



# Density functional study of hydrogen sulfide adsorption mechanism on activated carbon

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## ABSTRACT

A systematic theoretical study using the density functional theory was performed to provide molecular-level understanding on the adsorption of hydrogen sulfide (H<sub>2</sub>S) on activated carbon. Both zigzag and armchair edge sites of benzene ring models were considered as the possible active sites. The results indicate that the adsorption of H<sub>2</sub>S molecule on activated carbon is highly thermally favorable. The adsorption energies of H<sub>2</sub>S on zigzag and armchair edges are  $-664.9$  and  $-349.6$  kJ/mol, respectively. Activated carbon plays double role, not only facilitates the dissociation of H<sub>2</sub>S molecule but also offers active sites for H<sub>2</sub>S adsorption. The dissociative adsorption and evolution of H<sub>2</sub>S lead to the formations of C–S, C–S–C and C–SH, which is in agreement with experimental data. The shape of the local active site has a strong effect on H<sub>2</sub>S adsorption. The atomic charge of zigzag edge sites is more negative than that of armchair edge sites. Thus, the zigzag edge sites provide stronger force to attract H<sub>2</sub>S than the armchair edge sites. Direct adsorption of H<sub>2</sub>S leads to the formations of C–S or C–SH on activated carbon surface, followed by their evolution into C–S–C. These sulfur species including C–S, C–S–C and C–SH are stable on activated carbon.

## 1. Introduction

Gasification based clean coal technology is regarded as one of the most efficient and environmentally acceptable technologies for comprehensive utilization of coal [1,2]. However, several problems are still needed to be solved in order to realize the large commercial utilization of this technology. Hydrogen sulfide (H<sub>2</sub>S) included in gas products from the gasification process is one of the contaminants causing corrosion of turbine blades and poisoning of catalysts [3]. Therefore, the removal of H<sub>2</sub>S from the coal-derived flue gas is a key part in the gasification based clean coal technology.

The removal of H<sub>2</sub>S by using activated carbons as sorbents is considered as a safe and effective method for coal-derived flue gas desulfurization [4–9]. Various experimental studies have been conducted to investigate the removal of H<sub>2</sub>S by applying activated carbons [10]. However, the mechanism of H<sub>2</sub>S adsorption on carbon surface is still unclear. Moreover, there is even controversy on H<sub>2</sub>S adsorption. Guo et al. [11] studied the adsorption of H<sub>2</sub>S on activated carbons which derived from oil palm shell. They found that all H<sub>2</sub>S adsorbed on activated carbons could be desorbed at room temperature, suggesting a pure physisorption process involved. Köchermann et al. [12] reported that the adsorption of H<sub>2</sub>S on original carbons belonged to pure physisorption under dry and oxygen-free conditions. While Bouzaza et al.

[13] found that the oxidation of H<sub>2</sub>S on carbons could occur under a dry atmosphere. They suggested that the high H<sub>2</sub>S adsorption capacity of carbons could not owe solely to physisorption. Feng et al. [14] reported that H<sub>2</sub>S could be strongly bonded to the unsaturated active sites on carbon surface, which formed by the desorption of surface oxygen functionalities. This implies that chemisorption could occur during H<sub>2</sub>S adsorption on carbons. Although the removal of H<sub>2</sub>S by applying activated carbons has been studied experimentally, the adsorption mechanism of H<sub>2</sub>S on activated carbon has not been well established.

Understanding the detailed interactions of H<sub>2</sub>S with carbon surface is important to the design of more effective sorbents for H<sub>2</sub>S removal. Theoretical studies are needed to elucidate the mechanism of H<sub>2</sub>S adsorption on carbon surface [15]. Density functional theory (DFT) methods were extensively employed to investigate the adsorption mechanisms of gaseous molecules on solid materials [16–18]. It has become a widely used method because it provides a very good balance between accuracy and computational cost [19–22]. Therefore, theoretical calculations will be helpful in elucidating the mechanism of H<sub>2</sub>S adsorption process.

The adsorption of gaseous sulfur species on carbon surface has been studied previously by DFT calculations [23]. Yang et al. [24] investigated the carbon-catalyzed oxidation of SO<sub>2</sub>. They employed both the zigzag and armchair edges of graphene to represent the carbon

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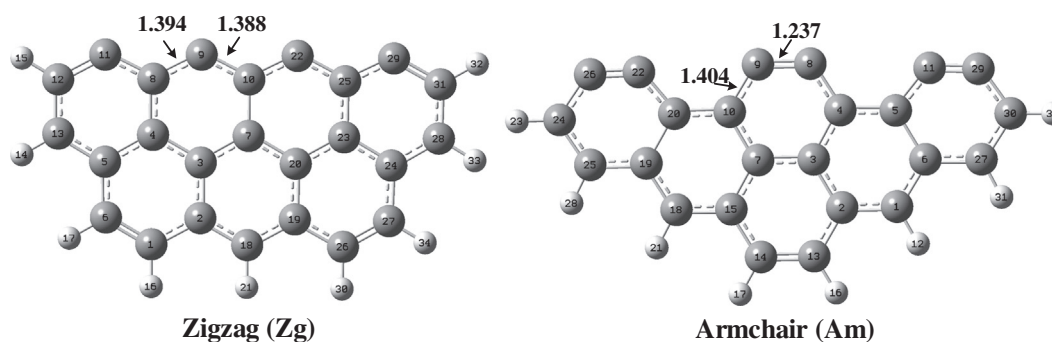


