Theoretical Study of As$_2$O$_3$ Adsorption Mechanisms on CaO surface

Yaming Fan $^{1,2,†}$, Qiyu Weng $^{2,3,4,†}$, Yuqun Zhuo $^{2,3,4,*}$, Songtao Dong $^1$, Pengbo Hu $^{2,3,4}$ and Duanle Li $^{2,3,4}$

1 Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, China; fanymthu@163.com (Y.F.); dongst.ripp@sinopec.com (S.D.)

2 Key Laboratory for Thermal Science and Power Engineering of the Ministry of Education, Department of Energy and Power Engineering, Tsinghua University, Beijing 100084, China; wqy17@mails.tsinghua.edu.cn (Q.W.); hupb18@mails.tsinghua.edu.cn (P.H.); liduanle@163.com (D.L.)

3 Tsinghua University-University of Waterloo Joint Research Center for Micro/Nano Energy and Environment Technology, Tsinghua University, Beijing 100084, China

4 Beijing Engineering Research Center for Ecological Restoration and Carbon Fixation of Saline–alkaline and Desert Land, Tsinghua University, Beijing 100084, China

* Correspondence: zhuoyq@mail.tsinghua.edu.cn
† These authors contributed equally to this work.

Received: 23 January 2019; Accepted: 18 February 2019; Published: 25 February 2019

Abstract: Emission of hazardous trace elements, especially arsenic from fossil fuel combustion, have become a major concern. Under an oxidizing atmosphere, most of the arsenic converts to gaseous As$_2$O$_3$. CaO has been proven effective in capturing As$_2$O$_3$. In this study, the mechanisms of As$_2$O$_3$ adsorption on CaO surface under O$_2$ atmosphere were investigated by density functional theory (DFT) calculation. Stable physisorption and chemisorption structures and related reaction paths are determined; arsenite (AsO$_3^{3−}$) is proven to be the form of adsorption products. Under the O$_2$ atmosphere, the adsorption product is arsenate (AsO$_4^{3−}$), while tricalcium orthoarsenate (Ca$_3$As$_2$O$_8$) and dicalcium pyroarsenate (Ca$_2$As$_2$O$_7$) are formed according to different adsorption structures.

Keywords: CaO; As$_2$O$_3$; DFT; adsorption

1. Introduction

Arsenic is a hazardous element existing in fossil fuels such as coal and petroleum [1]. According to the properties of arsenic and its compounds, it has been classified as volatile trace element by Clark and Sloss [2]. During combustion or chemical industry processes, gaseous arsenic is released into the environment. Excess amounts of arsenic can pollute water and soil. The exposure of arsenic to human may lead to hyperpigmentation, keratosis, skin and lung cancers with high possibility [3,4]. Arsenic compounds (including inorganic arsine) have been identified as hazardous air pollutants by the US government since 1990 [5]. The concentration of atmospheric arsenic in China is 51.0 ng/m$^3$, which is much higher than the limit of NAAQS (6.0 ng/m$^3$, GB 3095-2012) and the limit of WHO (6.6 ng/m$^3$, WHO) [6].

Combustion of fossil fuels, especially coal, is one of the main sources for anthropogenic emission of atmospheric arsenic [7]. It was estimated that 335.5 tons of atmospheric arsenic were emitted from Chinese coal-fired plants in 2010 [8]. In 2011, the US Environmental Protection Agency issued the Mercury and Air Toxics Standards (US, MATS, updated in 2016). An arsenic emission limit of $3.0 \times 10^{-3}$ lb/MWh (approximately 0.41 µg/m$^3$) was set for coal-fired power plants [9]. In Chinese coal-fired power plants, the control of arsenic still remains scarce, but there are increasing interests in understanding its transformation in flue gas and developing emission reduction techniques.
Under an oxidizing atmosphere, gaseous As$_2$O$_3$ should be the main form of arsenic combustion products [10]. It has been proven that CaO could adsorb As$_2$O$_3$ in the coal-fired flue gas, and the dominating products were arsenate (AsO$_4^{3−}$) [11–14]. CaO component in fly ash leads to the enrichment of arsenic [15–18]. R.O. Sterling [11] found that CaO could effectively adsorb As$_2$O$_3$ at 600 °C and 1000 °C; the adsorption products were Ca$_3$As$_2$O$_8$ when O$_2$ existed. Jadhav [12] studied the adsorption products of As$_2$O$_3$ on a CaO surface under O$_2$ atmosphere between 300 °C and 1000 °C. X-ray photoelectron spectroscopy (XPS) and X-ray Diffraction (XRD) reflected that, when temperature was lower than 600 °C, the adsorption product was Ca$_3$As$_2$O$_8$; when temperature was between 700 °C and 900 °C, the adsorption products was Ca$_2$As$_2$O$_7$; and when temperature was as high as 1000 °C, the adsorption product was Ca$_3$As$_2$O$_8$. He also revealed that SO$_2$ and HCl played a weak role in adsorption. Li [13,14] studied the influence of CO$_2$ and SO$_2$ on the capture of As$_2$O$_3$ by CaO. The existence of SO$_2$ and CO$_2$ did not change the form of arsenic in adsorption products. The previous study certified the strong adsorption of As$_2$O$_3$ on CaO surface and the important role O$_2$ played in the reaction. However, the acute toxicity and low concentration of arsenic significantly limit the experimental research of As$_2$O$_3$ adsorption. The adsorption mechanisms still remain unclear, especially the composition of adsorption active sites and product structures.

