



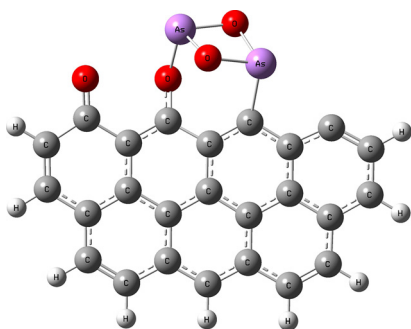
Effects of oxygen functional complexes on arsenic adsorption over carbonaceous surface

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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Carbonaceous surface
Arsenic
Oxygen functional complexes
Mayer bond order

ABSTRACT

The adsorption mechanism of As_2O_3 on carbonaceous surface modified with oxygen functional complexes was studied using density functional theory to understand the effect of oxygen functional complexes on arsenic adsorption. Full-parameter geometrical optimization and single point energy were calculated on B3LYP/def2-SVP and B3LYP/def2-TZVP level. Results showed that As_2O_3 adsorption on bare carbonaceous surface took place in physical as well as chemical way. The adsorption energies were between -2.07 kJ/mol to -480.20 kJ/mol. Compared to armchair model, zigzag model was more suitable as a carbonaceous sorbent. The participation of oxygen functional complexes greatly promoted the surface activity of carbonaceous surface and its adsorption capacity on arsenic. The adsorption energies of arsenic on carbonaceous surface with oxygen functional complexes were between -111.56 kJ/mol to -669.46 kJ/mol. The promotion order of oxygen functional complexes on surface activity was: phenol > lactone > carbonyl > semiquinone > carboxyl. Oxygen functional complexes promoted adsorption capacity of carbonaceous surface through enhancing the activities of neighboring carbon atoms rather than directly providing active sites. Mayer bond order was a reliable way to understand the adsorption process of arsenic on carbonaceous surface. This study provides a new idea for using modified carbonaceous sorbent to remove arsenic pollution from power stations.

1. Introduction

Arsenic is widely distributed in the natural environment and is regarded as one of the most toxic metals due to its carcinogenicity and

teratogenicity. Elemental arsenic is non-toxic, but its compounds are toxic and the toxicity are ranked as follows: $\text{AsH}_3 > \text{As}^{3+} > \text{As}^{5+} > \text{As}^0$ [1,2]. Contaminated air and food can enter the human body through both direct and indirect methods and

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<https://doi.org/10.1016/j.jhazmat.2018.08.029>

Received 19 May 2018; Received in revised form 7 August 2018; Accepted 9 August 2018

Available online 10 August 2018

0304-3894/ © 2018 Published by Elsevier B.V.

accumulate in the internal organs, causing chronic arsenic poisoning, while excessive intake of arsenic can even lead to death [3,4].

In coal-fired power station, arsenic vapor is easy to condense and be captured by fly ash particle and finally removed by dust remover as well as wet desulfurization device. Tang [5] has pointed out that for power station without desulfurization device, the rate of arsenic emission is as high as 17%. Moreover, since the operating temperature of denitration device is mostly between 300 °C–400 °C, a large amount of arsenic vapor is difficult to condense in this temperature range. Uncondensed arsenic vapor can easily diffuse into the surface and pores of selective catalytic reduction (SCR) catalyst [6]. The strong chemical adsorption at the active sites can cause arsenic poisoning of the catalyst, which is one of the most common causes of inactivation of SCR catalyst in a coal-fired boiler [7]. Therefore, an effective way is to add a solid adsorbent in front of the denitration device to convert gaseous arsenic into particulate state through adsorption or chemical reaction, thereby alleviating the arsenic poisoning of the SCR catalyst and reducing the total arsenic emissions into atmosphere.

Arsenic exists in many forms in flue gas, among which the gaseous oxides of arsenic, especially As_2O_3 (g), is considered to be the most common form [8]. Currently, arsenic removal in power plant mostly depends on various types of solid sorbents including calcium-based sorbent, metal oxide and carbonaceous sorbent [9–12]. Besides, a new adsorbent called metal organic framework [13,14] has gained extensive popularity in recent years due to its favorable adsorption capacity. Massoudinejad [15] conducted a series of experiment and found out the good removal efficiency of ethylenediamine-functionalized cubic ZIF-8 on arsenic from aqueous solution. Many studies have been focused on the arsenic removal performance of calcium-based materials during coal combustion. Chen [8] demonstrated that CaO can promote the diffusion of As_2O_3 and form $Ca_3(AsO_4)_2$ to remain in the coal ash, then reduce the arsenic volatilization into the atmosphere. Carbonaceous sorbent mainly includes the unburned carbon in fly ash and activated carbon. Fly ash is the tiny particles emitted during the combustion of fuel, mainly consisting of metal oxides and a small amount of unburned carbon which contains some microporous structures and tends to react with trace element as well as their compounds in flue gas. In recent years, activated carbon has gradually become a commonly used sorbent due to its multifunctionality and good adsorption properties. Experiment from López [16] has showed that arsenic has different degrees of retention on activated carbon depending on different atmosphere. Meanwhile, the retention efficiency of arsenic on activated carbon is lower than that of selenium and some other heavy metals, which may indicate the exist of competitive adsorption and the low adsorption capacity of activated carbon on arsenic. According to the high cost, poor thermodynamic stability and low removal efficiency of carbonaceous surface on arsenic, the modification of carbonaceous surface has become a key topic in recent years.