Fig. 1. Activated carbon surface models.

surface, and found that the oxidation of  $\text{SO}_2$  occurred on the zigzag edge sites, whereas the armchair edge sites were not feasible sites. Ashori et al. [25] studied the adsorption of  $\text{H}_2\text{S}$  on carbon nanocone, nanotube, and graphene. They found that the adsorption of  $\text{H}_2\text{S}$  on graphene belonged to physisorption, and the charge transfer between  $\text{H}_2\text{S}$  and graphene was negligible. However, they have only investigated the interaction of  $\text{H}_2\text{S}$  with the basal plane sites, which are quite limited in its potential for representing all of the possible active sites on carbon surface. It has been found that the active sites on the edge planes are more active than that on the basal planes [19]. Unfortunately, the detailed interactions of  $\text{H}_2\text{S}$  molecule with the active sites on the edge plane of activated carbon remain unclear, and the evolution processes of the probable products are still uncertain.

The objective of this study is to elucidate the adsorption mechanism of  $\text{H}_2\text{S}$  on carbon surfaces by DFT calculations. All of the possible approaches of  $\text{H}_2\text{S}$  adsorption on the edge sites of carbon surfaces were considered. Mulliken atomic charge analysis was used to evaluate the charge transfer between the bonding atoms. Energy profiles were provided to elucidate the possible pathways of  $\text{H}_2\text{S}$  evolution on carbon surfaces. To the authors' knowledge, this is the first theoretical study about the adsorption of  $\text{H}_2\text{S}$  on the activated carbon surface at the molecular level. This will be helpful for the design of more effective sorbents for  $\text{H}_2\text{S}$  removal from the coal-derived flue gas.

## 2. Computational details

### 2.1. Methodology

All of the calculations were performed with Gaussian 03 program package [26] implementation of DFT method. The geometry optimizations and energy calculations were carried out at B3PW91/6-31G(d) level of theory [27]. All of the structure geometries were fully optimized in their ground electronic states. The ground state was determined by performing single-point energy calculation at the same level of theory for different electronic states, and the ground state was the lowest-energy one. After geometry optimization, a frequency calculation was performed to ensure the stability of the optimized structure. Furthermore, the energies were calculated by adding the zero-point energy and thermal correction.

The adsorption energy ( $E_{\text{ads}}$ ) of  $\text{H}_2\text{S}$  on carbon surface is calculated as:

$$E_{\text{ads}} = E_{\text{AB}} - (E_{\text{A}} + E_{\text{B}}) \quad (1)$$

where  $E_{\text{AB}}$  is the total energy of the  $\text{H}_2\text{S}$ /substrate system in an equilibrium state;  $E_{\text{A}}$  is the total energy of the adsorbate  $\text{H}_2\text{S}$  molecule;  $E_{\text{B}}$  is the total energy of the substrate. A higher negative value of  $E_{\text{ads}}$  corresponds to a stronger adsorption. Normally, if the adsorption energy is less than  $-30$  kJ/mol, the interaction belongs to physisorption. If the adsorption energy is higher than  $-50$  kJ/mol, the interaction belongs to chemisorption [28,29].

### 2.2. Modeling the activated carbon surface

It is of great importance to establish a reasonable model for the sorbent surface in order to investigate the interactions of  $\text{H}_2\text{S}$  with activated carbon surfaces. Activated carbons are macrostructures formed mainly by aromatic clusters of different sizes. Solid-state  $^{13}\text{C}$  NMR characterization data shows that carbon has chemical structures consisting of 3–7 benzene rings [30]. It was found previously that the reactivity of the active sites strongly depended on its local shape rather than on the size of the cluster models [31,32]. Therefore, benzene ring cluster models with zigzag (Zg) and armchair (Am) edge shapes were employed in this study to simulate the carbon surface. The upper side carbon atoms in the cluster models are unsaturated to simulate the active sites and the carbon atoms on the other sides are terminated with hydrogen atoms [19]. In our previous studies [33,34], similar cluster models with different edge shapes and sizes have been used to represent carbon structures for mercury species adsorption.