Quantum chemistry calculation based on density functional theory (DFT) has become an effective method to simulate structures [19] and surface reaction of volatile trace elements [20]. For example, the adsorption of As$^0$ on a CaO (001) surface has been effectively studied by Zhang [21]. In this study, the adsorption structures and the detailed adsorption steps between the CaO surface and As$_2$O$_3$ (under O$_2$ atmosphere) have been studied by advanced DFT calculation, with the aim to offer microscopic information about critical reactions, and thus, to provide guidance to develop more efficient adsorbents and related control technologies.

2. Methods and Modeling

2.1. Methods

The material studio CASTEP [22,23] module was applied in the DFT calculation. The GGA (Generalized Gradient Approximation) and PBE [24] (Perdew-Burke-Ernzerhof) were chosen to describe the exchange and correlation interactions. The electronic wave functions were expanded on a plane wave basis with cut-off energy of 380 eV. The ultra-soft pseudo potential was referred to describe the interactions between electrons and the ionic cores [25]. The ‘spin-polarized’ option was selected for ‘spin-unrestricted’ calculations [26]. The BFGS (Broyden-Flechter-Goldfarb-Shanno) optimization algorithm was chosen for geometry optimization [27]. The transition state and reaction path (intermediate states) was determined by using the complete Linear Synchronous Transit/Quadratic Synchronous Transit (LST/QST) method [28] and confirmed by the Nudged-Elastic Band (NEB) method [29].

The convergence criteria of geometry optimization included: (a) self-consistent field (SCF) of $5.0 \times 10^{-7}$ eV/atom; (b) energy of $5 \times 10^{-6}$ eV/atom; (c) displacement of $5 \times 10^{-4}$ 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 NEB included: (a) energy of $1.0 \times 10^{-5}$ eV/atom; (b) max force of 0.05 eV/Å; and (c) max displacement of 0.004 Å.

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 adsorption product, $E_{slab}$ was the total energy of the slab model, and $E_{adsorbate}$ was the total energy of isolated adsorbate As$_2$O$_3$ or O$_2$ at its equilibrium geometry. A negative $E_{ads}$ value represented a stable adsorption system.
2.2. Modeling

The energy of CaO crystal cell was converged with $6 \times 6 \times 6$ $k$ points in the Monhorst-pack grid [30]. The equilibrium geometry of As$_2$O$_3$ and O$_2$ was examined in a cell of $20 \times 20 \times 20$ Å$^3$ periodic box. As shown in Table 1, the values of the calculated bond lengths, angles, and lattice parameters are consistent with the data reported from the previous study, indicating the reliability of the calculation.

| Substance | Previous Data | Simulated Data |
|-----------|---------------|----------------|
| CaO [31,32] | 4.836 Å/4.807 Å | 4.837 Å |
| As$_2$O$_3$ [33] | As–O bond 1.794 Å | As–O bond 1.814 Å |
| | As–O bond 1.610 Å | As–O bond 1.622 Å |
| | O–As–O angle 106.3° | O–As–O angle 111.2° |
| | As–O–As angle 133.8° | As–O–As angle 141.8° |
| O$_2$ [34] | O–O 1.210 Å | O–O 1.240 Å |

In our previous study, the CaO(001) slab model has been widely used for CO$_2$ [35], SeO$_2$ [36] and SeO$_2$ [37] heterogeneous adsorption reaction, in which the good consistency with experimental work has been proven. Similarly, a 4-layer $3 \times 3$-surface CaO (001) slab was modeled to describe the CaO surface between CaO and As$_2$O$_3$ in this study. The superficial two layers of atoms were relaxed while the rest layers were fixed [38]. The vacuum region between slabs was set to 10 Å to avoid interactions among periodic images [39]. The energy of slab models and related adsorption structures were converged with $2 \times 2 \times 1$ $k$ points in the Monhorst-pack grid. The detailed modeling process was put in the Supplementary Materials (Optimization of slab model section: Tables S1 and S2).

3. Results and Discussions

According to the spatial position of As$_2$O$_3$ and surface atoms distribution, three groups, including twenty-one possible As$_2$O$_3$ structures, were first modeled as the initial structures for optimization (provided in Figure S1). After the geometric optimization of the initial structures, plenty of adsorption structures were validated, then the possible reaction paths were calculated. Based on the minimal point of the reaction paths, additional stable structures were acquired. Most of the physisorption structures were similar in terms of structural pattern and close in terms of energy level; thus, three representative physisorption structures (adsorption energy higher than $-100$ kJ/mol [40]) were determined. Additionally, ten chemisorption structures (adsorption energy lower than $-100$ kJ/mol [40]) were identified. Based on these structures, various adsorption paths were finally confirmed. For briefness, the $n$th physisorption structure was abbreviated as $P_n$, while the $n$th chemisorption structure was abbreviated as $C_n$.

3.1. Stable Sorption Structures

3.1.1. Stable Physisorption Structures

Three representative physisorption structures have been shown in Table 2. The dominating differences are the number of As$_2$O$_3$’s O bonded with superficial Ca and the distribution of the superficial Ca occupied by As$_2$O$_3$’s O. Three types of physisorption follow the crystal orientation $<100>$, $<110>$ and $<110>$, respectively. Two or three superficial Ca is close to As$_2$O$_3$’s O, and the bond length is about 2.380 Å to 2.876 Å. The corresponding adsorption energy ranges from $-65.8$ kJ/mol to $-58.4$ kJ/mol. Based on electron density cloud, physisorption active sites are composed of superficial Ca atoms that interact with O of As$_2$O$_3$. 

