Fuel Processing Technology 171 (2018) 258–264

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Density functional study of hydrogen sulfide adsorption mechanism on activated carbon

Fenghua Shen, Jing Liu*, Zhen Zhang, Yuchen Dong, Chenkai Gu

State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

ARTICLE INFO

Keywords:
H_2S
Adsorption
Activated carbon
Density functional theory
Coal gasification

ABSTRACT

A systematic theoretical study using the density functional theory was performed to provide molecular-level understanding on the adsorption of hydrogen sulfide (H_2S) 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_2S molecule on activated carbon is highly thermally favorable. The adsorption energies of H_2S 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_2S molecule but also offers active sites for H_2S adsorption. The dissociative adsorption and evolution of H_2S 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_2S 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_2S than the armchair edge sites. Direct adsorption of H_2S 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_2S) 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_2S from the coal-derived flue gas is a key part in the gasification based clean coal technology.

The removal of H_2S 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_2S by applying activated carbons [10]. However, the mechanism of H_2S adsorption on carbon surface is still unclear. Moreover, there is even controversy on H_2S adsorption. Guo et al. [11] studied the adsorption of H_2S on activated carbons which derived from oil palm shell. They found that all H_2S 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_2S on original carbons belonged to pure physisorption under dry and oxygen-free conditions. While Bouzaza et al. [13] found that the oxidation of H_2S on carbons could occur under a dry atmosphere. They suggested that the high H_2S adsorption capacity of carbons could not owe solely to physisorption. Feng et al. [14] reported that H_2S 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_2S adsorption on carbons. Although the removal of H_2S by applying activated carbons has been studied experimentally, the adsorption mechanism of H_2S on activated carbon has not been well established.

Understanding the detailed interactions of H_2S with carbon surface is important to the design of more effective sorbents for H_2S removal. Theoretical studies are needed to elucidate the mechanism of H_2S 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_2S 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_2. They employed both the zigzag and armchair edges of graphene to represent the carbon

---

* Corresponding author.
E-mail address: liujing27@mail.hust.edu.cn (J. Liu).

https://doi.org/10.1016/j.fuproc.2017.11.026
Received 21 September 2017; Received in revised form 25 November 2017; Accepted 27 November 2017

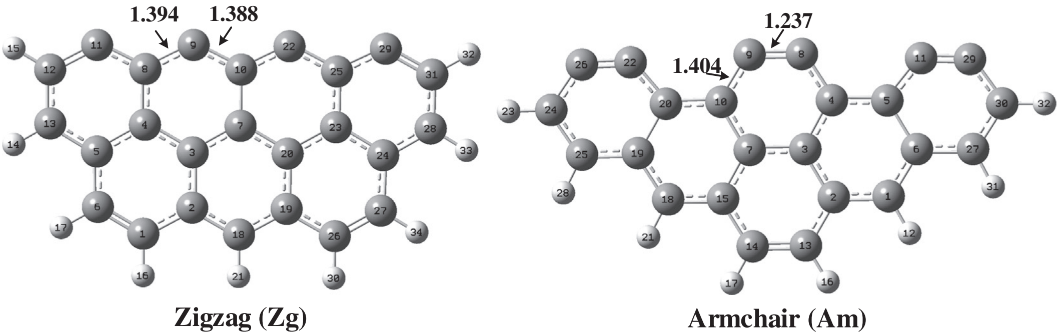

Fig. 1. Activated carbon surface models.

surface, and found that the oxidation of 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 H_2S on carbon nanocone, nanotube, and graphene. They found that the adsorption of H_2S on graphene belonged to physisorption, and the charge transfer between H_2S and graphene was negligible. However, they have only investigated the interaction of H_2S 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 H_2S 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 H_2S on carbon surfaces by DFT calculations. All of the possible approaches of H_2S 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 H_2S evolution on carbon surfaces. To the authors' knowledge, this is the first theoretical study about the adsorption of H_2S on the activated carbon surface at the molecular level. This will helpful for the design of more effective sorbents for H_2S 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_{ads}) of H_2S on carbon surface is calculated as:

$$E_{ads} = E_{AB} - (E_A + E_B) \tag{1}$$

where E_{AB} is the total energy of the H_2S/substrate system in an equilibrium state; E_A is the total energy of the adsorbate H_2S molecule; E_B is the total energy of the substrate. A higher negative value of E_{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 H_2S with activated carbon surfaces. Activated carbons are macrostructures formed mainly by aromatic clusters of different sizes. Solid-state ^{13}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 ∠C—C—C: 121°, ∠C—C—H: 120°) 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 ∠C—C—C: 121°, ∠C—C—H: 120°) were obtained. Both bond lengths and bond angels of the optimized structures were in good agreement with the experimental data (C—C: 1.42 Å, C—H: 1.07 Å, ∠C—C—C: 120°, ∠C—C—H: 120°) [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 H_2S 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 H_2S adsorption.

3. Results and discussion

3.1. Adsorption of H_2S molecule on activated carbon

H_2S adsorption on various sites and all possible adsorption orientations of H_2S on activated carbon surface were considered. In the case of zigzag edge sites, two stable surface intermediates are obtained,