



Effects of chemical functional groups on elemental mercury adsorption on carbonaceous surfaces

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ABSTRACT

A systematic theoretical study using density functional theory is performed to provide molecular-level understanding of the effects of chemical functional groups on mercury adsorption on carbonaceous surfaces. The zigzag and armchair edges were used in modeling the carbonaceous surfaces to simulate different adsorption sites. The edge atoms on the upper side of the models are unsaturated to simulate active sites. All calculations (optimizations, energies, and frequencies) were made at B3PW91 density functional theory level, using RCEP60VDZ basis set for mercury and 6-31G(d) pople basis set for other atoms. The results indicate that the embedding of halogen atom can increase the activity of its neighboring site which in turn increases the adsorption capacity of the carbonaceous surface for Hg⁰. The adsorption belongs to chemisorptions, which is in good agreement with the experimental results. For the effects of oxygen functional groups, lactone, carbonyl and semiquinone favor Hg⁰ adsorption because they increase the neighboring site's activity for mercury adsorption. On the contrary, phenol and carboxyl functional groups show a physisorption of Hg⁰, and reduce Hg capture. This result can explain the seemingly conflicting experimental results reported in the literature concerning the influence of oxygen functional groups on mercury adsorption on carbonaceous surface.

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1. Introduction

Mercury emissions are of global concern due to their toxicity, ability to be transported in the environment, and adverse effects on the ecosystem [1]. Coal-burning power plants are the largest source of mercury pollution in the USA, contributing to about 40% of the total mercury emissions [2]. Thus, reducing the emissions of mercury by coal-fired power plants has become an important environmental concern.

Mercury is present in flue gas in varying percentages of the three basic chemical forms: elemental mercury (Hg⁰), oxidized mercury, and particulate-bound mercury. Most of the particulate-bound mercury can be removed using air pollution control devices (electrostatic precipitators and fabric filters). Oxidized mercury is soluble in water and is therefore removed with high efficiency (>90%) by wet flue gas desulfurization (FGD) equipment. On the other hand, it is more difficult to remove Hg⁰ than the oxidized mercury from flue gas because Hg⁰ is water insoluble, high volatile, and chemical inert [1]. Therefore, among the three species of mercury found in coal-derived flue gas, elemental mercury (Hg⁰) is the most difficult species to eliminate. The injection of carbon

adsorbent upstream of the electrostatic precipitator or baghouse particulate collection device is a promising technology to control mercury emissions from coal-burning power plants [3]. Although very effective and reliable, the high cost involved hinders the practical application of this technology in mercury control. In order to lower the cost, improvements on the sorbent (either to increase the adsorption capacity or to decrease the cost) must be made to facilitate the application of this technology.

Previous pilot- and full-scale tests have demonstrated that the low chlorine concentration of most low-rank coals is a major limiting factor in the mercury control performance of conventional activated carbons (AC) [2,4]. For sub-bituminous or lignite-burning units producing a low concentration of HCl in the flue gas, the use of chemically treated activated carbons is an effective option to enhance mercury removal efficiency and lower the amount of carbon injection [4–6]. Halogen-embedded AC has been found to be effective for mercury removal [7,8]. Ghorishi et al. [9] have reported a significant increase in Hg⁰ removal by impregnating HCl onto activated carbon. In addition, brominated activated carbon has been tested in several full-scale systems and has demonstrated good performance such as more than 90% mercury removal efficiency at an injection level of less than 80 mg/m³ [5,10]. Maroto-Valer et al. [11] have investigated the effect of surface functionality on the mercury capacity of a fly ash carbon and its activated sample. They found that the presence of halogen species and oxygen functional groups on

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the surface of fly ash carbons may promote mercury adsorption, while the surface area does not seem to have a significant impact on their mercury capacity.

Study on X-ray absorption fine structure (XAFS) spectroscopy has shown that mercury bonding on the carbon surface appears to be associated with oxygen, and that surface oxygen complexes are most likely to provide the active sites for Hg⁰ bonding [12]. However, it is not clear what particular oxygen functional groups are participating in Hg⁰ adsorption due in part to the lack of information on the chemical characteristic of the carbons tested [13]. Furthermore, there is even a controversy on the effect of oxygen surface functionality of activated carbon sorbents on their mercury adsorption properties [7,11–14]. Some researchers [7,11–13,15] have concluded that oxygen surface complexes are the active sites for Hg⁰ capture after conducting a series of studies on various samples with different surface functionalities. Other studies [14] showed that oxygen functional groups reduce mercury capture by physisorption.