Table 2. Stable physisorption structures, adsorption energy, electron density cloud, and \( E_{ads} \).

| Name | Top View | Front View | Electron Density Cloud | Structure Details | \( E_{ads} \) |
|------|----------|------------|------------------------|------------------|-------------|
| P1   | ![P1 Top View](image) | ![P1 Front View](image) | ![P1 Density Cloud](image) | Bond12: 2.450 Å Bond14: 2.469 Å | -65.8 kJ/mol |
| P2   | ![P2 Top View](image) | ![P2 Front View](image) | ![P2 Density Cloud](image) | Bond12: 2.380 Å | -62.6 kJ/mol |
| P3   | ![P3 Top View](image) | ![P3 Front View](image) | ![P3 Density Cloud](image) | Bond12: 2.876 Å Bond14: 2.539 Å | -58.4 kJ/mol |

3.1.2. Stable Chemisorption Structures

Ten chemisorption structures were obtained, with \( E_{ads} \) ranging from -198.5 kJ/mol to -391.4 kJ/mol, which implies strong chemisorption. Superficial Ca is close to As\(_2\)O\(_3\)’s O, the bond length is about 2.269 Å to 2.528 Å, while superficial O is close to As\(_2\)O\(_3\)’s O, the bond length is 1.788 Å to 2.086 Å. According to electron density cloud and bond length, chemisorption active sites are superficial O atoms that interact with As of As\(_2\)O\(_3\). According to the adsorption energy and structure (i.e., the positions of As and O), four categories were classified in Table 3:

Category I: As\(_2\)O\(_3\)’s As is located on the hollow site
Category II: All of As\(_2\)O\(_3\)’s O is located on or close to superficial Ca top site
Category III: As\(_2\)O\(_3\) transforms into a spoon-shaped structure
Category IV: All of As\(_2\)O\(_3\)’s As is located on two neighboring superficial O top site

Table 3. Chemisorption structures, adsorption energy, electron density cloud and \( E_{ads} \).

| Category | Name | Top View | Front View | Electron Density Cloud | Structure Details | \( E_{ads} \) |
|----------|------|----------|------------|------------------------|------------------|-------------|
| I        | C\(_1\)  | ![C1 Top View](image) | ![C1 Front View](image) | ![C1 Density Cloud](image) | Bond12: 2.635 Å Bond14: 2.086 Å Bond35: 2.360 Å | -198.5 kJ/mol |
| II       | C\(_2\)  | ![C2 Top View](image) | ![C2 Front View](image) | ![C2 Density Cloud](image) | Bond12: 1.858 Å Bond14: 2.360 Å Bond56: 2.386 Å | -222.1 kJ/mol |
| II       | C\(_3\)  | ![C3 Top View](image) | ![C3 Front View](image) | ![C3 Density Cloud](image) | Bond12: 2.424 Å Bond14: 1.815 Å Bond56: 2.314 Å Bond78: 2.490 Å | -274.4 kJ/mol |
3.2. Transformation Process of Physisorption Structures to Chemisorption Structures

The transformation process from physisorption to chemisorption structures involves energy barriers that are typically low. This transformation can occur during one or two transition states. For instance, P1 to C7 (Figure 1a), P2 to C8 (Figure 1b) and P3 to C8 (Figure 1c). The energy barrier is not stable enough and could be easily transformed into chemisorption structures by thermal vibration.

### Table 3. Cont.

| Category | Name | Top View | Front View | Electron Density Cloud | Structure Details | $E_{ads}$ |
|----------|------|----------|------------|------------------------|-------------------|-----------|
| II       | C4   | ![C4 Top View](image) | ![C4 Front View](image) | ![C4 Electron Density Cloud](image) | Bond$_{12}$: 2.269 Å Bond$_{34}$: 1.949 Å Bond$_{56}$: 2.391 Å | $-292.0$ kJ/mol |
| II       | C5   | ![C5 Top View](image) | ![C5 Front View](image) | ![C5 Electron Density Cloud](image) | Bond$_{12}$: 2.293 Å Bond$_{34}$: 1.943 Å Bond$_{56}$: 2.298 Å | $-315.1$ kJ/mol |
| III      | C6   | ![C6 Top View](image) | ![C6 Front View](image) | ![C6 Electron Density Cloud](image) | Bond$_{12}$: 1.815 Å Bond$_{34}$: 2.355 Å | $-302.3$ kJ/mol |
| III      | C7   | ![C7 Top View](image) | ![C7 Front View](image) | ![C7 Electron Density Cloud](image) | Bond$_{12}$: 1.788 Å Bond$_{34}$: 2.528 Å Bond$_{56}$: 2.514 Å Bond$_{78}$: 2.422 Å | $-314.0$ kJ/mol |
| IV       | C8   | ![C8 Top View](image) | ![C8 Front View](image) | ![C8 Electron Density Cloud](image) | Bond$_{12}$: 2.357 Å Bond$_{34}$: 1.901 Å Bond$_{56}$: 2.298 Å | $-381.7$ kJ/mol |
| IV       | C9   | ![C9 Top View](image) | ![C9 Front View](image) | ![C9 Electron Density Cloud](image) | Bond$_{12}$: 2.472 Å Bond$_{34}$: 1.869 Å Bond$_{56}$: 2.503 Å | $-388.6$ kJ/mol |
| IV       | C10  | ![C10 Top View](image) | ![C10 Front View](image) | ![C10 Electron Density Cloud](image) | Bond$_{12}$: 2.382 Å Bond$_{34}$: 1.894 Å Bond$_{56}$: 2.299 Å Bond$_{78}$: 2.392 Å | $-391.4$ kJ/mol |

### 3.2. Adsorption Process

Due to the continuity of energy, the adsorption process can be characterized as an energy-drop process, including both physisorption and chemisorption.