Fig. 1 illustrates the cluster models used for this study. The edge carbon atoms on the upper sides were unsaturated to simulate the active sites on carbon surface, and the carbon atoms on the other sides were terminated with hydrogen atoms [35]. For zigzag edge shape, the optimized bond lengths (average C–C: 1.41 Å, C–H: 1.09 Å) and bond angles (average  $\angle\text{C–C–C}$ :  $121^\circ$ ,  $\angle\text{C–C–H}$ :  $120^\circ$ ) were obtained. For armchair edge shape, the optimized bond lengths (average C–C: 1.40 Å, C–H: 1.09 Å) and bond angles (average  $\angle\text{C–C–C}$ :  $121^\circ$ ,  $\angle\text{C–C–H}$ :  $120^\circ$ ) were obtained. Both bond lengths and bond angles of the optimized structures were in good agreement with the experimental data (C–C: 1.42 Å, C–H: 1.07 Å,  $\angle\text{C–C–C}$ :  $120^\circ$ ,  $\angle\text{C–C–H}$ :  $120^\circ$ ) [31].

Although net charge distribution within a molecule cannot be measured experimentally, this property is of great importance from the point view of chemistry [34,36,37]. Mulliken method was used to generate the atomic charge analysis by partitioning the electron density among the atoms in a molecular system. The results of Mulliken atomic charges for selected atoms are presented in Fig. 2. For the purpose of present discussion, suffice it to point out that C(9) and C(22) on the zigzag edge are more active than the other sites owing to their larger negative atomic charge. This implies that C(9) and C(22) are the most liable active sites for  $\text{H}_2\text{S}$  adsorption on zigzag edge sites. Furthermore, C(9) and C(22) on the zigzag edge are more active than those on the armchair edge because of the higher negative atomic charge. The activity of the active sites on the armchair edge is similar because of the same atomic charges. Thus, C(9) and neighboring vacancy on zigzag and armchair edges were used for  $\text{H}_2\text{S}$  adsorption.

## 3. Results and discussion

### 3.1. Adsorption of $\text{H}_2\text{S}$ molecule on activated carbon

$\text{H}_2\text{S}$  adsorption on various sites and all possible adsorption orientations of  $\text{H}_2\text{S}$  on activated carbon surface were considered. In the case of zigzag edge sites, two stable surface intermediates are obtained,

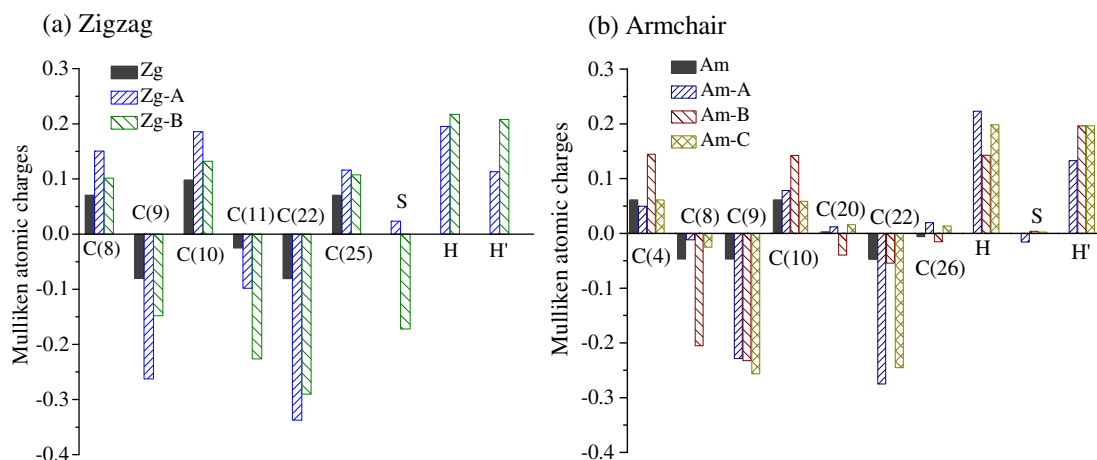


Fig. 2. Atomic charges of  $H_2S$  adsorption: (a) zigzag edge; (b) armchair edge.