Many experimental studies have been conducted to understand the effects of surface functional groups on mercury adsorption process on carbonaceous surfaces [6,9,11,13,14]. However, correlations between the physical and chemical characteristics of surface functional groups of carbonaceous surface and their Hg⁰ adsorption properties have not been well established, and the mechanisms involved in Hg⁰ adsorption are not well understood [13]. Theoretical understanding and prediction of the adsorption behavior and mechanism at the molecular level so far has been limited [16]. Such studies would help to give a better understanding of the effects of surface functional groups, and thus to improve the efficiency of the process. Progress in quantum chemical calculations has made it possible to make reliable predictions of molecular structures, relative energies, potential surfaces, reaction mechanisms, and so on. Quantum chemical methods, in the form of density functional theory, are increasingly used to understand mechanisms in both homogenous [17,18] and heterogeneous [19,20] systems.

The objective of the current study is to apply density functional theory to study the effects of halogen and oxygen functional groups on the mercury adsorption mechanism by the carbonaceous surface. This knowledge will have great value in developing effective sorbents for mercury removal.

2. Computational methodology

Quantum mechanical methods include *ab initio* methods and density functional theory (DFT) methods. QCISD (quadratic configuration interaction with single and double excitations) belongs to *ab initio* method. B3PW91 (Becke's three-parameter hybrid exchange functional with the correlation functional of Perdew and Wang) belongs to density functional theory (DFT) method. B3PW91 is hybrid methods of Hartree–Fock exchange with density functional exchange–correlation. Density functional theory was widely used because it provides a good balance between accuracy and computational cost [19]. Regarding basis set, mercury has eighty electrons, which makes the calculations computationally intensive. Therefore, the use of relativistic effective core potentials is necessary to make the calculations tractable while obtaining accurate theoretical adsorption energies [19]. The suitable combination of a method and basis set is very important for quantum mechanical calculation.

In our previous work [21], the use of quantum mechanical method and basis set combinations have been validated through a comparison of theoretically determined geometries, frequencies and reaction enthalpies involving mercury to experimental values found in the literature. The results showed that

QCISD/RCEP60VDZ combination leads to the most accurate results. Also, B3PW91/RCEP60VDZ combination provides reasonably accurate results for these systems B3LYP/LANL2DZ combination is not enough accurate. RCEP60VDZ is the basis set that uses a relativistic compact effective potential of Stevens et al. group [22], which replaces 60 of mercury's atomic core electrons, derived from numerical Dirac–Fock wavefunctions using an optimizing process based upon the energy-overlap functional [17]. The B3PW91 method of DFT is within acceptable errors for predicting geometries compared to the larger and more expensive calculation methods such as QCISD. Therefore, B3PW91/RCEP60VDZ was used for the Hg atom in this study. The Pople 6-31G(d) basis set was used for non-metal elements (C, F, Cl, Br, I, O and H). This level of theory is a reasonable compromise that minimized spin contamination, includes configuration interaction, and accomplishes the calculations at acceptable computational expense.

In this work, all of the calculations were carried out using the Gaussian 03 software package [23]. The calculation process includes geometry optimizations, vibrational frequency analysis and energy calculation. Full geometry optimizations, i.e., optimization over all atoms, were performed to optimize the hypothetical geometries of carbonaceous surface models and their corresponding Hg adsorbed intermediates to a minimal point on the potential surface at the B3PW91/RCEP60VDZ level of DFT in their ground states. The correct ground state was determined by performing single-point energy calculations for different electronic states, and a reasonable chemical structure, with the least spin contamination and the lowest energy electronic state was determined to be the selected ground state. The optimized geometric parameters for the adsorption models determine the bond length and bond angle. Once the geometry optimization was completed, vibrational frequency calculations followed in order to ensure that the final structure corresponds to a minimum on a potential energy surface and confirm its stability. The energies were calculated at the B3PW91/RCEP60VDZ level of DFT by adding the zero point energy (ZPE) and thermal (temperature dependent) corrections.