Research on modification of carbonaceous surface has been very mature in mercury removal experiment [17–22]. Li [23,24] has treated activated carbon with oxygen surface functional groups and implied that oxygen complexes provide active sites for Hg^0 adsorption. Toebes [25] has prepared carbon-nanofiber with oxygen-containing complex through experimental way, he concluded that oxygen functional complexes may influence the metal activity and selectivity and thus act as a catalyst. These suggest that the carbonaceous surface modified with oxygen functional complexes can increase its adsorption capacity on some metal elements, but the effect mechanism was not clear. Liu [26] has conducted a theoretical calculation on the effect of chemical functional groups on mercury adsorption over carbonaceous surface and found that modified carbonaceous surface has high adsorption capacity for elemental mercury, which is greatly corresponds to experimental data. She also implied that theoretical calculation can well explain the experimental phenomena and understand the adsorption mechanism. However, the mechanism of arsenic adsorption on carbonaceous surface is not clear so far. As we currently known, there is

hardly any theoretical study about the mechanism of arsenic adsorption on the carbonaceous surface. Thus, it is very necessary to reveal the adsorption mechanism and clarify the effect mechanism of different oxygen functional complexes on the arsenic adsorption over carbonaceous surface.

To further understand the effects of oxygen functional complexes on arsenic adsorption over carbonaceous surface, benzene clusters from single layer graphite structure were introduced to simulate carbonaceous surface. Quantum chemistry calculation was used to obtain the adsorption properties of arsenic on carbonaceous surface. Meanwhile, wave function analysis was performed to reveal the adsorption mechanism. This paper attempts to provide theoretical guidance for the arsenic removal by carbonaceous surface in coal-fired power plants.

2. Computational detail

Density functional theory (DFT) has been proved to be a favorable theory for calculating structural properties due to its good balance between computational efficiency and accuracy [27]. Therefore, density functional theory and B3LYP method were applied to all calculations by Gaussian 09 software package [28]. During full geometrical optimization and frequency calculation, Def2-SVP basis set was applied to C, H, O and As elements while the convergence was based on the software default value. Diego [29] has used Def2-SVP basis set for calculating the adsorption properties of harmful gas molecules on Fe-doped graphene and achieved reliable results. Relatively stable molecular configurations without negative frequency were obtained. Def2-TZVP basis set was applied to calculate the single-point energy of each system, which has been proved to be a more accurate basis set in quantum calculation. Meanwhile, Mayer bond order, electrostatic potential and electron transfer analysis were performed by Multiwfn program [30]. The adsorption of molecule A on the solid surface B is exothermic and the total energy of the system is calculated as follows [31]:

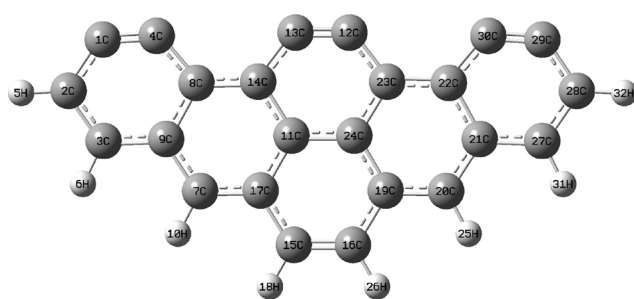
$$E_{ads} = E_{AB} - E_A - E_B$$

Where E_{AB} is the energy of compound AB, E_A and E_B correspond to the total energy of adsorbate A and solid sorbent B, respectively. There exist two types of adsorption, if the value of E_{ads} is between -30 to -10 kJ/mol, the reaction is classified as physical adsorption. Else if the value is between -960 to -50 kJ/mol, then it belongs to chemical adsorption. Basically, a higher value of E_{ads} corresponds to a stronger adsorption.

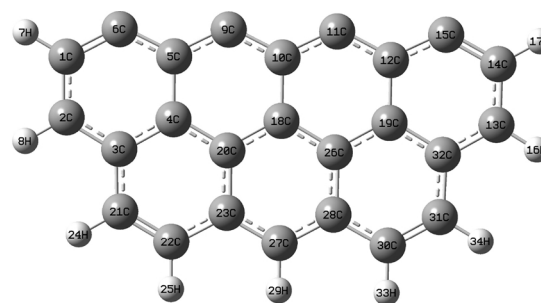
3. Result and discussion

3.1. Model establishment

In this study, finite benzene clusters from single layer graphite structure were used to simulate carbonaceous surface models. So far, this model has been successfully applied to many studies and obtained favorable results [17,27,31]. Chen [32] has already concluded that the most suitable model for simulating graphene structure contains 3–7 benzene rings (12–25 carbon atoms). In this range, the number of benzene rings does not have a significant effect on the characteristics of the model, which implied that the adsorption performance of carbonaceous surface does not depend on the size of model. Montoya [33] suggested that the surface reactivity mainly lies in the differences in the local active site structures such as armchair, zigzag, and tip shapes. To ensure adequate adsorption sites and the accuracy of the calculation, we took six benzene rings as armchair model and seven benzene rings as zigzag model, where the edge C atoms remained unsaturated to act as active sites, and other C atoms were saturated with H atoms. Fig. 1 shows two models of carbonaceous surface with different adsorption sites. After full geometrical optimization and vibrational frequency calculation, all models are optimized to the ground state, corresponding



1-1. Armchair model



1-2. Zigzag model

Fig. 1. Models of carbonaceous surface.

to a spin multiplicity of 1 for armchair model and 6 for zigzag model. Meanwhile the average C–C bond length and C–C–C bond angle were also obtained. For Armchair model, average bond length is 1.40 Å, average C–C–C bond angle is 120.1°, while for zigzag model, the average C–C bond length is 1.41 Å and the average C–C–C bond angle is 120.0°. These values are in great agreement with previous studies [32,34], indicating our models are reasonable in this way.