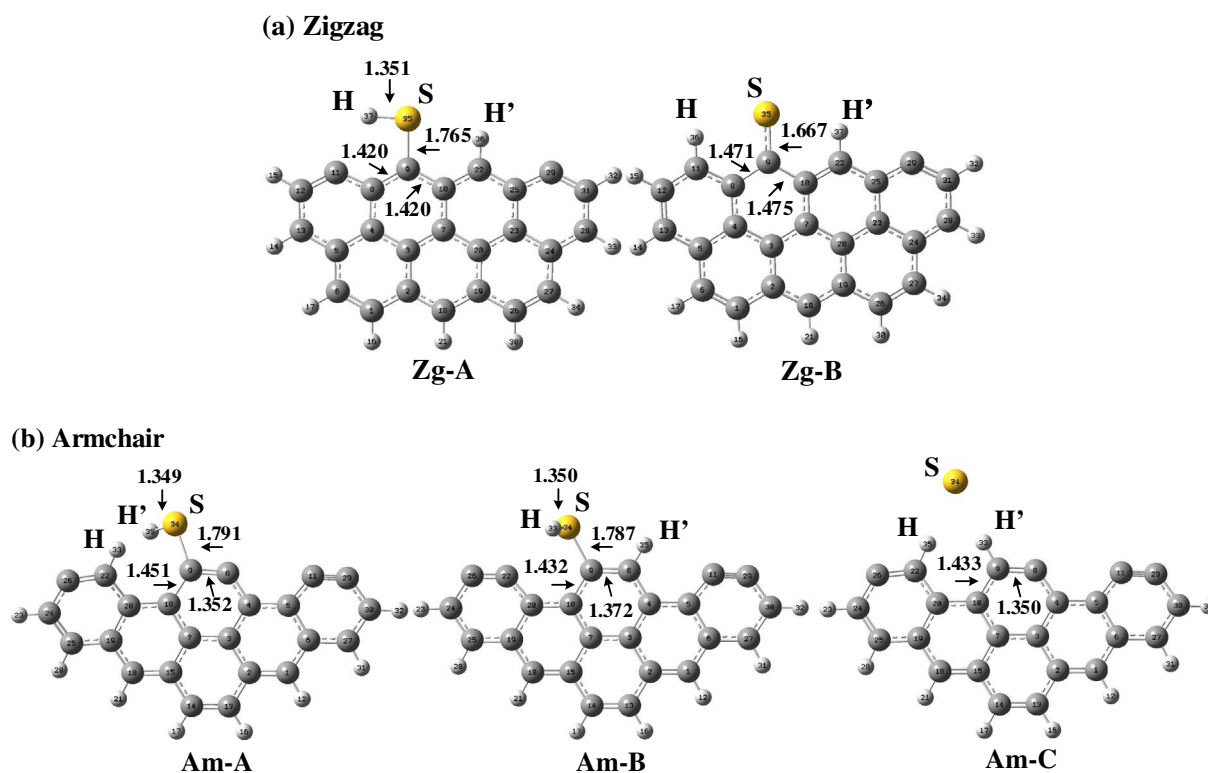


Fig. 3. Adsorption structures of  $H_2S$  on activated carbon: (a) zigzag edge; (b) armchair edge.

including Zg-A and Zg-B, as showed in Fig. 3(a). It is clear that  $H_2S$  is adsorbed dissociatively on the zigzag edge sites.  $H_2S$  molecule dissociates into SH and H atom in Zg-A, S atom and two H atoms in Zg-B. In both cases, visible C–S bonds are formed by the dissociative adsorption of  $H_2S$ . The bond length of C–S in Zg-B is found to be 1.667 Å, which is 0.098 Å shorter than that in Zg-A, indicating that C–S bond in Zg-B is stronger. Moreover, there are some obvious increases in C–C bond lengths where SH or S are directly involved, namely these C–S bonds are substantially weakened by  $H_2S$  adsorption. The adsorption energy of  $H_2S$  is found to be  $-442.0$  kJ/mol in Zg-A, and  $-664.9$  kJ/mol in Zg-B. The results indicate that the adsorption of  $H_2S$  on the zigzag edge sites belongs to chemisorption.

In the case of armchair edge sites, three stable surface intermediates are obtained, including Am-A, Am-B and Am-C, as showed in Fig. 3(b). Similar to zigzag edge sites,  $H_2S$  molecule is adsorbed dissociatively on armchair edge sites.  $H_2S$  molecule breaks down into SH and H atom in

Am-A and Am-B, and the two fragments are further adsorbed on surface C sites. In Am-A, SH and H atom are bonded with C atoms in non-adjacent benzene rings. In Am-B, SH and H atom are adsorbed on two adjacent C atoms in the same benzene ring. In Am-C, dissociated H atoms are bonded with C atoms, whereas S atom turns away from the surface. Since the S atom does not interact with surface C sites, Am-C will not be considered in the following discussions. The C–S bond length in Am-B is shorter than that in Am-A, suggesting that C–S bond in Am-B is stronger. The adsorption energy of  $H_2S$  is  $-227.1$  kJ/mol in Am-A, and  $-349.6$  kJ/mol in Am-B. The adsorption of  $H_2S$  on armchair edge sites belongs to chemisorption. The adsorption energy of  $H_2S$  on armchair edge sites is lower than that of zigzag edge sites, because of the lower negative atomic charge of active C sites on armchair edge.

The calculation results discussed above indicate that  $H_2S$  is adsorbed dissociatively on activated carbon surface. This is similar to the adsorption of  $H_2S$  on ZnO surface [38]. Activated carbon is able to

facilitate the dissociation of H<sub>2</sub>S molecule and offer active sites for H<sub>2</sub>S adsorption. Similar results have been reported experimentally by Feng et al. [14]. They found that the dissociative adsorption is involved in the adsorption of H<sub>2</sub>S on activated carbons. Moreover, the adsorption of H<sub>2</sub>S on activated carbon belongs to chemisorption. Sun et al. [39] studied experimentally the H<sub>2</sub>S removal abilities of various activated carbons and they suggested that H<sub>2</sub>S can react with the active sites on activated carbon by forming sulfur species. Cal et al. [40] performed H<sub>2</sub>S removal experiments by activated carbons, and suggested that H<sub>2</sub>S can react with active carbon sites. Feng et al. [41] conducted experiment to investigate the adsorption of H<sub>2</sub>S on activated carbons. They found that H<sub>2</sub>S could be adsorbed chemically on unsaturated active sites. The calculation results agree well with these experimental results that chemisorption occurs during H<sub>2</sub>S removal by activated carbons.