The adsorption energy (E_{ads}) of an adsorbate "A" on a solid surface "B" can be calculated as:

$$E_{\text{ads}} = E(\text{AB}) - (E(\text{A}) + E(\text{B}))$$

where $E(\text{A})$ is the total energy of the adsorbate, and $E(\text{B})$ is the total energy of the substrate, while $E(\text{AB})$ is the total energy of adsorbate/substrate system in equilibrium state. Adsorption of the adsorbate is exothermic if E_{ads} is negative. A higher negative value of E_{ads} corresponds to a stronger adsorption.

3. Results and discussion

3.1. Modeling the carbonaceous surface

In order to study the adsorption of Hg⁰ on carbonaceous surfaces at the molecular and theoretical levels, it is important to begin by establishing a model for the surface. The cluster models consisted of four–seven fused benzene rings have been used in several studies with different applications to simulate carbonaceous surfaces [19,24–28]. Chen and Yang have shown that the reactivity of the carbon model does not depend strongly on the molecular size [29]. In addition, Montoya et al. have shown that the reactivity of the active sites, which are the unsaturated carbon atoms at the edge of the graphene layers, depends strongly on the shape of the local active site rather than on the size of the molecular model [19,24]. Thus, on the basis of previous studies, it is a reasonable approximation to use the finite clusters of four–five fused benzene rings to simulate the carbonaceous surfaces. The zigzag and armchair models were used to simulate the different structures that can be

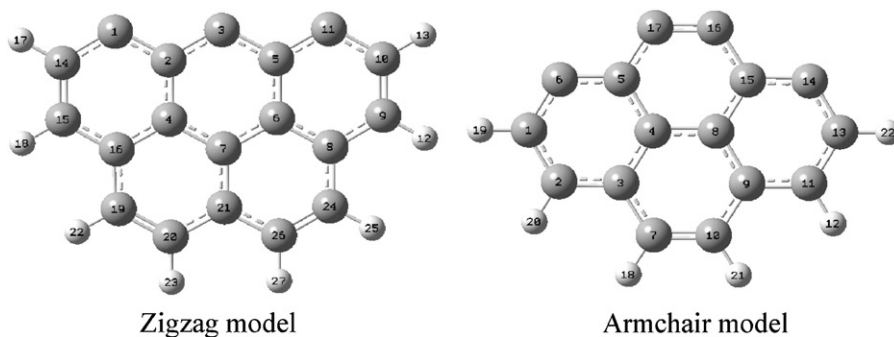


Fig. 1. Carbonaceous surface models.

found in a carbonaceous material. The calculations used provide a good balance between computational cost and accuracy [19].

Padak et al. [16] used four fused benzene ring to represent the active carbon surface with complete saturation with H atom at the B3LYP/LANL2DZ level. While Radovic and Bockrath [30] have concluded that “complete saturation with H or other heteroatoms is unrealistic and that not all graphene edge sites are saturated with H”. Furthermore, there has also been experimental evidence on the existence of partially-stabilized radical sites at graphene edges [19,31]. Therefore, in this study, the edge atoms on the upper side of the models are unsaturated to simulate carbon active sites while the other edge carbon atoms are terminated with hydrogen atoms.

Fig. 1 illustrates the structure of two types of carbon models; the first one has a zigzag structure while the other one has armchair edge site on the upper side of each model. Some carbon atoms are labeled to facilitate the discussion below. Note that the π -bond network is implied in the figure. The models shown in Fig. 1 are reasonable representation of the active site environment.

Full geometry optimization, i.e., optimization over all atoms, is performed. All optimizations end at a minimum on the potential surface, indicating the stability of our selected carbonaceous surface models [28].

Table 1

C–Hg bond lengths and adsorption energies of Hg^0 adsorption on carbonaceous surface.