3.2. As_2O_3 adsorption on carbonaceous surface

There are several active sites for As_2O_3 molecule adsorption on carbonaceous surface. Meanwhile, As_2O_3 adsorption can take place in horizontal and vertical way. In this study, all possible adsorption configurations have been established and only a few reasonable ones were obtained after optimization. As Fig. 2 shows, 2-1 and 2-2 are configurations of As_2O_3 adsorption on armchair model, while 2-3 and 2-4 are configurations of As_2O_3 adsorption on zigzag model. Table 1 lists adsorption energy of each configuration. As it can be seen in Table 1, configuration 2-2 has the highest adsorption energy of -2.07 kJ/mol, indicating a physical adsorption between As_2O_3 and carbonaceous surface. Configuration 2-1 seems to have a weak chemical reaction inside, corresponding to the adsorption energy of -41.41 kJ/mol. Meanwhile, adsorption energies of configuration 2-3 and 2-4 are -480.20 kJ/mol and -181.15 kJ/mol, which indicate a strong chemical adsorption between As_2O_3 and carbonaceous surface. These results are in great agreement with the experiment conducted by López [16], who has confirmed the retention ability of activated carbon on gaseous As_2O_3 . In configuration 2-4 the As_2O_3 molecule was vertically adsorbed on carbonaceous surface, it turned out to be less stable than configuration 2-3, where As_2O_3 molecule was horizontally adsorbed on carbonaceous surface.

Table 2 lists the bond length and Mayer bond order [35] (MBO, > 0.5) of main chemical bonds, Mayer bond order has proved to be a reliable method to understand the reaction between atoms in similar systems such as halogen-oxide and carbon-oxygen systems [36,37]. Practically, a lower value of bond length with a higher value of MBO correspond to a stronger chemical bond. The bond length of each C–As bond and C–O bond is more than 0.3 Å in configuration 2-2 and MBO is much less than 0.5, which obviously indicates that there is no new chemical bond formed between As_2O_3 and carbonaceous surface, and this result is in good agreement with adsorption energy in Table 1. As for zigzag model, it can be seen that the bond lengths between As_2O_3 and carbonaceous surface are almost the same, that is, 1.95 Å of C–As bond in configuration 2-3 and 1.97 Å of C–As bond in configuration 2-4. However, the bond length and MBO of C11–O38 are 1.34 Å and 1.36, result in a strong chemical adsorption on carbonaceous surface. It's worth mentioning that in configuration 2-3, two atoms are both connected with carbonaceous surface and As_2O_3 molecule to form a ring structure, which makes it become more stable and greatly correspond to

its lowest adsorption energy.

From Tables 1 and 2 it is worth noticing that As_2O_3 adsorption on zigzag model tends to be more stable than that on armchair model. In previous calculations, the ground state of the armchair model is 1, which means it's a closed-shell system without unpaired electrons. However, the ground state of zigzag model is 6, indicating that there may exist unpaired electrons in unsaturated C atoms on the edge. Correspondingly, it will lead to a more active surface property, so it can be roughly concluded that the surface activity of zigzag model is much better than that of armchair model.

3.3. As_2O_3 adsorption on carbonaceous surface containing oxygen functional complexes

Zhou [38] has applied Temperature Programmed Desorption (TPD) to analyze the oxygen-containing complexes on the surface of carbon nanofibers and coal-based activated carbon. Results showed that as temperature changed, there were different kinds of oxygen functional complexes existing on the carbonaceous surface, including carboxyl, lactone and so on. To figure out their impact about As_2O_3 adsorption, several models containing oxygen functional complexes had been established to simulate carbonaceous surface, that was, armchair model with semiquinone, phenol, lactone, carboxyl groups and zigzag model with semiquinone, phenol, lactone, carbonyl groups, respectively. Fig. 3 illustrates eight configurations that As_2O_3 molecule adsorption on carbonaceous surface with the presence of oxygen functional complexes. Adsorption energies of each configuration are listed in Table 3.

Apparently, all configurations belong to chemical adsorption since the adsorption energies are in the range of -960 kJ/mol to -50 kJ/mol. In terms of armchair model, a significant difference can be seen before and after the participation of oxygen functional complexes. When As_2O_3 adsorption takes place on bare carbonaceous surface, the adsorption energies are higher than -50 kJ/mol. However, after the participation of oxygen functional complexes, the adsorption energies rapidly decreased to -154.68 kJ/mol, -271.76 kJ/mol, -261.14 kJ/mol and -111.56 kJ/mol. Since a more negative value of adsorption energy corresponds to a better adsorption capacity, the influence order of various oxygen functional complexes on the adsorption capacity of carbonaceous surface (armchair model) can be obtained, that is phenol $>$ lactone $>$ semiquinone $>$ carboxyl.

As for zigzag model, it is worth mentioning that As_2O_3 molecule adsorption on carbonaceous surface in a horizontal way in configuration 3-5 and 3-6 and in a vertical way in configuration 3-7 and 3-8. Comparing configuration 2-3 with 3-6, both of them are horizontal adsorption. When the adsorption occurs on the bare carbonaceous surface, the adsorption energy is -480.20 kJ/mol. But after the participation of phenol group, the adsorption energy rapidly decreases to -669.46 kJ/mol. This huge difference clearly indicates a great improvement of adsorption capacity. However, that difference is not

