DFT Study on Adsorption of Arsenic by Oxides in Fly Ash

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Abstract. Based on density functional theory (DFT), the adsorption properties of arsenic (As) via the five most abundant oxides in fly ash were investigated. It has been proved that the iron oxide (Fe₂O₃) in fly ash is the effective active component during the adsorption process. This paper verifies the feasibility of using fly ash as the adsorbent to control As pollution in power plants, and also provides some reference for the subsequent experimental research.

1 Introduction

Coal is the most important energy source in China, which can not be replaced for a long time. With the burning of coal, the corresponding pollutants are generated. Traditional pollutants of coal-fired flue gas, such as nitrogen oxide (NO_x), sulfur dioxide (SO₂) and dust, have been widely studied by scholars [1, 2]. However, there are few researches focus on the trace heavy metal pollutants in coal-fired flue gas. The content is not high, but their emissions into the atmosphere has considerable damage to the ecological environment, and is difficult to control [3, 4]. At present, studies mainly focus on mercury (Hg), cadmium (Cd), chromium (Cr) and other heavy metals, but relatively few studies on arsenic (As) emission. The As forms in flue gas and its treatment methods are still in the exploration stage.

Adsorption method is a potential way to reduce emission of coal-fired pollutants. It is characterized by the use of some specific adsorbents to adsorb the target pollutants in the flue gas, so as to achieve the purpose of fixing pollutants. He et al. [5] found that chlorine modified activated carbon helps enhance the adsorption of mercury. But its high cost limits the industrial application. In comparison, fly ash, as a by-product of coal combustion, has incomparable advantages. Fly ash is almost cost-free and the production is huge. The effective use of fly ash to remove pollutants from flue gas is beneficial to the recycling of resources, so as to improve the economic benefits of power plants. However, the complex composition of fly ash makes it difficult to study the mechanism of pollutant removal reaction. It is hard to determine which active component of fly ash plays the main role, so it is difficult to further modify fly ash to improve the efficiency of pollutant removal. On the other hand, if the experiment is carried out directly on the site of power plant, the cost must be very high and affects the work of the flue gas treatment system of the power plant. If studied in a laboratory, the preparation of simulated smoke containing gaseous As requires a large initial investment and a big time cost.

All these factors bring difficulties to the study of As adsorption by fly ash.

The computation based on the density functional theory (DFT) is a popular method in quantum chemistry. It is the method to study the electronic structure of multi-electron system, which can effectively simulate the crystal surface of adsorbent and evaluate the adsorption ability. Through DFT calculation, the main active components that adsorb As atom in fly ash can be preliminarily screened out, which can provide certain reference for subsequent laboratory-scale research and reduce the time and cost of experimental research. Liu et al. [6] found that the five most abundant oxides in fly ash were: SiO₂, Al₂O₃, Fe₂O₃, CaO and MgO. In this work, the five most abundant oxides in fly ash are used as potential adsorbents for As adsorption. Each oxide was cleaved into a representative crystal surface, and the As atoms were placed on some potential adsorption points. The stability of adsorption was evaluated via the adsorption energy and the active components of fly ash were confirmed. This paper verified the feasibility of using fly ash as the adsorbent to removal As pollutant, while it also provides some reference for subsequent experimental research.

2 Calculation method

The Density Functional Theory (DFT) calculation were taken on the Cambridge Serial Total Energy Package (CASTEP) codes. The exchange and correlation effects were described by the Perdew-Burke-Ernzerhof (PBE) functional within generalized gradient approximation (GGA). An energy cutoff was set as 381.0 eV and the k-point set as 1*1*1. The convergence criteria were as follows: maximal force on the atoms 0.1 eV/Å, maximal stress on the atoms 0.2 GPa, maximal atomic displacement 0.005 Å, and maximal energy 5.0×10⁻⁵ eV/atom. The absorption energy is calculated by the following formula:

$$E_{ad}=E(AB)-E(A)-E(B) \quad (1)$$

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where E_{ad} represents the adsorption energy. $E(AB)$ is the total energy of B molecule adsorbed by A molecular surface. $E(A)$ and $E(B)$ represent the total energy of isolated A and B molecule, respectively. Commonly, a negative adsorption energy indicates that the structure is spontaneous. And a lower adsorption energy indicates that the adsorption configuration is more stable.

3 Results and discussion

3.1 SiO₂

The β -SiO₂ model is used in this work. After geometric optimization, the SiO₂ bulk is cleaved into the (100) surface. To mitigate the effects of adjacent adsorbed atoms, a supercell size with 2*2*1 is used. The vacuum layer is set as 15 Å to reduce the impact of the neighbouring layers. As shown in Fig. 1, the surface of SiO₂(110) has four silicon atoms in its outermost layer, and forming a rectangle between them. It is initially speculated that the SiO₂(100) surface consists of five highly symmetrical positions, which may be the potential adsorption points: Si top site (Si_T), O top site (O_T), long bridge site (LB), short bridge site (SB) and hollow site (H). The As atoms are placed on the above five locations for geometric optimization, and the final configuration is obtained as shown in Fig. 2, while the corresponding adsorption energy is also marked in the diagram.

Fig. 1. The geometry optimized structure and potential adsorption sites of the SiO₂(100) surface: (a) top view from (100) facet; (b) 3D view.

From Fig. 2a, when As atom starts on Si_T or O_T site, the final structure is on the Si_T site, and the adsorption energy is -3.930 eV. The distance between As and Si_T atom is 2.170 Å. When the initial structure is on the LB site, the As atom has shifted a lot after the geometry optimization and it's close to the Si_T atom (Fig. 2b). The adsorption energy is -3.927 eV and the As-Si_T distance is 2.226 Å. While when As atom starts at SB or H site, it ends up at SB site with the adsorption energy of -4.068 eV (Fig. 2c). The As atom is preferentially adsorbed at short bridge position, followed by Si top position.

