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SeO_2 adsorption on CaO surface: DFT study on the adsorption of a single SeO_2 molecule

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ABSTRACT

Selenium is a hazardous element in coal. During coal combustion, most of the selenium will convert to SeO_2 in the flue gas. Ca-based adsorbents, especially CaO, have been considered as a potential sorbent to adsorb SeO_2 due to its low cost. In this paper, the adsorption mechanisms of single SeO_2 on CaO surface were investigated by density functional theory (DFT) calculation. Both the physisorption and chemisorption structures were determined. It has been identified that the adsorption of SeO_2 on CaO surface is primarily chemisorption, while physisorption takes effects at the initial stage of the process. Under O_2 atmosphere, selenate is hard to form. Most of the adsorption products are selenite. Additionally, the electron density maps were obtained to reveal the surface active sites. The partial density of states (PDOS) was calculated for analyzing the electronic structural change of SeO_2 and CaO surface during adsorption. The results provide fundamental information of the adsorption process, which could be meaningful for the development of new absorbents.

1. Introduction

Selenium is hazardous element existing in coal and mineral. According to the chemistry properties of selenium and its compounds, it has been classified as one of the most volatile trace elements by Clarke and Sloss [1]. During coal combustion and smelting processes, gaseous selenium will be released into the environment. Excess amounts of selenium can pollute water and soil, and its overabundance in food chains will lead to severe selenosis [2]. Selenium compounds have been included as one of 189 toxic air pollutants by US government (US, 1990 Clean Air Act Amendments) [3]. Combustion of coal accounts for 50% anthropogenic emission of atmospheric selenium [4]. In 2011, US Environmental Protection Agency issued the Mercury and Air Toxics Standards (US, MATS, updated in 2016). A selenium emission limit of 5.0×10^{-2} lb/MWh (approximately 6.8 $\mu g/m^3$) was set for coal-fired power plants [5].

Under oxidative atmosphere, gaseous SeO_2 is the main form of selenium combustion products [6]. Ca-based adsorbents, especially CaO, have been proved effective for the adsorption of SeO_2 in laboratory scale [7–9]. The main explanation was the reaction between solid CaO and gaseous SeO_2. The reaction products were selenite (Se^{4+}). Due to its low cost and possible desulfurization [10] and decarbonization [11] capabilities, CaO has been considered as a promising sorbent for SeO_2 capture. The CaO in fly ash will adsorb SeO_2, leading to the enrichment of selenium in fly ash [12,13]. The main selenium in fly ash is selenite (Se^{4+}) with a minor presence of selenate (Se^{6+}) [14]. However, the detailed surface reaction steps between CaO surface and SeO_2 under O_2 atmosphere still remain unclear and need further insightful investigation.

Advanced DFT calculation is a recently developed computational chemistry technology [15]. By simplifying wave function into electron density functional, the Schrodinger equation could be resolved accordingly. The adsorption mechanisms of other volatile trace elements, especially Hg [16,17] and As [18] have been extensively studied by DFT method. In this study, the DFT method was attempted to investigate the adsorption of gaseous SeO_2 on the CaO(001) slab model surface, with the aim to offer microscopic information of the adsorption of SeO_2 on CaO under O_2 atmosphere, thus to provide guidance to develop more efficient sorbents in the future.

2. Theory and model

2.1. Computational details

All the DFT calculations applied in this study were performed by using CASTEP [19,20] module of Material Studio software. The

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Table 1
Calculated lattice parameters, bond lengths and bond angles.

Substance	Previous data	Simulated data
SeO_2	Se-O bond 1.608 Å [28] O-Se-O angle 113.8° [28]	Se-O bond 1.615 Å O-Se-O angle 115.6°
CaO	4.836 Å [29], 4.807 Å [30]	4.837 Å

Table 2
Change of physical and chemical properties of different surface size.

Surface size	Δz_{layers}, Å	Δz_{Ca-O}, Å	ΔE_{ads}, kJ/mol
1 × 1	7.3×10^{-2}	1.0×10^{-4}	115.5
2 × 2	7.1×10^{-2}	9.2×10^{-5}	4.0
3 × 3	5.0×10^{-2}	9.0×10^{-5}	0.7
4 × 4	7.2×10^{-2}	1.0×10^{-4}	3.3

GGA (Generalized Gradient Approximation) Scheme and PBE [21] (Perdew–Burke–Ernzerhof) functional were used to describe the exchange and correlation interactions. Ultra-soft pseudopotential [22] was used to describe the interactions between electrons and ionic cores. The spin-polarized option was selected for 'spin-unrestricted' calculation [23]. BFGS optimization algorithm was chosen for the geometry optimization [24]. The transition state was determined using the complete LST/QST method [25] and confirmed by Nudged-Elastic Band (NEB) method [26].

The energy of CaO crystal cell was converged with 6 × 6 × 6 *k* points in a Monhorst-pack grid [27]. The equilibrium geometry of SeO_2 was examined in a large cell of $20 \times 20 \times 20\,Å^3$ periodic box. The electronic wave functions were expanded on a plane wave basis with a cut-off energy of 380 eV. The convergence criteria of geometry optimization included: a) self-consistent field (SCF) of 5.0×10^{-7} eV/atom; b) energy of 5×10^{-6} eV/atom; c) displacement of 5×10^{-4} Å; d) force of 0.01 eV/Å; and e) stress of 0.02 GPa. The convergence of complete LST/QST method (RMS, root mean square) was set to 0.05 eV/Å. The convergence criteria of Nudged-Elastic Band (NEB) included: a) energy 1.0×10^{-5} eV/atom, b) max force of 0.05 eV/Å, and c) max displacement of 0.004 Å.