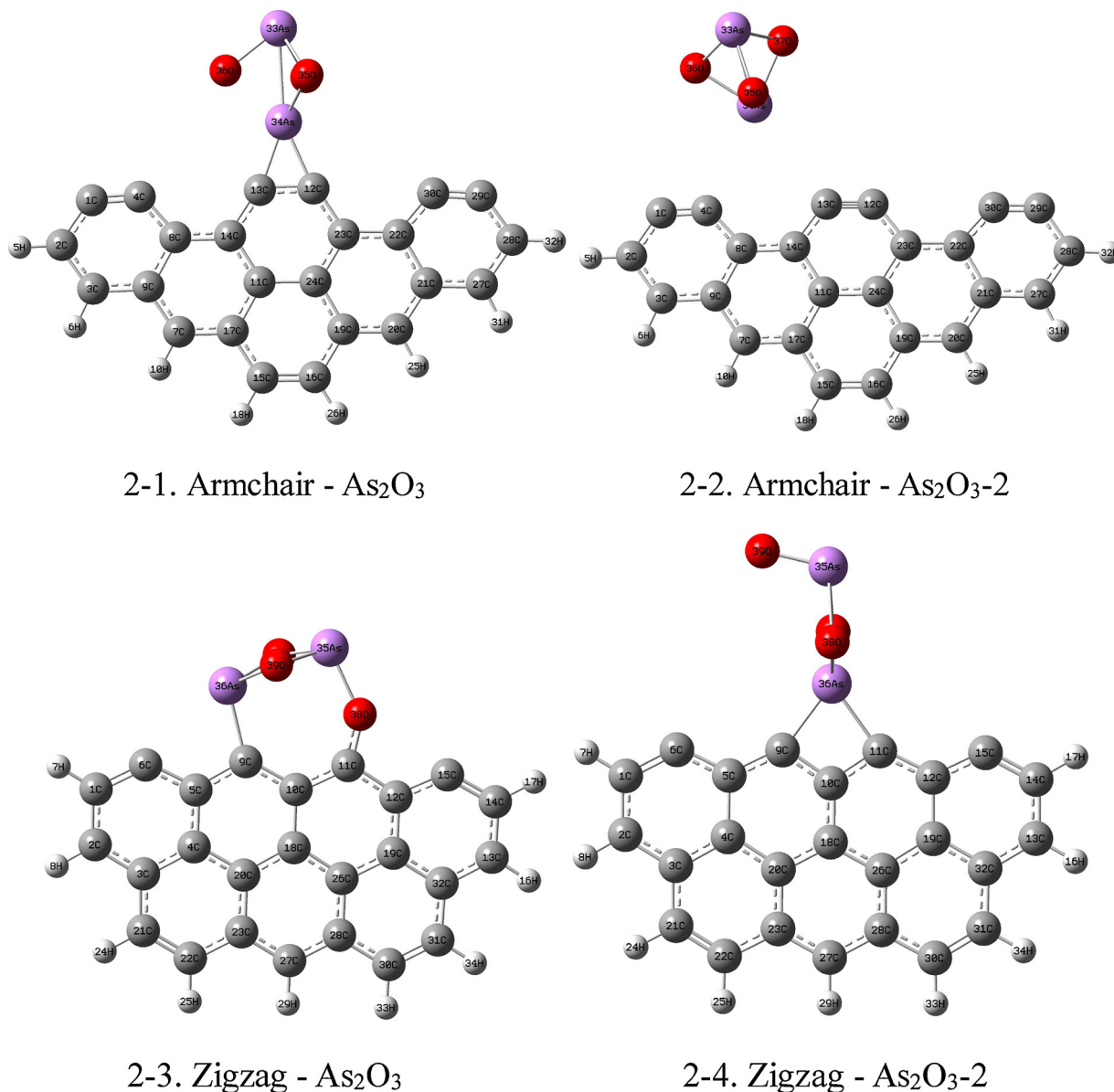
Fig. 2. Configurations of As_2O_3 adsorption on carbonaceous surface.

Table 1
Adsorption energy of As_2O_3 on carbonaceous surface.

Configuration	E_{ads} (kJ/mol)
2-1. Armchair - As_2O_3	-41.41
2-2. Armchair - As_2O_3 -2	-2.07
2-3. Zigzag - As_2O_3	-480.20
2-4. Zigzag - As_2O_3 -2	-181.15

Table 2
Bond length and MBO of As_2O_3 adsorption on carbonaceous surface.

Configuration	Bond	Bond length(Å)	MBO
2-1. Armchair - As_2O_3	C12-As34	1.90	0.77
	C13-As34	1.87	0.95
2-2. Armchair - As_2O_3 -2	C4-As34	3.04	0.06
2-3. Zigzag - As_2O_3	C9-As36	1.95	0.89
	C11-O38	1.34	1.36
2-4. Zigzag - As_2O_3 -2	C9-As36	1.98	0.76
	C11-As36	1.97	0.79

distinct between configuration 2-3 and 3-5, where the adsorption energies are -480.20 kJ/mol and -477.64 kJ/mol, indicating that the semiquinone group may not contribute to the enhancement of adsorption capacity. The adsorption energy of configuration 3-7 is -357.07 kJ/mol, showing that the lactone group also has a positive effect on the adsorption capacity of carbonaceous surface. In addition, the adsorption energy of configuration 3-8 is -307.44 kJ/mol, compare to -181.15 kJ/mol of configuration 2-4, we can see the presence of carbonyl also increase the adsorption capacity of carbonaceous surface. The above discussion supports the claim from Maroto-Valer [39], who has carried out the experiment to find the relationship between surface oxygen functionality and mercury adsorption on fly ash carbon and its activated sample. He came to the conclusion that the oxygen functionality on the surface of carbonaceous surface can promote mercury adsorption. The influence order of various oxygen functional complexes on the adsorption capacity of carbonaceous surface (zigzag model) can be obtained, that is: phenol > lactone > carbonyl > semiquinone. Combining armchair and zigzag model, the promotion order of oxygen functional complexes on surface activity of carbonaceous surface is: phenol > lactone > carbonyl > semiquinone >