Model	C–Hg bond lengths (Å)	E_{ads} (kJ/mol)
Zigzag-A	2.29	–29.6
Zigzag-BC	2.32	–44.6
Armchair	2.23	–48.0

3.2. Hg^0 adsorption on carbonaceous surface

The interactions of Hg with different sites on the zigzag and armchair models of carbonaceous surface were studied. There are three sites for Hg adsorption on the zigzag model, and one site on the armchair model, as shown in Fig. 2. The different sites of Hg^0 on the zigzag model are shown as “a”, “b” and “c”. Both “b” and “c” formed the same structure zigzag-BC and “a” formed the structure zigzag-A. The optimized C–Hg bond lengths and the adsorption energies on the carbonaceous surface are presented in Table 1. For the zigzag model, the adsorption energy of Hg^0 on zigzag-BC is higher than that of zigzag-A, which indicates that zigzag-BC (Hg binding with C1 and C3 atom) is the main binding mode for Hg^0 adsorption on

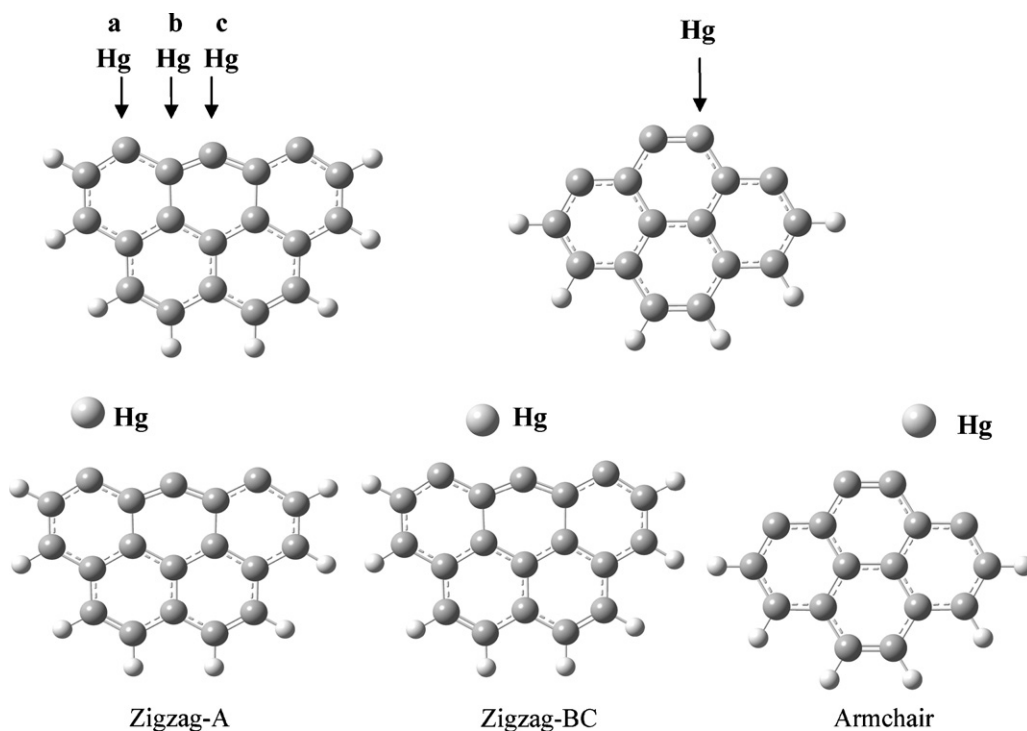


Fig. 2. Adsorption of Hg at different sites of zigzag and armchair models.

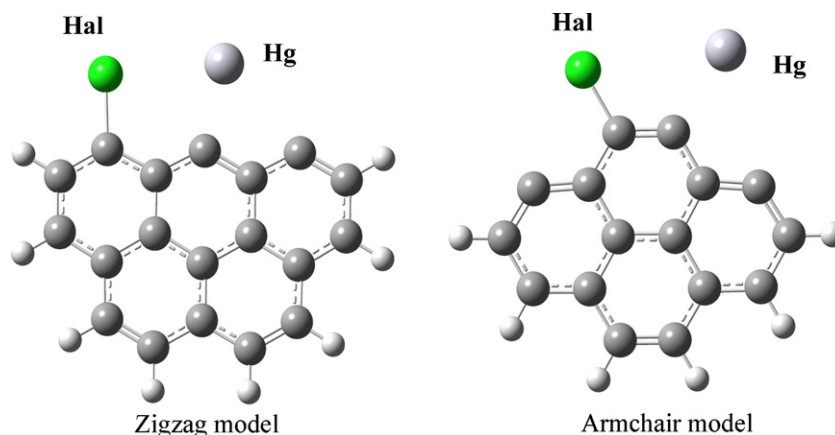


Fig. 3. Adsorption of Hg on carbonaceous surface embedded halogen (Hal: F, Cl, Br and I).