In order to further evaluate the bond strength in H<sub>2</sub>S adsorbed structures, Mulliken population analyses are performed to analysis the interaction between atoms. Generally, if the value of the bond population is highly positive, the bond will be a strong covalent bond; whereas if it is close to zero, no interaction will be occurred between the atoms [19,42]. Some pertinent bond populations of H<sub>2</sub>S adsorption on zigzag edge sites are listed in Table 1. The dissociation of H<sub>2</sub>S molecule can be further verified by the bond population between S atom and H atom. In Zg-A, the bond population of S–H is 0.254, suggesting a strong interaction of S with H. However, S does not interact with H' in Zg-A as indicated by S–H' bond population (zero). This implies that H<sub>2</sub>S molecule decomposes into SH and H atom in Zg-A. In Zg-B, both the bond populations of S–H and S–H' are zero, implying that H<sub>2</sub>S molecule breaks down into S atom and two H atoms. Moreover, the bond population of C–S in Zg-B is higher compared with that in Zg-A. This suggests that C–S bond in Zg-B is stronger. The high positive value of C–S bond populations in these structures indicates that S and SH are strongly bonded with surface C atoms. In addition, the bond populations of C(8)–C(9) and C(9)–C(10) are decreased upon the adsorption of H<sub>2</sub>S. For example, the bond population of C(8)–C(9) in Zg-B decreases from 0.334 to 0.231, and the bond population of C(9)–C(10) decreases from 0.341 to 0.226. This indicates that C(8)–C(9) and C(9)–C(10) have been weakened by H<sub>2</sub>S adsorption.

The bond populations of H<sub>2</sub>S adsorption on armchair edge sites are listed in Table 2. Similar to the adsorption of H<sub>2</sub>S on zigzag edge sites, C–C bonds are weakened where SH or H is directly adsorbed. The bond population of C–S in Am-B is higher compared to that in Am-A. This indicates that the interaction of S atom with C atom is stronger in Am-B. Moreover, the bond populations of C–S in Am-A and Am-B are found to be highly positive, indicating a strong interaction of S atom with surface C site.

The results of Mulliken population analyses suggest that stable C–S and C–SH species could be formed by the adsorption of H<sub>2</sub>S molecule on activated carbon. XPS analysis results found that sulfur species can incorporate into the carbon matrix, resulting in the formation of C–S, C–S–C and C–S–H [43,44]. Shi et al. [45] analyzed the adsorption of H<sub>2</sub>S on activated carbon by using XPS. They found that C–S groups can

**Table 1**  
Bond populations of H<sub>2</sub>S and dissociated species on zigzag (Zg) edge of activated carbon.

	Zigzag edge		Dissociated species on zigzag edge			
	Zg	Zg-A	Zg-B	Zg-C	Zg-D	Zg-E
C(8)–C(9)	0.334	0.279	0.231	0.224	0.232	
C(9)–C(10)	0.341	0.336	0.226	0.319	0.237	0.304
C(10)–C(22)						0.373
C(9)–S		0.279	0.493	0.294	0.477	0.231
C(22)–S						0.231
S–H		0.254	0	0.248	0	0
S–H'		0	0	0	0	0

**Table 2**  
Bond populations of H<sub>2</sub>S and dissociated species on armchair (Am) edge of activated carbon.

	Armchair edge			Dissociated species on armchair edge			
	Am	Am-A	Am-B	Am-C	Am-D	Am-E	Am-F
C(8)–C(9)	0.652	0.440	0.436	0.437	0.420	0.427	0.399
C(9)–C(10)	0.461	0.373	0.408	0.441	0.373	0.405	0.336
C(8)–S						0.285	
C(9)–S		0.246	0.282		0.283		0.340
S–H		0	0.247	0	0	0.248	0
S–H'		0.248	0	0	0.247	0	0

be formed by H<sub>2</sub>S adsorption. The calculation results are consistent with the XPS analysis results. Feng et al. [46] studied the adsorption of H<sub>2</sub>S on activated carbons, and found that sulfur species adsorbed on carbon surface could not be removed entirely under high temperature (800 °C) in an inert environment. They suggested that sulfur species formed by H<sub>2</sub>S dissociative adsorption could be embedded into the carbon matrix with the formation of C–S bond. The calculation results agree well with the experimental results.