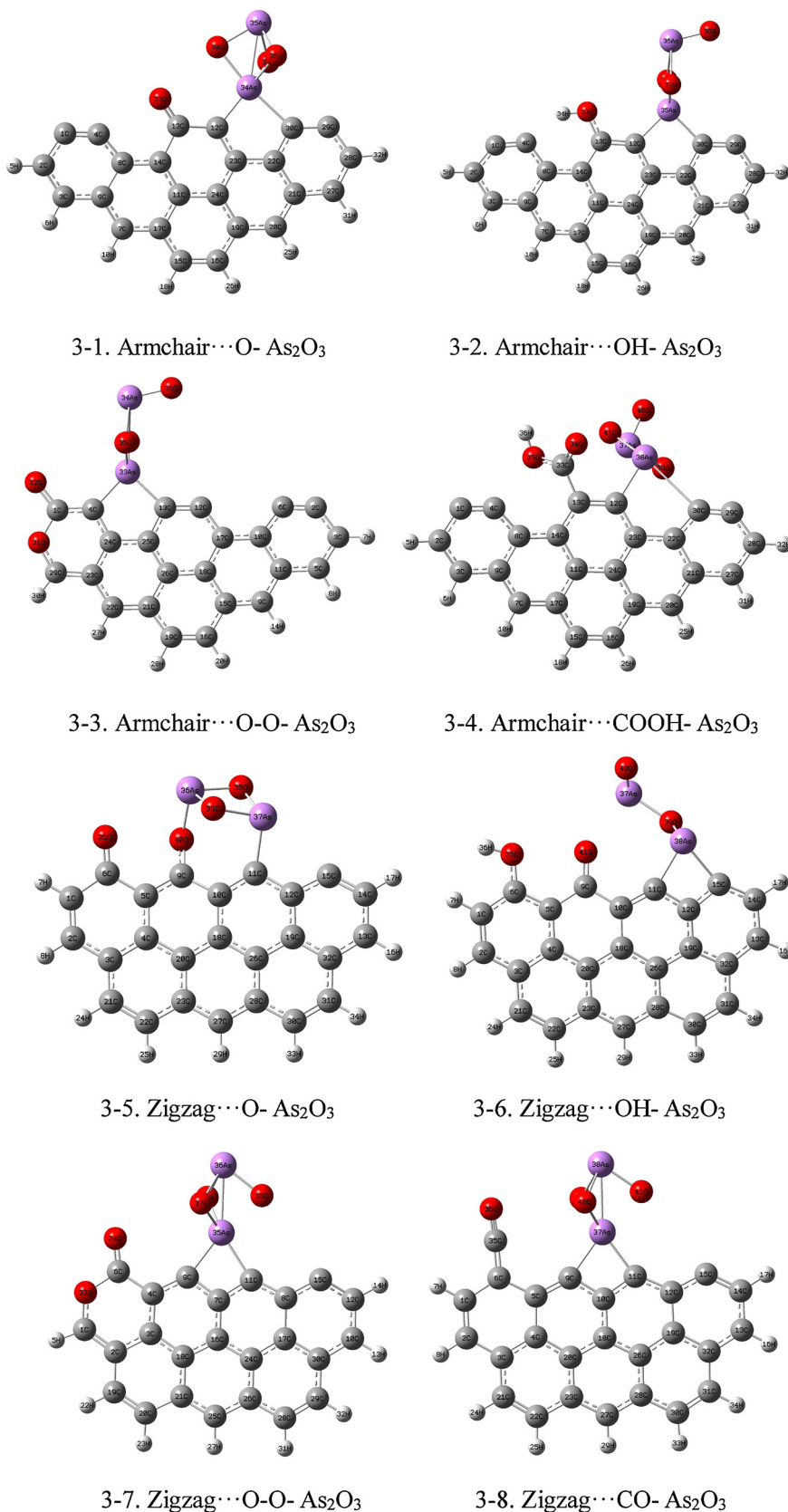


Fig. 3. Configurations of As_2O_3 adsorption on carbonaceous surface containing oxygen functional complexes.

carboxyl. Li [23] has conducted Temperature programmed desorption to investigate the mercury adsorption on activated carbon with the participation of oxygen surface functional groups and found that the

phenol and carbonyl groups might inhibit mercury adsorption while other groups increased the mercury adsorption. This implies the different promotion effect of oxygen functional complexes on arsenic

Table 3
Adsorption energy of As₂O₃ on carbonaceous surface containing oxygen functional complexes.

Configuration	E _{ads} (kJ/mol)
3-1. Armchair...O–As ₂ O ₃	–154.68
3-2. Armchair...OH–As ₂ O ₃	–271.76
3-3. Armchair...O–O–As ₂ O ₃	–261.14
3-4. Armchair...COOH–As ₂ O ₃	–111.56
3-5. Zigzag...O–As ₂ O ₃	–477.64
3-6. Zigzag...OH–As ₂ O ₃	–669.46
3-7. Zigzag...O–O–As ₂ O ₃	–357.07
3-8. Zigzag...CO–As ₂ O ₃	–307.44

Table 4
Bond length and MBO of As₂O₃ adsorption on carbonaceous surface containing oxygen functional complexes.

Configuration	Bond	Bond length(Å)	MBO
3-1. Armchair...O–As ₂ O ₃	C12–As34	1.90	1.05
	C30–As34	2.13	0.57
3-2. Armchair...OH–As ₂ O ₃	C12–As35	1.93	0.91
	C30–As35	1.95	0.91
3-3. Armchair...OO–As ₂ O ₃	C4–As33	1.93	0.91
	C13–As33	1.96	0.89
3-4. Armchair...COOH–As ₂ O ₃	C12–As38	2.01	0.85
	C30–As38	2.75	0.12
3-5. Zigzag...O–As ₂ O ₃	C9–O40	1.33	1.21
	C11–As37	1.99	0.88
3-6. Zigzag...OH–As ₂ O ₃	C9–O41	1.23	1.96
	C11–As38	2.01	0.82
3-7. Zigzag...OO–As ₂ O ₃	C15–As38	2.05	0.89
	C9–As35	2.01	0.66
3-8. Zigzag...CO–As ₂ O ₃	C11–As35	1.99	0.78
	C9–As37	2.02	0.59
	C11–As37	1.98	0.84

adsorption and mercury adsorption, but there is almost no experimental study has been conducted to demonstrate this result hitherto. Further experiments will be expected to investigate the effect of oxygen functional complexes on arsenic adsorption over carbonaceous surface

