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Effect of SO_3 on elemental mercury adsorption on a carbonaceous surface

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ABSTRACT

The effect of SO_3 on elemental mercury adsorption on a carbonaceous surface is investigated by the density-functional theory calculations. A nine-fused benzene ring model is employed to represent the carbonaceous surface. The edge atoms on the upper side of the model remain unsaturated to simulate the active sites for reaction. All of the possible approaches in which SO_3 is adsorbed on the carbonaceous surface are conducted to evaluate their effects on Hg adsorption. The results indicate that the carbonaceous surface is energetically favorable for SO_3 adsorption, which causes that SO_3 competes for the active sites on the carbonaceous surface. But adsorption of SO_3 decreases the adsorption capacity of the carbonaceous surface for Hg^0 since SO_3 suppresses the activity of its next-nearest-neighbor carbon atom and negatively affects on the frontier molecular orbitals and LUMO–HOMO energy gap of the carbonaceous surface.

1. Introduction

Mercury is one of the most toxic metals with adverse effects on the important bodily processes and ecosystem [1]. Coal-fired power plants are regarded as the greatest anthropogenic source of mercury emission [2,3]. Hence, reducing the emission of mercury from coal-fired power plants has already become a major environmental and regulatory concern.

During combustion, mercury is transferred into different forms in flue gas, mainly including oxidized mercury, particulate-bound mercury and elemental mercury (Hg^0) [4]. Oxidized mercury can be captured with high efficiency by flue gas desulfurization scrubbing units because of its water-soluble feature. Particulate-bound mercury can be removed by electrostatic precipitators and fabric filters [5]. However, elemental mercury (Hg^0) is water insoluble, high volatile and chemical inert and is therefore relatively difficult to be eliminated from coal-derived flue gas [6]. Many studies have been performed to design effective sorbent to capture Hg^0 from the combustion flue gas. Activated carbon injection (ACI) into the flue gas is considered as one of most mature and favorable technology to capture mercury through adsorption processes [7–9].

Currently, many experimental studies have been carried out to understand the mechanism of mercury adsorption on the carbonaceous surface [10,11]. These previous efforts indicate that acidic functional group in coal-fired flue gas greatly affects the mercury adsorption [12,13]. Most field sampling data from power plants have demonstrated that the cobenefit of exiting de-SO_x technology decreases the adsorption capacity of ACI for Hg^0 [14]. Full-scale sorbent injection tests show the mercury capture of ACI from 85% (no SO_3 injection) to 17% (SO_3 injection set at 10.7 ppm) [15]. Hence, ACI cannot be successful in mercury adsorption at sites with substantial concentrations of SO_3 [16]. Then, investigations preformed by Krishnakumar and Niksa [17] have examine the effect of SO_3 on mercury adsorption. They have concluded that the SO_3 inhibits mercury oxidation and thus decreases mercury removal. Additionally, Zhuang et al. [18] have reported that SO_3 vapor competes against mercury vapor for the active sites on the carbonaceous surface, which causes that the adsorption capacity of ACI for Hg^0 decays exponentially with increasing SO_3 level. Therefore, reducing SO_3 vapor concentration can be regarded as the best candidate of improving ACI performance on Hg^0 capture, but it is still a challenge for entire SO_3 removal from flue gas.

On the other hand, the experimental observations indicate that surface oxygen complexes can increase the activity of its neighboring sites and thus present a positive effect on mercury adsorption [19]. Meanwhile, mercury is also adsorbed easily at particular sites where high sulfur concentration exists [7,20]. However, SO_3 consisted of oxygen and sulfur atom exhibits the obvious discrepancies in the effect on Hg^0 adsorption. Currently, it is still difficult to evaluate the mechanism of mercury on surface via experimental test. To our knowledge, correlations between SO_3 and carbonaceous surface have not been well established. Little is known at the molecular level about the interaction of mercury and SO_3 with carbonaceous surface. It is still not clear why SO_3 adsorption on the carbonaceous surface presents a negative impact of mercury capture. Quantum chemical methods are increasingly used to clarify the mechanism

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of mercury adsorption [4,5,21,22], which prove to be powerful tools and can solve the problem beyond the limited experiments.

This state of the art has motivated the present study. The purpose of this work is to investigate the effect of SO_3 on Hg^0 adsorption capacity of the carbonaceous surface by the density functional theory (DFT) calculation. All of the possible approaches of SO_3 adsorption on the carbonaceous surface are examined to find the possible sites and structure of the adsorbed species. Then the Hg^0 adsorption by the carbonaceous surface with and without SO_3 is discussed using Mulliken total atomic charges, equilibrium geometrical parameters and LUMO–HOMO energy gap.