The atomic charges of H<sub>2</sub>S adsorption on the zigzag edge are showed in Fig. 2(a). It is clear that the atomic charges of active C atoms in those structures become more negative after H<sub>2</sub>S adsorption. This indicates that the adsorption of H<sub>2</sub>S on the zigzag edge leads to charge transfer among atoms. For example, in Zg-B, the atomic charge of C(9) increases from –0.081 to –0.148. Furthermore, S atom in the free H<sub>2</sub>S molecule has a negative charge of –0.258, and it decreases to –0.172 after H<sub>2</sub>S adsorption. The atomic charges of H<sub>2</sub>S on the armchair edge are illustrated in Fig. 2(b). Similar to zigzag edge, the adsorption of H<sub>2</sub>S on armchair edge leads to charge transfer among atoms. This conclusion is obvious that the atomic charges of C atoms, which bonded with SH and H, are more negative after H<sub>2</sub>S adsorption. For example, in Am-A, the atomic charge of C(9) changes from –0.047 to –0.229. The results of atomic charge indicate that charge transfer among atoms occurs during H<sub>2</sub>S adsorption, and thus enhancing the interaction of S atom with surface C atoms. The electrons of S and H atoms in the molecular H<sub>2</sub>S transfer to the surface C atoms. The charge transfer proves the chemisorption of H<sub>2</sub>S on activated carbon surface.

Further, the interactions in these stable configurations are characterized by the electron density difference contour, as shown in Fig. 4. Solid line areas correspond to an increased density in the complex, while losses are denoted by the dotted line regions. In these H<sub>2</sub>S adsorbed structures, obvious solid line areas exist between S atom and C atom, indicating the formation of covalent bond due to the electron transfer. This electron transfer decreases the electron density of the S–H bond, which results in the weakening or breaking of S–H bond.

To evaluate the H<sub>2</sub>S removal ability of activated carbon, the comparison of activated carbon with various adsorbents were carried out from the point view of adsorption energy, and summarized in Table 3. It is clear that the adsorption energy of H<sub>2</sub>S on activated carbon surface is higher than that of the other adsorbents, indicating a higher H<sub>2</sub>S removal ability.

### 3.2. Co-adsorption of dissociated species of H<sub>2</sub>S on activated carbon

In order to investigate the adsorption and evolution processes of H<sub>2</sub>S on activated carbon surface, it is necessary to investigate the co-adsorption of dissociated species of H<sub>2</sub>S on non-neighboring sites, namely, the co-adsorption of SH and H, as well as the co-adsorption of S, H and H, respectively.

The surface intermediates formed by dissociated species of H<sub>2</sub>S co-adsorption on zigzag edge are presented in Fig. 5(a). Zg-C represents the intermediate formed by SH and H co-adsorption on zigzag edge. The

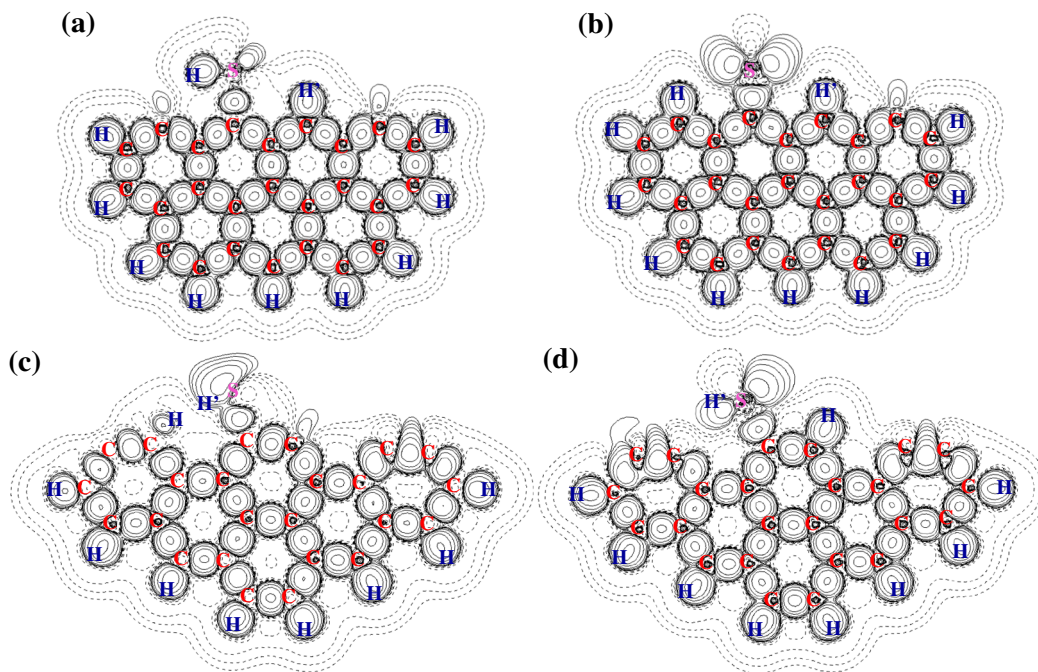


Fig. 4. Electron density difference contour plot of H<sub>2</sub>S on activated carbon: (a) Zg-A; (b) Zg-B; (c) Am-A; (d) Am-B.

Table 3

The comparison of the adsorption energy of the most stable structure of H<sub>2</sub>S on activated carbon with the other adsorbents.