Table 4 lists the major bond length and Mayer bond order (> 0.5) between As₂O₃ molecule and carbonaceous surface. In configuration 3-2, the bond length of C12–As35 and C30–As25 are 1.93 Å and 1.95 Å, the MBO are both 0.91, indicating two quite stable chemical bonds. As far as configuration 3-3, bond C4–As33 has the same length and MBO with C12–As35 in configuration 3-2, but bond C13–As33 has a length of 1.96 Å and MBO of 0.89, indicating a relatively weak interaction between As33 atom and C13. This slight difference leads to a distinction in adsorption energy between these two configurations. In configuration 3-1 the length of C30–As34 bond is 2.13 Å and MBO is 0.57, this extremely weak chemical bond results in a higher value of adsorption energy, which is –154.68 kJ/mol. Meanwhile, the length of C30–As38 bond in configuration 3-4 is 2.75 Å and MBO is only 0.12, leading to the highest adsorption energy of –111.56 kJ/mol. The same pattern can be found in configurations of As₂O₃ adsorption on zigzag model. There are three chemical bonds formed between As₂O₃ molecule and carbonaceous surface in configuration 3-6: C9–O41 bond, C11–As38 bond and C15–As38 bond, with the length and MBO of 1.23 Å, 2.01 Å, 2.05 Å and 1.96, 0.82, 0.89, respectively. Three strong formed chemical bonds make it become the most stable configuration with the adsorption energy of –669.46 kJ/mol.

The adsorption energies of the armchair model are generally higher than the adsorption energies of zigzag model, indicating that the zigzag model of carbonaceous surface is more favorable for As₂O₃ adsorption. Meanwhile, this study has tried to adsorb As₂O₃ on the oxygen atom of oxygen functional complexes rather than neighboring carbon atoms of carbonaceous surface, but it turned out that the stable configuration could not be obtained during the optimization process, which implied

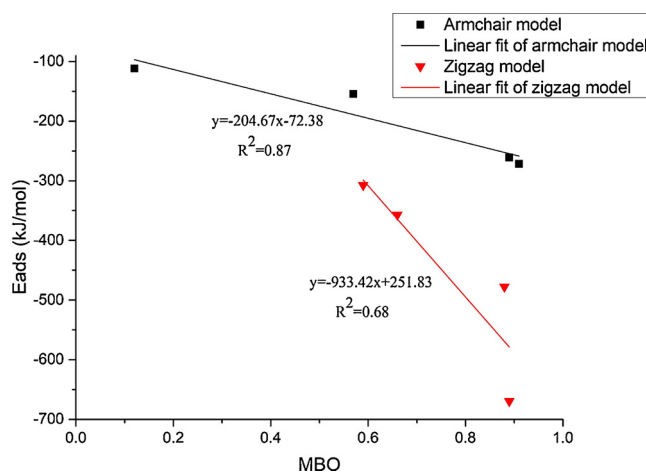


Fig. 4. The relationship between MBO and adsorption energy.

that the oxygen functional complexes itself cannot provide a reaction site for the adsorption of As₂O₃ molecule. Although Maroto [39] has suggested that surface oxygen complexes provide active sites for metal bonding on activated carbon, the result from theoretical calculation may not support his claim. Results from previous calculations are consistent with Liu's [26] conclusion about the mercury adsorption on the carbonaceous surface with chemical functional groups, in which the Hg atom tends to move to the surrounding C atoms rather than to the O atom of chemical functional group.

3.4. Relationship between MBO and adsorption energy

In order to further understand the difference in promotion effect of oxygen functional complexes on surface activity, the relationship between MBO and adsorption energy was studied. To ensure the rationality of the results, the relatively smaller MBO in each configuration was selected for fitting. As Fig. 4 shows, there obviously exists a linear relationship between MBO and adsorption energy, where adsorption energy become lower with the proportional increase of MBO. The deviation of the linear fit of zigzag model is because there are three chemical bonds formed between As₂O₃ with carbonaceous surface in configuration 3-6. Thus, it can be proved that the MBO is a suitable way to explain the changes in adsorption energy. In addition, compared to linear fit of armchair model, the slope of linear fit of zigzag model turns to be much steeper, implying that the effect of MBO on the adsorption energy of zigzag model is greater than its effect on the adsorption energy of armchair model. In short, Mayer bond order is a method worthy of consideration to understand the arsenic adsorption process on carbonaceous surface.

3.5. Electrostatic potential analysis

In order to explore how oxygen functional complexes affect the adsorption capacity of carbonaceous surface, the electrostatic potential (ESP) was taken into consideration in this study. Hundreds of literatures have shown its reliability of understanding both electrophilic and nucleophilic processes, including hydrogen-bonding interactions [40,41].

In this study, Multiwfn program was applied to produce electrostatic potential on carbonaceous surface. Figs. 5 and 6 show the carbonaceous surface area ratio in different range of electrostatic potentials. It can be seen from Fig. 5, the distribution of electrostatic potential on bare surface of armchair model is concentrated in the range of –80 ~ 120 kJ/mol. Regions with a relatively high absolute electrostatic potential (> 80 kJ/mol) account for about 7% of the surface. However, the participation of oxygen functional complexes greatly changes the distribution of electrostatic potential on carbonaceous surface. In

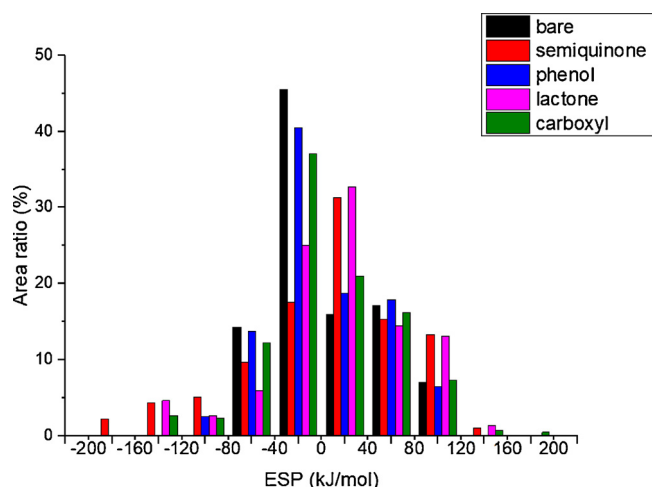


Fig. 5. Armchair model surface area ratio of different ESPs.