#### 3.2.1. Transformation Process of Physisorption Structures to Chemisorption Structures

In the following part, the transition state number $n$ is abbreviated as $T_{Sn}$, and the intermediate position number $n$ is abbreviated as $IP_{n}$ for short.

As shown in Figure 1, when $\text{As}_2\text{O}_3$ approaches the surface with vibration along the surface, the physisorption structure transforms into a chemisorption structure during one or two transition states. For instance, P$_1$ to C$_7$ (Figure 1a), P$_2$ to C$_8$ (Figure 1b) and P$_3$ to C$_8$ (Figure 1c). The energy barrier is low, from 1.4 kJ/mol to 13.9 kJ/mol, suggesting that the physisorbed $\text{As}_2\text{O}_3$ is not stable enough and could be easily transformed into chemisorption structures by thermal vibration.
Firstly, category with another reaction path, the related energy barrier is 7.4 kJ/mol. The relatively low energy barrier paths were calculated. The four categories of chemisorption structures can be sorted by the $E_{ads}$ suggests that Category I is not stable enough, and could easily transform to Category II, III and IV.

$\Delta E_{IV} \approx 7.4 \text{ kJ/mol}$, and $\Delta E_{II} \approx 10.8 \text{ kJ/mol}$, respectively. As shown in Figure 2, Category I transforms into Category IV along with another reaction path, the related energy barrier is 7.4 kJ/mol. The relatively low energy barrier suggests that Category I is not stable enough, and could easily transform to Category II, III and IV.

### 3.2.2. Transformation Process of Chemisorption Structures

Chemisorbed As$_2$O$_3$ gradually transforms into more stable structures. Different possible reaction paths were calculated. The four categories of chemisorption structures can be sorted by the $E_{ads}$ of each as Category IV $\approx$ Category III $<_{\text{rel}}$ Category II $<_{\text{rel}}$ Category I.

Category I has relatively high energy, i.e., relatively low stability, its transformation to Category II, III and IV could be triggered by molecular thermal vibration.

The pathway that Category I transforms to Category II is shown in Figure 2. Firstly, $C_1$ transforms into $C_6$ (Category II) and then $C_5$ (Category III), with the energy barrier of 10.8 kJ/mol, 16.7 kJ/mol, and 6.7 kJ/mol, respectively. As shown in Figure 2, Category I transforms into Category IV along with another reaction path, the related energy barrier is 7.4 kJ/mol. The relatively low energy barrier suggests that Category I is not stable enough, and could easily transform to Category II, III and IV.

#### Figure 1. Structures and energies during transformation process of physisorption structures to chemisorption structures. (a) Reaction path of physisorption structure 1; (b) Reaction path of physisorption structure 2; (c) Reaction path of physisorption structure 3.
Figure 2. Transformation path of Category I. (a) Category I to Category II and III; (b) Category I to Category IV.

The reaction path of Category II is shown in Figure 3. $C_3$ firstly transforms into intermediate and then converts to $C_5$. The corresponding energy barrier is 16.1 kJ/mol and 83.0 kJ/mol, proving that Category II transforms to Category IV with the special direction of thermal vibration.

Figure 3. Transformation path of Category II.

Structures of Category III can transform into Category II, as shown in Figure 4. The spoon-shaped structure of As$_2$O$_3$ in $C_7$ disappears and then overcomes a 48.3 kJ/mol energy barrier to transform to $C_5$, indicating the conversion of Category III to Category II.

Figure 4. Transformation path of Category III.
Category IV is the most stable category. $C_8$, $C_9$, and $C_{10}$ can transform into each other (shown in Figure 5). As$_2$O$_3$’s As does not move during the transformation. When all of As$_2$O$_3$’s O in $C_8$ vibrate, $C_8$ converts to $C_9$, and the energy barrier is 41.6 kJ/mol (Figure 5a). When one of As$_2$O$_3$’s O in $C_8$ vibrates, $C_8$ converts to $C_{10}$, and the energy barrier is 153.3 kJ/mol (Figure 5b). When one of the oxygen atoms of As$_2$O$_3$ in $C_9$ vibrates, $C_9$ converts to $C_{10}$, and the energy barrier is 154.4 kJ/mol (Figure 5c). The difference in energy barrier is caused by the movement distance of As$_2$O$_3$’s O being motivated by thermal vibration. In the first reaction, the movement distance of As$_2$O$_3$’s O is shorter than that in the second and third reactions, which demands relatively lower energy to overcome the energy barrier.