Sorbents	Adsorption energy (kJ/mol)	Reference
Fe <sub>2</sub> O <sub>3</sub>	− 107.5	[47]
Gallium nitride	− 31.8	[48]
Pt-SWCNT	− 481.6	[49]
TiO <sub>2</sub>	− 169.8	[50]
Cu <sub>2</sub> O	− 86.4	[51]
ZnO	− 131.6	[38]
Activated carbon	− 664.9	Present study

co-adsorption energy of SH and H in Zg-C is − 421.1 kJ/mol. Zg-D and Zg-E represent the structures of S, H and H co-adsorption on zigzag edge. The co-adsorption energy of S, H and H is − 621.3 kJ/mol in Zg-D, and is − 646.2 kJ/mol in Zg-E. The co-adsorptions of dissociated species of H<sub>2</sub>S on zigzag edge sites are highly exothermic processes.

The surface intermediates formed by dissociated species of H<sub>2</sub>S co-adsorption on armchair edge are illustrated in Fig. 5(b). Am-D and Am-E represent the intermediates formed by SH and H co-adsorption on armchair edge. The co-adsorption energy of SH and H is − 216.3 kJ/mol in Am-D, and is − 256.6 kJ/mol in Am-E. Am-F represents the structure of S, H and H co-adsorption on armchair edge. The co-adsorption energy of S, H and H is − 386.3 kJ/mol in Am-F. The co-adsorptions of dissociated species of H<sub>2</sub>S on armchair edge are highly exothermic processes. Similar to the adsorption of H<sub>2</sub>S molecule, the co-

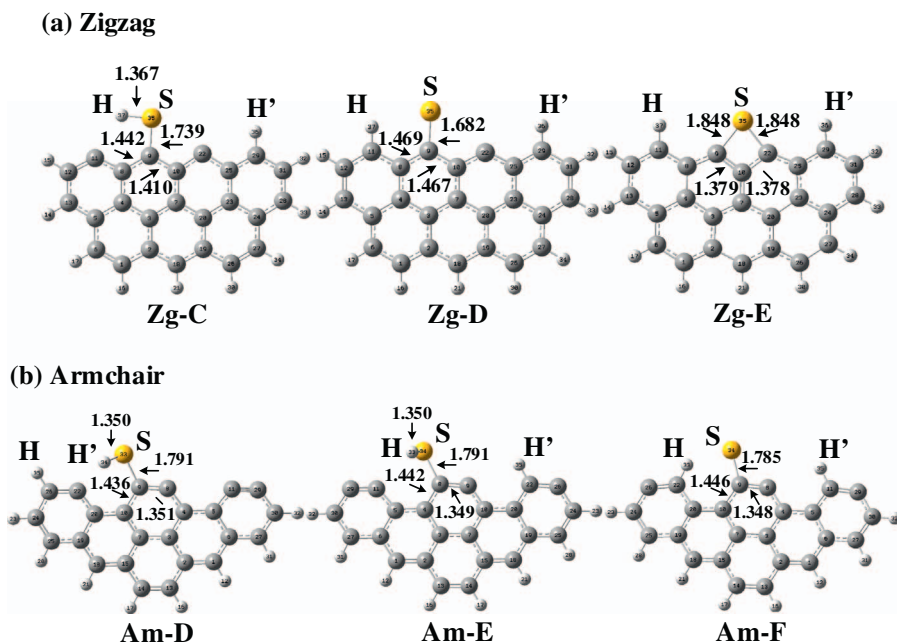


Fig. 5. Co-adsorption structures of dissociated species of H<sub>2</sub>S on activated carbon: (a) zigzag edge; (b) armchair edge.

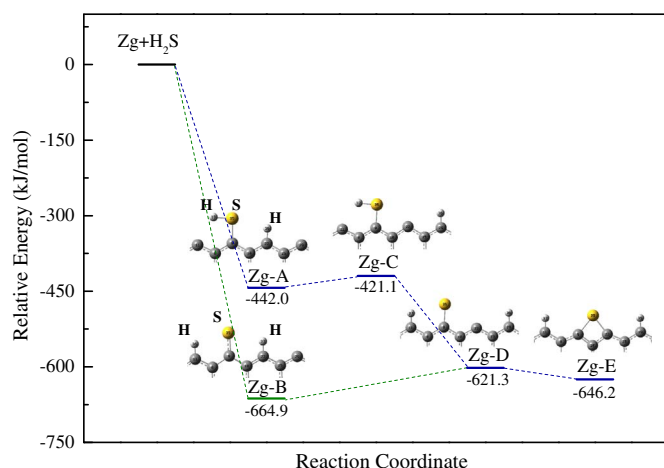


Fig. 6. Evolution processes and energy profiles of H<sub>2</sub>S on zigzag edge of activated carbon.