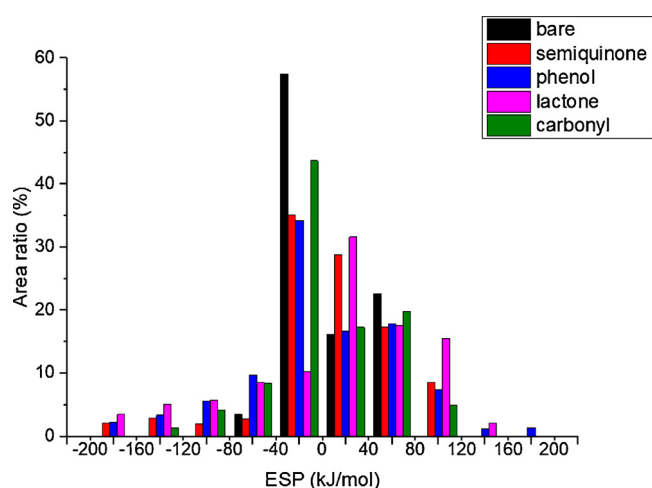


Fig. 6. Zigzag model surface area ratio of different ESPs.

particular, the distribution of electrostatic potential with larger absolute value is increases. As we can see, after the participation of semiquinone, the area ratio of electrostatic potentials between $-200 \sim -80$ kJ/mol and $80 \sim 200$ kJ/mol increases from 0 to 11.67% and 7.03%, which indicates the enhancement of the overall level of electrostatic potential of carbonaceous surface, making it much easier to adsorb As_2O_3 molecule. According to the degree of increase on electrostatic potential, these four oxygen functional complexes can be ranked as: semiquinone > lactone > carboxyl > phenol.

In Fig. 6, the electrostatic potential is between $-80 \sim 80$ kJ/mol on bare surface of zigzag model, where the area ratio of electrostatic potential in the range of $-40 \sim 40$ kJ/mol is as high as 73.71%. However, after the participation of phenol, area ratio in that range decrease to 51.05%, while the ratios of electrostatic potential in the range of $-200 \sim -120$ kJ/mol and $120 \sim 200$ kJ/mol increase from 0 to 5.64% and 11.28% and 10.05%, which also indicates the higher possibilities of adsorption reaction on carbonaceous surface. Same regularities can be found in other oxygen functional complexes, showing their role in improving the adsorption capacity of carbonaceous surface. The enhancement degree of each oxygen functional complexes can be ranked as: lactone > phenol > carbonyl > semiquinone.

The enhancement degree of oxygen functional complexes on the surface activity of the carbonaceous surface obtained by electrostatic potential analysis is different from the above results obtained by adsorption energy, this is because what electrostatic potential illustrates is the overall electrostatic level of the carbonaceous surface including the

interior of benzenes and marginal carbon atoms, while the particular electrostatic potential of the unsaturated carbon atoms on the top cannot be numerically reflected. Another reason is that electrostatic potential is a powerful tool for analyzing various weak interactions dominated by static electricity, but for a chemical reaction system, the results may be not precise. But the change of surface area ratio of different ESPs can still characterize the promotion effect of modified carbonaceous surface on its surface activity. Therefore, it can be concluded that the presence of oxygen functional complexes improves the surface activity of carbonaceous surface, but electrostatic potential analysis maybe not a suitable way for understanding the degree of oxygen functional complexes' effect on the arsenic adsorption over carbonaceous surface.

3.6. ADCH charge analysis

Electron transfer process is believed to be involved in the As_2O_3 adsorption on carbonaceous surface. Lu [30] has compared a variety of mainstream atomic charge calculation methods and found that Atomic Dipole Moment Corrected Hirshfeld (ADCH) charge has both accuracy and stability under most circumstances. Feng [42] and Fahimeh [43] used ADCH charge to study the interactions between metal elements with modified graphene as well as carbon nanotubes and have achieved favorable results. In this study ADCH charge was introduced to analyze the electron transfer. To further understand how oxygen functional complexes effect As_2O_3 adsorption on carbonaceous surface, the ADCH charges of each active sites on armchair model and zigzag model containing oxygen functional complexes were obtained. Fig. 7 shows the ADCH charge of C4, C12, C13 and C30 of armchair model with the presence of different oxygen functional complexes, while Fig. 8 shows the ADCH charge of C6, C9, C11 and C15 of zigzag model with the presence of each oxygen functional complexes.