Figure 5. Transformation path of Category IV. (a) Reaction path of $C_8$ to $C_9$; (b) Reaction path of $C_8$ to $C_{10}$; (c) Reaction path of $C_9$ to $C_{10}$.

3.3. Path of the Reaction

According to above-mentioned processes, the reaction paths can be concluded as follows; firstly, the isolated As$_2$O$_3$ is physisorbed on a CaO surface (As$_2$O$_3$’s O weakly interacts with superficial Ca); secondly, the physisorbed As$_2$O$_3$ transforms to chemisorbed As$_2$O$_3$. (As$_2$O$_3$’s As interacts with superficial O); and thirdly, due to thermal vibration, the chemisorbed As$_2$O$_3$ transforms into more stable chemisorbed As$_2$O$_3$ (the position of As$_2$O$_3$’s O changed).
The adsorption path of As$_2$O$_3$ was summarized as the process shown in Figure 6. These reactions could be classified as three types according to the energy barrier with the aim to reflect the intensity of the required reaction temperature. The number of superficial CaO occupied by As$_2$O$_3$ is also considered in order to describe the adsorption reaction equation.

Figure 6. Overall adsorption paths of As$_2$O$_3$ on CaO.

Blue arrow: energy barrier is in the range of 0–40 kJ/mol, suggesting that reaction is likely to occur under a relatively low-temperature condition.

Yellow arrow: energy barrier is in the range of 40–100 kJ/mol, suggesting that reaction is likely to occur under a relatively medium-temperature condition.

Red arrow: energy barrier is in the range of 100–200 kJ/mol, suggesting that reaction is likely to occur under a relatively high-temperature condition.

Figure 6 reveals that three main reaction paths may exist:

1. As$_2$O$_3$ → P$_1$ → C$_7$ → C$_9$ → C$_{10}$;
2. As$_2$O$_3$ → P$_2$ or P$_3$ → C$_8$ → C$_9$ → C$_{10}$;
3. As$_2$O$_3$ → P$_2$ or P$_3$ → C$_8$ → C$_{10}$.

Under a relatively low-temperature condition (blue arrow, 0–40 kJ/mol), the main products are C$_7$ and C$_8$ (blue grid). Three superficial Ca and one or two superficial O are involved in the reaction, representing three CaO participates in the adsorption. The adsorption equation could be written as:

$$\text{As}_2\text{O}_3 + 3 \text{CaO} \rightarrow \text{Ca}_3\text{As}_2\text{O}_6$$  \hspace{1cm} (2)

Under a relatively medium-temperature condition (yellow arrow, 40–100 kJ/mol), the main products are C$_9$. Two superficial Ca and two superficial O participate in the structure. The adsorption equation could be written as:

$$\text{As}_2\text{O}_3 + 2 \text{CaO} \rightarrow \text{Ca}_2\text{As}_2\text{O}_5$$  \hspace{1cm} (3)

Under a relatively high-temperature condition (red arrow, 100–200 kJ/mol), the main product is C$_{10}$. Three superficial Ca and two superficial O are involved in the reaction (hollow Ca represents 1/2 Ca atom). The adsorption equation could be written as:

$$\text{As}_2\text{O}_3 + 3 \text{CaO} \rightarrow \text{Ca}_3\text{As}_2\text{O}_6$$  \hspace{1cm} (4)

With the reaction temperature increases, adsorption product changes from Ca$_3$As$_2$O$_6$ to Ca$_2$As$_2$O$_5$ and back to Ca$_3$As$_2$O$_6$ again. Different microcosmic adsorption structures lead to different macroscopic products and reaction equation.

Besides, as shown in Figure S2, the paths of C$_1$ transforming to other structures have been also been found. However, no possible paths which isolated or physisorbed As$_2$O$_3$ transforms to C$_1$ has been found, implying C$_1$ is unstable or nonexistent.
3.4. Partial Density of States (PDOS)

The change PDOS of As$_2$O$_3$ and CaO was put in the Supplementary Materials (Figure S3). For As$_2$O$_3$, the PDOS of physisorption structure 1, 2, and 3 are similar to each other. As the physisorption structure transforms to C$_7$, the p state orbitals near Fermi level (from $-0.6$ eV to $1.9$ eV) drift to lower energy level, meanwhile get energy splitting and orbital reorganization, caused by the changing of As$_2$O$_3$ structure and the combination between As$_2$O$_3$’s As and superficial O. When C$_7$ transforms to C$_5$, s state orbital ($-17.2$ eV) energy level splits into two peaks of $-18.0$ eV and $-16.9$ eV, which is caused by the As-O bond breaking and the bonding between As and superficial O. When C$_5$ transform to C$_8$, the p state orbital ($3.7$ eV) and s state orbital ($-17.9$ eV) energy level both split slightly. This is the result of the slight change in the surface distribution of As$_2$O$_3$. As the adsorption products have close energies and structures, PDOS of C$_9$ and C$_10$ are basically similar to C$_8$.

For CaO slab surface, when an As$_2$O$_3$ molecule is physisorbed on the surface, little change of PDOS is detected. When As$_2$O$_3$ is chemisorbed, it can be seen that the superficial p orbitals around Fermi level (from $-2.7$ eV to $0.4$ eV) drift to a lower energy range (from $-5.8$ eV to $0.2$ eV). Moreover, a small peak ($-16.8$ eV) is separated from s orbitals (peak at $-14.6$ eV), proving that s orbitals participate in the chemisorption to some extent. Superficial p state orbitals near Fermi level play an important role in the chemisorption of As$_2$O$_3$. It suggests that the CaO surface’s property of capturing As$_2$O$_3$ might be improved by increasing the quantities of superficial p orbitals near Fermi level.