2. Model and computational details

2.1. Carbonaceous surface model

First, a valid model for the sorbent surface is very important to study Hg^0 adsorption on carbonaceous surface at the molecular level. Chen and Yang [23] have proposed six graphite models with increasing sizes up to seven rings, and then their properties are studied using the HF method. The conclusion has shown that the calculated chemical performances of the graphene model are in agreement with the experimental results. On the other hand, Montoya et al. [24] have found that the reactivity of the carbonaceous model does not depend strongly on the molecular size. Therefore, a single graphene layer has been usually employed to serve as a representative cluster species to simulate the carbonaceous surface [4,5,21,25,26]. Thus, a nine-fused benzene ring is conducted to model the carbonaceous surface in our simulation.

The experimental evidences have shown that there are some partially-stabilized radical sites at graphene edges [27]. Therefore, in this work, the edge atoms on the upper side of the single graphene layer remain bare or unterminated to simulate carbon active sites for reaction, and the hydrogen termination is used in saturating the other edge atoms. Although analysis of the chemical nature of graphene edges indicates that complete saturation with H or other heteroatoms is unrealistic and not all graphene edge sites are saturated with H [28], the use of hydrogen remains the best choice in consideration of both the charge balance and suitable chemical environment [23]. On the other hand, a hydrogen atom on the boundary terminal has been proven its adequacy in many applications [21,29]. Hence, it is a reasonable approximation in this work to simulate the carbonaceous surface by a nine-fused benzene ring in which its bottom edges are saturated by hydrogen atoms.

2.2. Computational methods

All of the possible approaches of SO_3 adsorption on the active sites of carbonaceous surface are considered to examine their effects on Hg adsorption using quantum chemical method. Their geometries are fully optimized in the electronic ground states. Furthermore, Mulliken population is calculated to determine the charge distribution. Then the adsorption capacity of carbon atom is evaluated by its atomic charge. That is to say, if one carbon atom becomes more electronegative, its propensity for Hg adsorption is reinforced [21].

All calculations are performed using the DFT calculation, which are implemented by a simulating tool of Dmol3 code [30]. The gradient-corrected exchange-correlation functional (GGA) theory is applied in combination with the BLYP gradient-corrected functional method [31,32]. The 1.0×10^{-5} Ha quality is to set the threshold which is used to determine whether a self-consistent field (SCF) has converged. During the geometry optimization, the convergence thresholds for the maximum energy change, the maximum force and the maximum displacement are set as 2×10^{-5} Hartree, 0.004 Hartree Å^{-1} and 0.005 Å, respectively. The atomic orbital basis set is specified as double numerical plus d-functions (DND) [33]. All calculations are performed with spin polarization. The energies of the frontier molecular orbitals, viz., the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbital (LUMO) are determined.

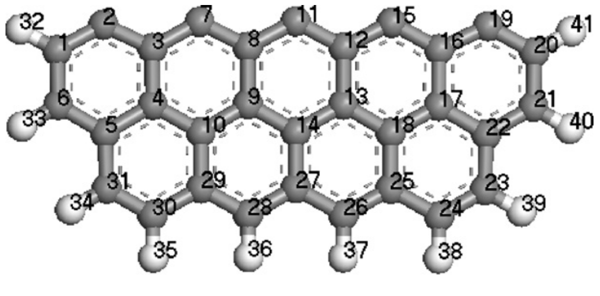

Fig. 1. Optimized geometry of carbonaceous surface. The gray balls denote carbon; and the white balls denote hydrogen.

The absorption energy is calculated using the following formula:

$$E_{\text{ads}} = E(\text{AB}) - E(\text{A}) - E(\text{B}) \tag{1}$$

where E_{ads} is adsorption energy. E (AB) is the total energy of B molecule adsorbed by A molecular surface. E (A) and E (B) denote the total energy of A and B molecule, respectively.

It is noted that our work maybe show some discrepancies in the magnitude of the calculated adsorption energy and bond length reported in the previously theoretical literature using the Gaussian software package [4], which may result from the different computational algorithm and software programs. Hence, a comparison of their absolute values is not a significant meaning, and their relative values are considered to be useful.

3. Results and discussion

3.1. SO_3 adsorption on the carbonaceous surface

Fig. 1 illustrates the optimized geometries of the graphene model (Model A). The carbon atoms are labeled to facilitate the discussion below. The optimized parameters of Model A are given in Table 1. The calculated bond lengths and bond angles are in good agreement with the experimental observed data [23]. The dihedral angles are all either 0° or 180°, indicating that the carbonaceous surface is characteristic of an expected single plane sheet structure.

Mulliken total atomic charges of some atoms in Model A are listed in Table 2. The atoms C(3), C(8), C(12), and C(16) exhibit a remarkable excess of negative charge than the other carbon atoms, suggesting that they present a strong propensity for Hg adsorption [21].

Then, all of the possible approaches of SO_3 adsorption on a carbonaceous surface are discussed in order to evaluate the SO_3 effect on Hg^0 adsorption. It can be seen that the atoms C(2) and C(19) locate at the corner of the cluster model. Such sites cannot provide

Table 1
Optimized parameters of the carbonaceous surface.

Average parameter	Model A	Exp
C—C(Å)	1.40	1.42
C—H(Å)	1.09	1.07
∠C—C—C (°)	120	120
∠C—C—H (°)	120	120