As shown in Table 1. The calculated Se–O bond length of SeO_2 is 1.615 Å, and the angle of O–Se–O is 115.6°, which agree well with the experimental data [28] of 1.608 Å and 113.8°. The optimized CaO lattice parameter is consistent with the previous work. The relative parameter error was 0.02% and 0.62% respectively, proving the accuracy of our work.

CaO (001) is a typical surface which can effectively describe the solid and gas reaction between CaO and gas such as NO [31] and gaseous Hg^0 [32]. The surface layer of atoms was relaxed while the rest layers were fixed [33]. As shown in Fig. 1, a series of *a*-layers *b* × *b*-surface slab models were modeled to describe CaO (*a* = 2–6, *b* = 1–4). The vacuum region between slabs was set to 10 Å, to avoid interactions among periodic images [34]. The energy of slab models and related adsorption structures were converged with 2 × 2 × 1 *k* points in a Monhorst-pack grid. The convergence criteria were same with that of CaO crystal cell.

The adsorption energy (E_{ads}) was defined as follows:

$$E_{ads} = E_{pro} - (E_{slab} + E_{adsorbate}) \tag{1}$$

where E_{pro} was the total energy of the adsorption product, E_{slab} was the total energy of the slab model, and $E_{adsorbate}$ was the total energy of the isolated adsorbate SeO_2 at its equilibrium geometry. A negative E_{ads} value represented a stable adsorption system.

2.2. Optimization of slab model

The surface size (1 × 1, 2 × 2, 3 × 3, 4 × 4) and layer (2, 3, 4, 5 and 6) of the slab models were optimized. The stability of the surface physical and chemical properties was considered. The physical property included the layer thickness Δz_{layers} and surface average Ca–O distance Δz_{Ca-O}. The chemical property was characterized by the adsorption energy of Se^0, which can reflect relationship between Se and CaO at a low computing cost.

The Δz_{layers} and Δz_{Ca-O} were defined as follows:

$$\Delta z_{layers} = |z_{layers\_relaxed} - z_{layers\_fixed}| \tag{2}$$

$$\Delta z_{Ca-O} = |z_{Ca-O_{r}elaxed} - z_{Ca-O_{f}ixed}| \tag{3}$$

$$\Delta E_{ads} = |E_{ads} - E_{ads\_mean}| \tag{4}$$

where z_{layers}, z_{Ca-O} and E_{ads_mean} represented the slab model thickness, surface average Ca–O bond length and average adsorption energy, respectively. Suffix of 'fixed' represented that the surface layer of the slab models was fixed, while 'relaxed' represented the contrary.

The surface size was firstly optimized. *n* × *n*-surface (*n* = 1, 2, 3 and 4) models (4 layer) were constructed. The changes of surface physical and chemical properties are shown in Table 2. For physical properties, the 3 × 3-surface model had the lowest Δz_{layers} (5.0×10^{-2} Å) and Δz_{Ca-O} (9.0×10^{-5} Å). The average adsorption energy $E_{ads\text{-}mean}$ did not include the 1 × 1-surface model due to the obvious large difference. For chemical properties, ΔE_{ads} of 3 × 3-surface model was also the lowest (0.7 kJ/mol). Therefore, the

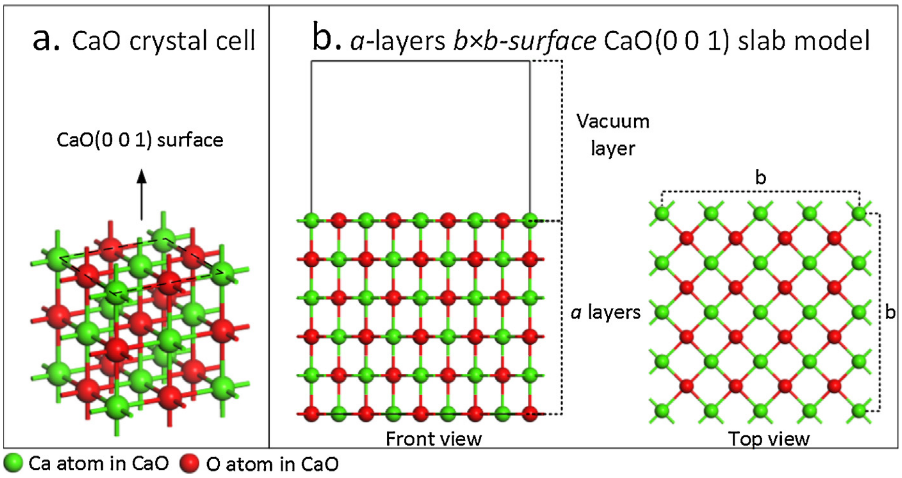

Fig. 1. (a) CaO crystal cell and (b) *a*-layers *b* × *b*-surface CaO (001) slab model.