3.5. Influence of O$_2$ on Adsorbed As$_2$O$_3$

Under the flue gas atmosphere, especially O$_2$-containing atmosphere, O$_2$ reacts with chemisorbed As$_2$O$_3$; i.e., arsenite (AsO$_3^{3-}$) is oxidized to arsenate (AsO$_4^{3-}$). As an example, two stable chemisorption structures (C$_8$, C$_9$) identified previously were presented in Table 4. The distance between As$_2$O$_3$’s As and O$_2$’s O is 1.763–1.764 Å, which is close to the As-O bond length of As$_2$O$_3$ (1.628 Å). The distance between O$_2$’s O and superficial Ca is 2.247–2.263 Å. According to the electron density cloud, one of O$_2$’s O overlaps with As$_2$O$_3$’s As. The other O of O$_2$ overlaps slightly with the superficial Ca.

| Name | Top View | Front View | Electron Density Cloud | Structure Details | $E_{ads}$ |
|------|----------|------------|------------------------|-------------------|---------|
| C$_5$ under O$_2$ | ![C$_5$ under O$_2$ Top View](image) | ![C$_5$ under O$_2$ Front View](image) | ![C$_5$ under O$_2$ Electron Density Cloud](image) | Bond$_{12}$: 1.764 Å Bond$_{34}$: 1.452 Å Bond$_{56}$: 2.263 Å | $-165.2$ kJ/mol |
| C$_8$ under O$_2$ | ![C$_8$ under O$_2$ Top View](image) | ![C$_8$ under O$_2$ Front View](image) | ![C$_8$ under O$_2$ Electron Density Cloud](image) | Bond$_{12}$: 1.763 Å Bond$_{34}$: 1.599 Å Bond$_{56}$: 2.427 Å | $-174.4$ kJ/mol |

Based on Figure 6 and Table 4, the reaction equation of adsorption under O$_2$ atmosphere can be written as Equations (5)–(7), corresponding to low-temperature, medium-temperature, and high-temperature adsorption, respectively.

$$3\text{CaO} + \text{As}_2\text{O}_3 + \text{O}_2 \rightarrow \text{Ca}_3\text{As}_2\text{O}_8$$ (5)
The adsorption products of As can be described as follows: the isolated As2O3 molecule is firstly adsorbed on the CaO surface by physisorption, and then physisorbed As2O3 will transform to chemisorbed As2O3. Due to thermal vibration, the chemisorbed As2O3 would overcome the energy barrier and transform to a more stable chemisorbed As2O3 state. The adsorption product is AsO3\(^{3-}\);

\[
\begin{align*}
2\text{CaO} + \text{As}_2\text{O}_3 + \text{O}_2 & \rightarrow \text{Ca}_2\text{As}_2\text{O}_7 \\
3\text{CaO} + \text{As}_2\text{O}_3 + \text{O}_2 & \rightarrow \text{Ca}_3\text{As}_2\text{O}_8
\end{align*}
\]

With the increase of reaction temperature, adsorption product changed from Ca3As2O8 to Ca2As2O7 and then to Ca3As2O8 in an O2-containing atmosphere. According to this research, the product under low-temperature and high-temperature conditions is Ca3As2O8 with different structures, i.e., crystalline form. Under a medium-temperature condition, the main product is Ca3As2O7.

Previous experimental research consistently reflected that the adsorption product with O2 existence is AsO4\(^{3-}\), while different opinions existed regarding the adsorption structures. The study of Jadhav [12] found that the adsorption product obtained under 500 °C was mainly Ca3As2O8 (JCPDS No.01-0933). Under 700 °C and 900 °C, the product was Ca2As2O7 (JCPDS No.17-0444). When the temperature increased to 1000 °C, the reaction product was Ca3As2O8 (JCPDS No.26-0295). Mahuli [41] (600 °C and 1000 °C) and Sterling [11] (800 °C) found that the adsorption product was Ca3As2O8 (JCPDS No. 26-0295), while the sorbent used by Mahuli was Ca(OH)\(_2\). Li [13] found that the product obtained under 600 °C mainly belonged to Ca3As2O8 crystal structure (JCPDS No. 01-0933), and another kind of Ca3As2O8 crystal (JCPDS No. 73-1928) was identified for the products obtained under 800 °C and 1000 °C.

The role of temperature on adsorption product transformation is qualitatively described. The more detailed description of the product layer development is associated with many other factors, such as the concentration and flow rate of As2O3 and O2, and the quantity and granular size of CaO. The quantitative description of the adsorption process is still a very difficult challenge. Nevertheless, the DFT calculation findings revealed by this study could directly explain the experimental results obtained by previous researchers, which might provide some meaningful insight to understand the process of As2O3 adsorption on CaO.

