_2$  prompted the atomic activation in the surface layer, and the oxygen atoms in  $\text{CO}_2$  molecules could interact with the neighboring Ca atoms. This is discussed in the following section. Under the same conditions, adsorption of one  $\text{CO}_2$  molecule on the  $2 \times 2 \times 1$  CaO (100) super crystal cell surface did not lead to any change in the space between surface and subsurface. However, the space between subsurface and the third layer as well as the  $\text{C}-\text{O}_{\text{surf}}$  bond length reduced. The calculated results obtained by this model were similar to the results by Gaussian [6, 7], indicating that after the  $\text{CO}_2$  molecules were adsorbed on the CaO (100) surface, strong adsorption bond was formed between the carbon atoms in  $\text{CO}_2$  molecules and the oxygen atoms on the CaO (100) surface under certain conditions, resulting in the changes in the electronic configuration of the atoms on the surface layer. Subsequently, the subsurface layer was changed by Coulomb force, resulting in the reduction of the layer space. This could also be confirmed from the increase in  $\text{C}-\text{O}_{\text{CO}_2}$  bond length. Later, when four  $\text{CO}_2$  molecules were adsorbed on the  $2 \times 2 \times 1$  CaO (100) super crystal cell surface, the layer space was further reduced; however, the  $\text{C}-\text{O}_{\text{surf}}$  bond length increased by 0.0162 nm. It was mainly attributed to the intermolecular repulsion between  $\text{CO}_2$  molecules. The energy of this type of adsorption bond was low, and that was not conducive to the adsorption of  $\text{CO}_2$ . Moreover, the  $\text{Ca}_{\text{surf}}$  and  $\text{Ca}_{\text{sub}}$  atoms which were closely connected with  $\text{O}_{\text{surf}}$  atoms were affected by the changes in outer electronic configuration of  $\text{O}_{\text{surf}}$  atoms, resulting in different  $\text{O}_{\text{surf}}-\text{Ca}_{\text{surf}}$  and  $\text{O}_{\text{surf}}-\text{Ca}_{\text{sub}}$  bond lengths compared to the average interlayer space.

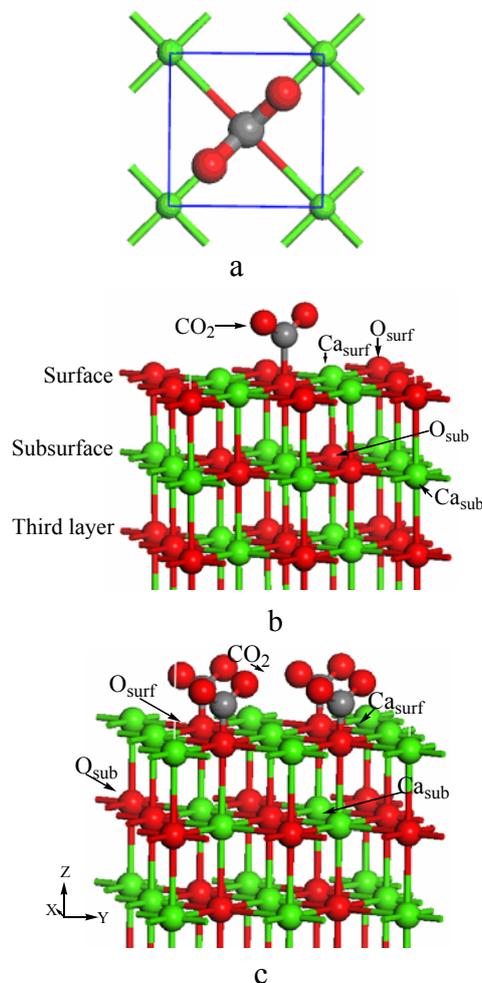


Fig. 1. Adsorption model of CaO, CaO (100) and  $\text{CO}_2$  adsorbed CaO(100) supercell

Light red, green and grey balls represent O, Ca and C atoms, respectively.  $\text{O}_{\text{surf}}$  and  $\text{Ca}_{\text{surf}}$  represent two different O and Ca sites of top surface;  $\text{O}_{\text{sub}}$  and  $\text{Ca}_{\text{sub}}$  represent two different O and Ca sites of subsurface.

Table 2 Geometrical parameters for CO<sub>2</sub> adsorbed on CaO (100) surface at GGA-PW91 level (in nm)

Model	Distance <sup>a</sup> <sub>(1-2)</sub>	Distance <sup>b</sup> <sub>(2-3)</sub>	C-O <sub>surf</sub>	C-O <sub>CO2</sub>	O <sub>surf</sub> -Ca <sub>surf</sub>	O <sub>surf</sub> -Ca <sub>sub</sub>
1×1×1 CaO(100)	0.2383	0.2421	--	--	0.2405	0.2369
CO <sub>2</sub> on 1×1×1CaO(100)	0.2476	0.2458	0.1725	0.1215	0.2409	0.2370
CO <sub>2</sub> on 2×2×1 CaO(100)	0.2383	0.2396	0.1438	0.1269	0.2513	0.2539
4CO <sub>2</sub> on 2×2×1 CaO(100)	0.2368	0.2314	0.1600	0.1220	0.2410	0.2289

<sup>a</sup> Stands for layer distance for surface to subsurface; <sup>b</sup> Stands for layer distance for subsurface to third layer.

#### 4. Conclusions

The density function theory GGA-PW91 method was used to simulate the CO<sub>2</sub> molecule adsorption behavior on the most stable sites of the 1 × 1 × 1 and 2 × 2 × 1 CaO (100) super crystal cell. The configuration optimization was conducted for the adsorption of one, two, and four CO<sub>2</sub> molecules on the 2 × 2 × 1 CaO (100) super crystal cell. The properties of electronic structure were analyzed. The results indicated that the most stable adsorption bond could be formed between the carbon atom and the O<sub>surf</sub> atom when CO<sub>2</sub> was adsorbed on the 2 × 2 × 1 CaO (100) surface, with the adsorption bond of 0.1438 nm.

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