zigzag edge site of the surface. Therefore, the zigzag-A (Hg binding with C1 atom) model was not considered in the following calculations associated with the effects of halogen and oxygen functional groups on Hg⁰ adsorption on the carbonaceous surfaces. In addition, the values of Hg⁰ adsorption energies on the zigzag model are relatively lower and belong to physisorption. This result is in agreement with the available experimental results in the literature [32–34].

Comparing the zigzag with armchair model, the adsorption energy of Hg⁰ on armchair model is higher than that on zigzag model, and the C–Hg bond length of armchair model is shorter than that of zigzag model. This difference indicates that the armchair sites are more favorable for Hg⁰ adsorption than the zigzag sites, due to the existence of unpaired electrons on zigzag edges, while no such electrons are found on armchair edges [35].

3.3. Effect of halogen on Hg⁰ adsorption on carbonaceous surface

In the same manner indicated above, the interactions of Hg⁰ with zigzag and armchair edge sites of the halogen-embedded carbonaceous surface were studied. Different halogens (fluorine, chlorine, bromine, and iodine) were considered. The resultant carbonaceous cluster structures having Hg and halogen at the zigzag and armchair edges are illustrated in Fig. 3, and the optimized C–Hg bond lengths and the adsorption energies are presented in Table 2.

From the theoretical calculation, we found that the mercury atom moved to the carbon atom that is the neighboring site of the halogen atom, instead of moving to the halogen atom for adsorption, which demonstrates that mercury–carbon interactions are much more favorable than mercury–halogen interactions, and Hg⁰ has a preferred interaction with carbon atom in the neighboring site of the halogen atom. Furthermore, the adsorption energies of elemental mercury on the carbonaceous surface with halogen are much higher than that without halogen, indicating that the embed-

ding of halogen can increase the activity of its neighborhood site to increase the adsorption capacity of carbonaceous surface for Hg⁰. This observation is in good agreement with the experimental results in the literature [34,6,36]. The adsorptions belong to chemisorption where the acting forces are strong valence forces resulting in chemical bonding and can be either exothermic or endothermic which can be temperature-favorable in some cases. Comparing the adsorption energies reported in Table 2 reveals that the mercury adsorption energies are in the trend of F > Cl ≈ Br > I.

3.4. Effect of oxygen functional groups on Hg⁰ adsorption on carbonaceous surface

The XANES (X-ray absorption near-edge structure) results suggest that carbon-bound oxygen on the surface captures Hg⁰ during the adsorption experiments, and different types of oxygen surface groups are believed to exist on carbonaceous surfaces [12]. Depending on their history of formation and activation temperature, they could be carboxyl, lactone, phenolic, and carbonyl groups [12]. Hence oxygen functional groups have been investigated for their impact on elemental mercury adsorption on the carbonaceous surface sites. Five oxygen functional groups (carbonyl, lactone, carboxyl, semiquinone and phenol groups) were placed on the cluster models to simulate a carbonaceous surface. Each functional group has been studied to see its effect on elemental mercury adsorption [16]. The carbonaceous cluster structures having mercury and different oxygen functional groups at the zigzag and armchair edges are illustrated in Fig. 4, and the optimized C–Hg bond lengths and the adsorption energies are presented in Table 3.

From the theoretical calculation, the mercury atom tends to move to the carbon atom that is the neighboring site of the oxygen functional group, instead of moving to the oxygen atom for adsorption, which demonstrates that Hg⁰ has a preferred interaction with

Table 2
C–Hg bond lengths and adsorption energies of Hg⁰ adsorption on carbonaceous surface with halogens.