4. Conclusions

The mechanisms of As5O3 adsorption on a CaO surface have been studied by using DFT calculation; conclusions are as follows:

1. Physisorption active sites are composed of superficial Ca atoms that interact with O of As2O3. Chemisorption active sites are superficial O atoms that interact with As of As2O3;
2. The adsorption process can be described as follows: the isolated As2O3 molecule is firstly adsorbed on the CaO surface by physisorption, and then physisorbed As2O3 will transform to chemisorbed As2O3. Due to thermal vibration, the chemisorbed As2O3 would overcome the energy barrier and transform to a more stable chemisorbed As2O3 state. The adsorption product is AsO3\(^{3-}\);
3. The adsorption products of As2O3 under an O2-containing atmosphere are AsO4\(^{3-}\). The adsorption product’s structure is influenced by the adsorption temperature. Under relatively low-temperature, the product is Ca3As2O8; under relatively medium-temperature, the product is Ca3As2O7; and under relatively high-temperature, the product is Ca3As2O8.

The consistency between DFT calculation and the previous experiments proves high possibilities to design and optimized the CaO-based adsorbents by modifying O sites or other elements. Besides, other flue gases such as SO2 or CO2 can be involved in the following study to achieve materials design under real flue gas conditions. The optimized CaO-based adsorbents should be of high industrial value, could be applied in the injection of limestone into the furnace, CaO looping reactor, and dry desulfurization, etc.

**Supplementary Materials**: The following are available online at http://www.mdpi.com/1996-1944/12/4/677/s1. Table S1: Changes in physical and chemical properties of different surface size; Table S2: Changes in physical and chemical properties of different layers; Figure S1: Initial adsorbate structures; Figure S2: Paths and structures of
the physisorption and chemisorption reaction from chemisorption structure 1; Figure S3: PDOS of As$_2$O$_3$ and CaO surface during physisorption and chemisorption (a. PDOS of As$_2$O$_3$ molecule; and b. PDOS of CaO surface).

**Author Contributions:** Research Design, Y.F. and Y.Z.; Data collection, Y.F.; Data analysis, Y.F., Q.W., S.D., P.H. and D.L.; Figures and Tables, Q.W.; Manuscript draft, Y.F., Q.W., Y.Z. and S.D.; Manuscript revise, P.H. and D.L.

**Funding:** This work was financially supported by the National Natural Science Foundation of China No. 51776107.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Liu, R.; Yang, J.; Xiao, Y.; Liu, Z. Fate of Forms of arsenic in Yima coal during pyrolysis. *Energy Fuels* **2009**, *23*, 2013–2017. [CrossRef]
2. Clarke, L.B.; Sloss, L.L. *Trace Elements-Emissions from Coal Combustion and Gasification*; IEA Coal Research: London, UK, 1992; Volume 8, pp. 1822–1826.
3. Gao, J.; Yu, J.; Yang, L. Urinary arsenic metabolites of subjects exposed to elevated arsenic present in coal in Shaanxi province, China. *Int. J. Environ. Res. Public Health* **2011**, *8*, 1991–2008. [CrossRef] [PubMed]
4. Kapaj, S.; Peterson, H.; Liber, K.; Bhattacharya, P. Human health effects from chronic arsenic poisoning—A review. *J. Environ. Sci. Health Part A* **2006**, *41*, 2399–2428. [CrossRef] [PubMed]
5. 1990 Clean Air Act Amendment. Public Law; 1990. Available online: https://www.gpo.gov/fdsys/pkg/USCODE-2013-title42/html/USCODE-2013-title42-chap85-subchap-partA-sec7412.htm (accessed on 11 February 2019).
6. Duan, J.; Tan, J.; Hao, J.; Chai, F. Size distribution, characteristics and sources of heavy metals in haze episod in Beijing. *J. Environ. Sci.* **2014**, *26*, 189–196. [CrossRef]
7. Pacyna, J.M.; Pacyna, E.G. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ. Rev.* **2001**, *9*, 269–298. [CrossRef]
8. Tian, H.; Liu, K.; Zhou, J.; Lu, L.; Hao, J.; Qiu, P.; Gao, J.; Zhu, C.; Wang, K.; Hua, S. Atmospheric Emission Inventory of Hazardous Trace Elements from China’s Coal-Fired Power Plants Temporal Trends and Spatial Variation Characteristics. *Environ. Sci. Technol.* **2014**, *48*, 3575–3582. [CrossRef] [PubMed]
9. Mercury and air toxics Standards (MATS). Public Law; 2013. Available online: https://www.epa.gov/mats (accessed on 11 February 2019).
10. Helsen, L. Sampling technologies and air pollution control devices for gaseous and particulate arsenic: A review. *Environ. Pollut.* **2005**, *137*, 305–315. [CrossRef] [PubMed]
11. Sterling, R.O.; Helble, J.J. Reaction of arsenic vapor species with fly ash compounds: Kinetics and speciation of the reaction with calcium silicates. *Chemosphere* **2003**, *51*, 1111–1119. [CrossRef]
12. Jadhav, R.A.; Fan, L. Capture of gas-phase arsenic oxide by lime: Kinetic and mechanistic studies. *Environ. Sci. Technol.* **2001**, *35*, 794–799. [CrossRef] [PubMed]
13. Li, Y.; Tong, H.; Zhuo, Y.; Li, Y.; Xu, X. Simultaneous removal of SO$_2$ and trace As$_2$O$_3$ from flue gas: Mechanism, kinetics study, and effect of main gases on arsenic capture. *Environ. Sci. Technol.* **2007**, *41*, 2894–2900. [CrossRef] [PubMed]
14. Li, Y. Experimental Study on Simultaneous Removal of Trace Selenium and Arsenic in Flue Gas Desulphurization within Medium Temperature Range; Tsinghua University: Beijing, China, 2006.
15. López-Antón, M.A.; Díaz-Somoano, M.; Spears, D.A.; Martínez-Tarazona, M.R. Arsenic and selenium capture by fly ashes at low temperature. *Environ. Sci. Technol.* **2006**, *40*, 3947–3951. [CrossRef] [PubMed]
16. Shah, P.; Strezov, V.; Stevanov, C.; Nelson, P.F. Speciation of arsenic and selenium in coal combustion products. *Energy Fuels* **2007**, *21*, 506–512. [CrossRef]
17. Huggins, F.E.; Senior, C.L.; Chu, P.; Ladwig, K.; Huffman, G.P. Selenium and arsenic speciation in fly ash from full-scale coal-burning utility plants. *Environ. Sci. Technol.* **2007**, *41*, 3284–3289. [CrossRef] [PubMed]
18. Tian, C.; Gupta, R.; Zhao, Y.; Zhang, J. Release Behaviors of Arsenic in Fine Particles Generated from a Typical High-Arsenic Coal at a High Temperature. *Energy Fuels* **2016**, *30*, 6201–6209. [CrossRef]
19. Jialin, Y.; Jingjing, X.; Qinfang, Z.; Binwen, Z.; Baolin, W. First-principles studies on the structural and electronic properties of As clusters. *Materials* **2018**, *11*, 1596.
20. Li, Z.; Yangwen, W.; Jian, H.; Qiang, L.; Yongping, Y.; Laibao, Z. Mechanism of mercury adsorption and oxidation by oxygen over the CeO$_2$ (111) surface: A DFT study. *Materials* **2018**, *11*, 485.
21. Zhang, S.; Hu, X.; Lu, Q.; Zhang, J. Density functional theory study of arsenic and selenium adsorption on the CaO (001) surface. *Energy Fuels* **2011**, *25*, 2932–2938. [CrossRef]