Fig. 2. The adsorption structures of As atoms at different adsorption sites.

3.2 Al₂O₃

Al₂O₃ is also an important part of fly ash, so it is necessary to discuss its adsorption property of As. After geometric optimization, the Al₂O₃ bulk is cleaved and exposed to the (110) surface. The supercell size is 2*2*1 and the vacuum layer is 15 Å. As shown in Fig. 3, the representative potential surface adsorption sites are selected as Al top site (Al_T), O top site (O_T) and hollow site (H). The As atoms are placed on these three sites for geometric optimization, and the final structures are shown in Fig. 4. The corresponding adsorption energy is also marked.

Fig. 3. The geometry optimized structure and potential adsorption sites of the Al₂O₃(110) surface: (a) top view from (110) facet; (b) 3D view.

From Fig. 4a, when putting As on the Al_T site, after optimization the As atom deviates from Al_T site and advances in the direction of O_T site. The As-Al_T distance is 2.948 Å and the As-O_T distance is 1.993 Å. The adsorption energy is -2.295 eV in this case. While when the initial structure of As absorption is on the O_T site, the final structure is still on O_T site (Fig. 4b). The distance between As and O_T atoms is 1.945 Å and the adsorption energy is -2.432 eV. Nevertheless, the hollow site shows a relatively strong adsorption capacity for As atom which adsorption energy is -2.704 eV (Fig. 4c).

Fig. 4. The adsorption structures of As atoms at different adsorption sites.

3.3 Fe₂O₃

The Fe₂O₃ is a common metal oxide in fly ash and is also an important catalyst with many applications. The Fe₂O₃(100) plane is selected as a representative surface in this work. The supercell size is 2*1*1 and the vacuum layer is 15 Å. As shown in Fig. 5, the representative potential surface adsorption sites are selected as Fe top site (Fe_T), O top site (O_T) and hollow site (H). The As atoms are placed on the above sites and the final structures are shown in Fig. 6, while the corresponding adsorption energy is also given.

Fig. 5. The geometry optimized structure and potential adsorption sites of the Fe₂O₃(100) surface: (a) top view from (100) facet; (b) 3D view.

From Fig. 6a, the Fe_T site can adsorb As atom stably, that has a adsorption energy of -4.614 eV with the As-Fe_T distance of 2.089 Å. When As atom is beginning at O_T or hollow site, the final position is close to the hollow site with the adsorption energy of -13.860 eV, which is the lowest within the five oxides (Fig. 6b). The As atom attaches first to hollow site, followed by Fe_T site. The hollow site in Fe₂O₃(100) has a strong adsorption ability of As atom.

Fig. 6. The adsorption structures of As atoms at different adsorption sites.

3.4 CaO

CaO, which is less abundant in fly ash, is also studied the adsorption property of As [7]. Fig. 7 shows the (001) surface of CaO with the supercell size of 2*1*1 and the vacuum layer of 15 Å. Three highly symmetrical positions are selected as the potential adsorption sites: Ca top site (Ca_T), O top site (O_T) and hollow site (H). The final structures are shown in Fig. 8.

Fig. 7. The geometry optimized structure and potential adsorption sites of the CaO(001) surface: (a) top view from (001) facet; (b) 3D view.

When As atom starts on Ca_T site, after geometric optimization it is still on the Ca_T site (Fig. 8a). The adsorption energy is -1.281 eV and the As-Ca_T distance is 2.921 Å. The adsorption energy is relatively high and the adsorption effect is not good. While when As atom starts on O_T or H site, after geometric optimization it is on the O_T site (Fig. 8b). The adsorption energy is -3.851 eV and the As-O_T distance is 1.921 Å. The As atom is preferentially adsorbed at O_T site than Ca_T site.

Fig. 8. The adsorption structures of As atoms at different adsorption sites.

3.5 MgO

MgO, with low content in fly ash, is also analyzed via the (110) surface (Fig. 9) [8]. The supercell size is $2 \times 2 \times 1$ and the vacuum layer is 15 Å. Four highly symmetrical positions are selected as the potential adsorption sites: the Mg top site in the upper (Mg_{T1}), the Mg top site in the subsurface (Mg_{T2}), the O top site in the upper (O_{T1}) and the O top site in the subsurface (O_{T2}). The final structures are shown in Fig. 10, and the corresponding adsorption energy is given.

Fig. 9. The geometry optimized structure and potential adsorption sites of the MgO(110) surface: (a) top view from (110) facet; (b) 3D view.

The As atom can be adsorbed stably at all these four adsorption sites (Fig. 10). The adsorption energy of As atom at Mg_{T2} site is the minimum, reaching -3.881 eV. The adsorption of As at O_{T1} site is also good, with the adsorption energy of -3.652 eV and the As- O_{T1} distance of 1.931 Å. This may be because the surface oxygen atoms in MgO interact strongly with the As atom. When the As atom is at Mg_{T2} site, the two adjacent oxygen atoms could interact with it, so the adsorption is relatively stable (Fig. 10b).

Fig. 10. The adsorption structures of As atoms at different adsorption sites.

4 Conclusions

In general, among the five oxides in fly ash, the As atom adsorbs most readily on the Fe_2O_3 and the optimal adsorption energy is -13.860 eV. The adsorption ability of Al_2O_3 to As atom is the weakest, which is in the range of -2.295~-2.704 eV. Therefore, the Fe_2O_3 in fly ash can be considered as the main active component to adsorb gaseous As. This paper proves the feasibility of using fly ash as the adsorbent to control As pollution preliminarily, and also provides some help for the subsequent experimental research.

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