Model		C–Hg bond lengths (Å)	E_{ads} (kJ/mol)
Zigzag	Carbonaceous surface-F	2.29	–81.4
	Carbonaceous surface-Cl	2.31	–76.5
	Carbonaceous surface-Br	2.32	–77.0
	Carbonaceous surface-I	2.33	–66.9
	Carbonaceous surface-F	2.26	–101.9
Armchair	Carbonaceous surface-Cl	2.27	–92.7
	Carbonaceous surface-Br	2.30	–88.7
	Carbonaceous surface-I	2.31	–84.6

Table 3
C–Hg bond lengths and adsorption energies of Hg⁰ adsorption on carbonaceous surface with different oxygen functional groups.

Model		C–Hg bond lengths (Å)	E_{ads} (kJ/mol)
Zigzag	Carbonyl	2.33	–137.6
	Carboxyl	2.36	–16.3
	Lactone	2.27	–164.3
	Phenol	2.29	–43.6
	Semiquinone	2.28	–126.8
Armchair	Carbonyl	2.32	–174.2
	Sarboxyl	2.28	–34.7
	Phenol	2.26	–51.1
	Semiquinone	2.27	–120.1

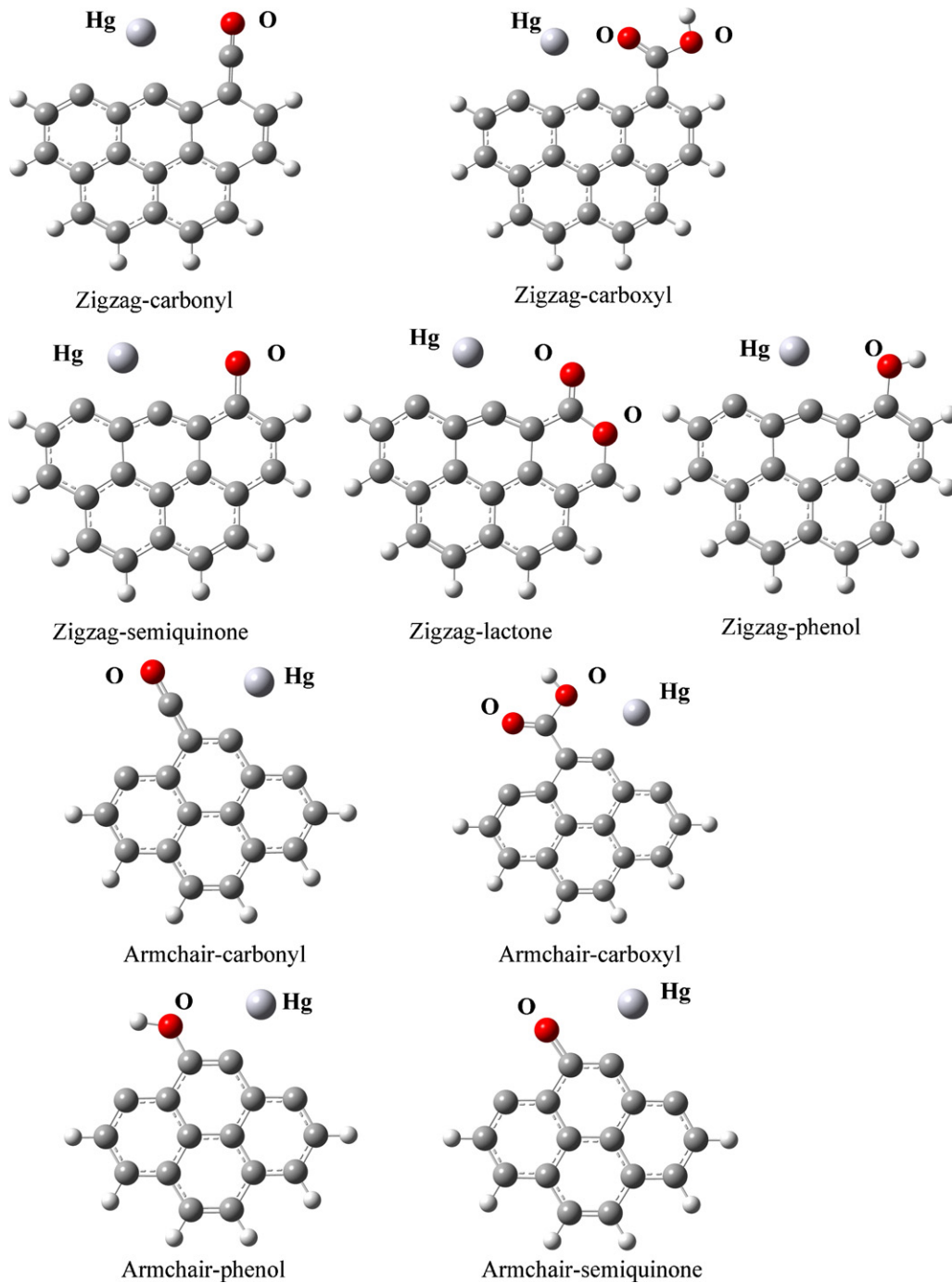


Fig. 4. Adsorption of Hg on carbonaceous surface with oxygen functional groups: lactone, phenol, carboxyl, carbonyl and semiquinone.

carbon atom in the neighboring site of the oxygen functional group. Comparing the Hg^0 adsorption energies on the carbonaceous surface of different oxygen functional groups, we found that different oxygen functional groups have different effects. The adsorption energies for lactone, carbonyl and semiquinone are higher, respectively, while phenol and carboxyl groups have relatively lower adsorption energies. Therefore, we present a mechanism: lactone, carbonyl and semiquinone functional groups favor the chemisorption of Hg^0 because they increase the neighboring site's activity rather than directly provide the active sites. Phenol and carboxyl groups show a physisorption of Hg^0 . Electron transfer processes are likely to be involved during the chemisorption of Hg^0 , and different oxygen groups can participate in the electron transfer processes

on carbon surfaces [12]. Extended π bonding in the extensive aromatic network of carbons permits electron clouds and charges to be highly delocalized, and certain surface functional groups could take up electrons from Hg^0 at specific conditions [12].

The theoretical studies presented above are in good agreement with the experimental results [11–13]. Study on X-ray absorption fine structure (XAFS) spectroscopy has shown that some surface oxygen complexes may affect surface conditions or create certain active sites for Hg^0 bonding [12]. Li et al. [13] have investigated the effect of varying physical and chemical properties of activated carbons on adsorption of elemental mercury (Hg^0) by treating two activated carbons to modify their surface functional groups. They found lactone and carbonyl groups promote mercury adsorp-