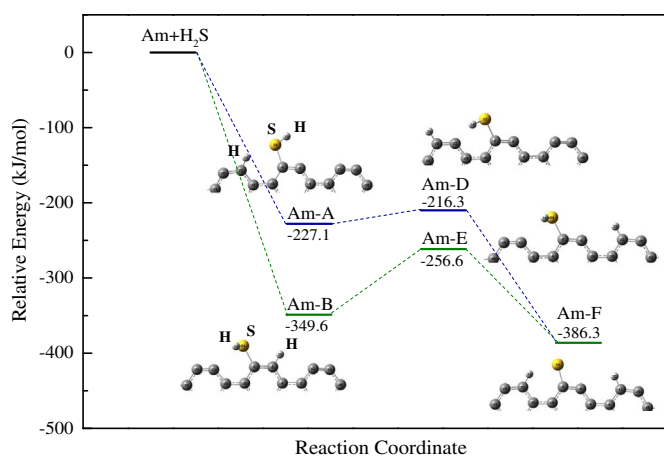


Fig. 7. Evolution processes and energy profile of H<sub>2</sub>S on armchair edge of activated carbon.

adsorption of dissociated species of H<sub>2</sub>S on zigzag edge is more exothermic than that on armchair edge.

Table 1 display the corresponding bond populations of co-adsorption of dissociated species of H<sub>2</sub>S on zigzag edge. In Zg-E, the bond populations of C(9)–S and C(22)–S are both 0.231. This indicates that S atom is interacting with the two C atoms C(9) and C(22), namely C–S–C is formed. In addition, the high positive values of C–S bond populations in these intermediates indicate that C–S, C–SH and C–S–S formed by the co-adsorption of dissociated species of H<sub>2</sub>S on activated carbon surface are stable.

### 3.3. The evolution process and energy of different pathways of H<sub>2</sub>S on activated carbon surface

To characterize the probable reaction pathways of H<sub>2</sub>S on activated carbon surface, schematic energy profiles of H<sub>2</sub>S adsorption and evolution were examined. The energies of these optimized structures are relative to the reactants. The evolution processes and energy profiles of H<sub>2</sub>S on zigzag edge are presented in Fig. 6. It is clearly that the intermediate Zg-B is the most likely structure to be formed by H<sub>2</sub>S molecule adsorption on zigzag edge because its pathway is more exothermic. If the intermediate Zg-B transforms into the intermediate Zg-D with H atom migrating to C(29), only an energy of 43.6 kJ/mol is needed. Moreover, the intermediate Zg-A is also likely to be formed because the pathway is highly exothermic. The transformation of the intermediate Zg-A into the intermediate Zg-C requires an energy of 20.9 kJ/mol.

Although the migration of H atom on carbon surface is endothermic, this process would proceed possibly because the fuel gases have higher temperatures. In addition, the reaction energy of H<sub>2</sub>S adsorption can also compensate for the required energy. After the migration of H, the intermediate Zg-E will be formed because its pathway is exothermic. The total energy of C–S–C forming pathway is 18.7 kJ/mol for intermediate Zg-B, and –204.2 kJ/mol for intermediate Zg-A.

The reaction pathways of H<sub>2</sub>S adsorption and evolution on armchair edge are presented in Fig. 7. The above calculation results show that only C–SH species can be formed by the direct adsorption of H<sub>2</sub>S molecule on armchair edge. So the evolution process of C–SH species is necessary to be investigated. In Am-F, C–S species is formed by the co-adsorption of S, H and H on armchair edge. Am-F can be obtained from Am-B via Am-E, and an energy of 93.0 kJ/mol is required. Meanwhile, C–S species can also be obtained from Am-A via Am-D. The total energy of C–S forming on armchair edge from intermediate Am-A is –159.2 kJ/mol. The calculation results indicate that C–S, C–S–C and C–SH can be formed by H<sub>2</sub>S adsorption on activated carbon surface, which is in agreement with XPS analysis results [43,44].

## 4. Conclusions

The density functional theory calculation and cluster model were employed to investigate the adsorption mechanism of H<sub>2</sub>S on activated carbon surface at the molecular level. The adsorption of H<sub>2</sub>S on carbon surface is a dissociative process and belongs to chemisorption. The active sites on the zigzag edge are more active for H<sub>2</sub>S adsorption than those on the armchair edge, because of their higher negative atomic charges. Thus, the adsorption of H<sub>2</sub>S on zigzag edge sites is more exothermic. The direct adsorption of H<sub>2</sub>S molecule leads to the forming of C–S or C–SH on the zigzag edge, and C–SH on the armchair edge. During the process of H<sub>2</sub>S adsorption, charge transfer occurs and electrons of S and H atoms in the molecular H<sub>2</sub>S transfer to the surface C atoms. The co-adsorption of SH and H, as well as the co-adsorption of S, H and H are highly exothermic processes. Stable C–S–C can be formed by the co-adsorption of S, H and H on activated carbon surface. The evolution processes and energy profiles of H<sub>2</sub>S on activated carbon surface were obtained. The results indicates that activated carbon plays double role, first as a catalyst for H<sub>2</sub>S molecule dissociation, and second as a sorbent offering active sites for H<sub>2</sub>S adsorption.

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