22. Segall, M.D.; Lindan, P.J.; Probert, M.A.; Pickard, C.J.; Hasnip, P.J.; Clark, S.J.; Payne, M.C. First-principles simulation: Ideas, illustrations and the CASTEP code. *J. Phys. Condens. Matter* **2002**, *14*, 2717. [CrossRef]

23. Clark, S.J.; Segall, M.D.; Pickard, C.J.; Hasnip, P.J.; Probert, M.I.; Refson, K.; Payne, M.C. First principles methods using CASTEP. *Cryst. Mater.* **2005**, *220*, 567–570. [CrossRef]

24. Burke, K.; Ernzerhof, M.; Perdew, J.P. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

25. Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B Condens. Matter* **1990**, *41*, 7892. [CrossRef] [PubMed]

26. Von Barth, U.; Hedin, L. A local exchange-correlation potential for the spin polarized case. *I. J. Phys. C Solid State Phys.* **1972**, *5*, 1629. [CrossRef]

27. Press, W.H.; Teukolsky, S.A.; Vetterling, W.T.; Flannery, B.P. *Numerical Recipes in C*; Cambridge University Press: Cambridge, UK, 1996; Volume 2.

28. Halgren, T.A.; Lipscomb, W.N. The synchronous-transit method for determining reaction pathways and locating molecular transition states. *Chem. Phys. Lett.* **1977**, *49*, 225–232. [CrossRef]

29. Henkelman, G.; Jónsson, H. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J. Chem. Phys.* **2000**, *113*, 9978–9985. [CrossRef]

30. Monkhorst, H.J.; Pack, J.D. Special points for Brillouin-zone integrations. *Phys. Rev. B Condens. Matter* **1976**, *13*, 5188. [CrossRef]

31. Ghebouli, M.A.; Ghebouli, B.; Bouhemadou, A.; Fatmi, M.; Bouamama, K. Structural, electronic, optical and thermodynamic properties of SrxCa1−xO, BaxSr1−xO and BaxCa1−xO alloys. *J. Alloys Compd.* **2011**, *509*, 1440–1447. [CrossRef]

32. Verbraeken, M.C.; Suard, E.; Irvine, J.T. Order and disorder in Ca2Nd0.90H0.10–A structural and thermal study. *J. Solid State Chem.* **2011**, *184*, 2088–2096. [CrossRef]

33. Ghebouli, M.A.; Ghebouli, B.; Bouhemadou, A.; Fatmi, M.; Bouamama, K. Structural, electronic, optical and thermodynamic properties of SrxCa1−xO, BaxSr1−xO and BaxCa1−xO alloys. *J. Alloys Compd.* **2011**, *509*, 1440–1447. [CrossRef]

34. Liu, H.; Xiang, H.; Gong, X.G. First principles study of adsorption of O2 on Al surface with hybrid functionals. *J. Phys. Chem. B* **2011**, *115*, 2399–2405. [CrossRef] [PubMed]

35. Nørskov, J.K.; Studt, F.; Abild-Pedersen, F.; Bligaard, T. *Fundamental Concepts in Heterogeneous Catalysis*; John Wiley & Sons: Hoboken, NJ, USA, 2014.

36. Mahuli, S.; Agnihotri, R.; Chauk, S.; Ghosh-Dastidar, A.; Fan, L.-S. Mechanism of Arsenic Sorption by Hydrated Lime. *Environ. Sci. Technol* **1998**, *31*, 3226–3231. [CrossRef]