tion, while phenol groups may inhibit Hg⁰ adsorption. The high Hg⁰ adsorption capacity of a carbon sample is also found to be associated with a low ratio of the phenol/carbonyl groups. This calculation result can also explain the seemingly conflicting experimental results reported in the literature concerning the influence of oxygen functional groups on Hg adsorption on carbonaceous surface since different experiments possibly deals with different oxygen functional group.

4. Conclusions

In this study, we carried out a density functional theory study to understand the effects of halogen and oxygen functional groups on adsorption mechanism of Hg⁰ on carbonaceous surface. The embedding of halogen atom can increase the activity of its neighboring site which in turn increases the adsorption capacity of the carbonaceous surface for Hg⁰, which is in good agreement with the experimental results. For the effects of oxygen functional groups, we propose a mechanism: lactone, carbonyl and semiquinone favor the chemisorption of Hg⁰, because they increase their neighboring site's activity rather than directly provide the active sites. Phenol and carboxyl functional groups show a physisorption of Hg⁰. The important roles of halogen and oxygen functional groups in the adsorption mechanisms of Hg⁰ by carbonaceous surface provides useful information for reducing mercury emissions from coal-fired power plants. It is important to note that the current investigation focuses on adsorption energy study. In the actual experiments, there could be other factors to affect the overall adsorption performance, such as adsorption rate, oxidation of Hg⁰ to Hg²⁺. Further investigations will be carried out to study the effect of Hg oxidation and adsorption rate and incorporate them into a complete mercury adsorption mechanism. The current investigation showed that density functional method is an effective method to optimize and select sorbents for removing mercury in flue gas.

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