As Fig. 7 shows, ADCH charges of C4, C13, C12 and C30 are -0.043 , -0.034 , -0.034 and -0.043 . After the adsorption of oxygen functional complexes, the ADCH charge of C13 increase because of the larger electronegative of oxygen, which makes carbon atoms prone to lose electrons. It is especially obvious in configuration 3-5, where the charge of C13 rapidly increase to 0.486. It is worth mentioning that the lactone is adsorbed on the edge of benzene, so it is normal for the charge of C13 to be negative. The ADCH charge of C30 seems to be stable while that of the neighboring atoms C4 and C12 have changed. In configuration 3-1, ADCH charges of C4 and C12 decrease to -0.079 and -0.042 , so they become more active for arsenic adsorption. Meanwhile, after the presence of phenol, the charges of C4 and C12 in configuration 3-2 decrease to -0.086 and -0.042 , showing that the

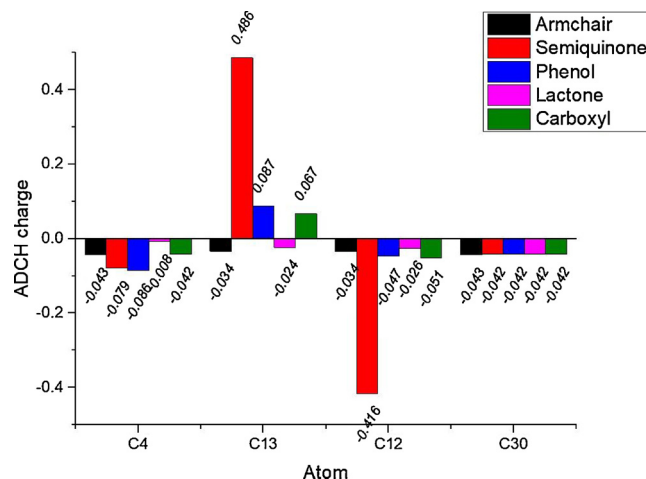


Fig. 7. ADCH charge transfer of armchair model containing oxygen functional complexes.

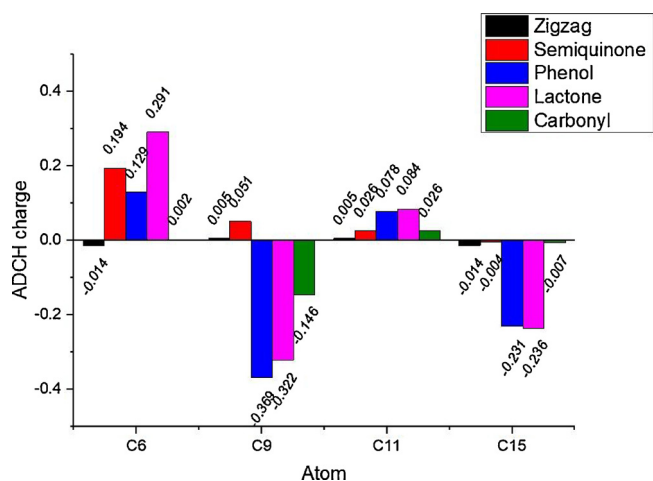


Fig. 8. ADCH charge transfer of zigzag model containing oxygen functional complexes.

participation of phenol increased the activity of neighboring carbon atoms. Similarly, in configuration 3-4, the charges of neighboring C12 decrease to -0.051 .

In Fig. 8, same regularity can be found in other configurations, suggesting that the participation of oxygen functional complexes reduce the ADCH charges of neighboring carbon atoms and make them more favorable to react with As_2O_3 molecule. Combining the fact that oxygen functional complexes cannot provide any active sites for As_2O_3 adsorption, it can be concluded that oxygen functional complexes enhance the adsorption capacity of carbonaceous through increasing the activities of neighboring carbon atoms rather than providing adsorption sites itself. In addition, the change of ADCH charges of neighboring carbon atoms in armchair model is, in general, not as large as that change in zigzag model, implying that the effect of oxygen functional complexes on the surface activity of armchair model is smaller than that of zigzag model, which is greatly consistent with previous conclusion obtained from adsorption energies. Compared with armchair model, the powerful advantages of zigzag model in terms of adsorption capacity lays the foundation for the modification of carbonaceous adsorbents.

4. Conclusion

In this paper, five kinds of oxygen functional complexes including semiquinone, phenol, lactone, carboxyl and carbonyl were introduced to investigate the effect of modified carbonaceous surface on arsenic adsorption. Benzene clusters from single layer graphite with unsaturated hydrogens were used to simulate the armchair model and zigzag model of carbonaceous surface. All calculations were performed under B3LYP level based on density functional theory. Adsorption energy, Mayer bond order, electrostatic potential and ADCH charge were introduced to deeply understand the influence mechanism of oxygen functional complexes on the arsenic adsorption capacity of carbonaceous surface.

Results from adsorption energy show that the As_2O_3 adsorption on bare carbonaceous surface occurs in two ways: physical adsorption and chemical adsorption, the adsorption energies of zigzag model are quite lower than that of armchair model. After the participation of oxygen functional complexes, adsorption energies decrease rapidly, which indicates a significant improvement in adsorption capacity of the carbonaceous surface. The order of improvement is: phenol > lactone > carbonyl > semiquinone > carboxyl. Results from electrostatic potential show that the participation of oxygen functional complexes enhances the overall level of electrostatic potential, while ADCH charge proves that the participation of oxygen functional complexes increases the adsorption capacity of carbonaceous surface by enhancing the

activity of neighboring carbon atoms rather than directly providing active sites.

In conclusion, zigzag model has a higher surface activity and is more suitable as a carbonaceous adsorbent. Oxygen functional complexes have a promotion effect on the adsorption capacity of carbonaceous surface, in which the phenol promotes the most. This paper provides a favorable way for arsenic removal in coal-fired power station with carbonaceous surface modified by oxygen functional complexes. The good linear relationship between MBO and adsorption energy shows that Mayer bond order is a quite reliable method to understand the adsorption mechanism of metal oxide on carbonaceous surface. Further studies will be carried out to investigate other types of modified carbonaceous surface and their effect on arsenic removal.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 91545122), Beijing Natural Science Foundation (2182066) and the Fundamental Research Funds for the Central Universities (JB2015RCY03 and 2017XS121). Computational resources from the Lvliang Supercomputer Center were acknowledged.

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