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Density Functional Theory Study on Mechanism of Mercury Removal by CeO₂ Modified Activated Carbon

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Abstract: Doping of CeO₂ on activated carbon (AC) can promote its performance for mercury abatement in flue gas, while the Hg⁰ removal mechanism on the AC surface has been rarely reported. In this research, density functional theory (DFT) calculations were implemented to unveil the mechanism of mercury removal on plain AC and CeO₂ modified AC (CeO₂-AC) sorbents. Calculation results indicate that Hg⁰, HCl, HgCl and HgCl₂ are all chemisorbed on the adsorbent. Strong interaction and charge transfer are shown by partial density of states (PDOS) analysis of the Hg⁰ adsorption configuration. HCl, HgCl and HgCl₂ can be dissociatively adsorbed on the AC model and subsequently generate HgCl or HgCl₂ released to the gas phase. The adsorption energies of HgCl and HgCl₂ on the CeO₂-AC model are relatively high, indicating a great capacity for removing HgCl and HgCl₂ in flue gas. DFT calculations suggest that AC sorbents exhibit a certain catalytic effect on mercury oxidation, the doping of CeO₂ enhances the catalytic ability of Hg⁰ oxidation on the AC surface and the reactions follow the Langmuir–Hinshelwood mechanism.

Keywords: flue gas mercury removal; activated carbon sorbent; CeO₂ doping; density functional theory(DFT) calculations

1. Introduction

Mercury pollution has attracted widespread attention due to the toxic effect, mobility, persistence, and bioaccumulation [1]. In 2013, the Minamata Convention was concluded among more than 90 countries to control mercury emission, which meant the arrival of a new stage in global mercury pollution control [2,3]. Flue gas is regarded as one of the major sources of mercury emitted to the atmosphere. In China, the Emission Standard of Air Pollutants for Thermal Power Plant (GB13223-2011) released in 2011, prescribes the emission of mercury species from coal-fired boilers as below 0.03 mg/m³ [4–6]. Mercury mainly exists in flue gas as elemental form (Hg⁰), oxidized form (Hg²⁺), and particulate form (Hg^P) [7]. Hg²⁺ and Hg^P can be removed by existing pollutant control equipment in coal-fired power stations, while Hg⁰ is hard to control since it is chemically stable and insoluble in water [8–10]. Consequently, Hg⁰ removal from flue gas is a research hotspot for mercury pollution control in coal-fired power stations.

Activated carbon injection (ACI) is regarded as a mature technology to control Hg⁰ in flue gas, but the high cost makes it insupportable for coal-fired power plants [11,12]. Modification of carbon based sorbents can enhance the adsorption capacity for Hg⁰ in flue gas and reduce the consumption of AC sorbents, saving a large amount of operating expenses for coal-fired power plants. Therefore,

various modification methods on AC sorbent have been studied recently. CeO_2 is a promising catalytic oxidation material which is widely used in the field of denitrification and mercury removal [13–16]. Experimental studies have shown that the doping of metal oxides such as CeO_2 can change the physical and chemical conditions on the AC surface and significantly enhance its mercury removal efficiency in coal-fired flue gas [17–23]. Tian et al. tested the mercury removal performance of CeO_2 doped AC in a simulated flue gas efficiency test and characterization results showed that CeO_2 had good dispersibility on the AC surface and significantly improved the mercury removal efficiency by introducing a large number of functional groups which can be helpful for Hg^0 oxidation [18]. Zhang et al. investigated the mercury removal performance in simulated flue gas by MnO_x and CeO_2 modified semi-coke. It was found that although the pore structure of semi-coke was slightly reduced after loading metal oxide, the mercury removal of semi-coke adsorbent was significantly improved, which was consistent with Wu's research on modification of AC by MnO_x and CeO_2 [22,23].

However, it is difficult to understand how the surface condition of the adsorbent after CeO_2 doping is changed on the microscopic scale and also to reveal the interaction mechanism between Hg^0 and the AC surface, especially when only experimental evidence can be relied on. In addition, during the process of Hg^0 removal, there may be complex processes such as chemical adsorption and oxidation of Hg^0 catalyzed by activated carbon, yet the mechanism of these processes has not been clearly unveiled. To date, few theoretical researches on Hg^0 removal by CeO_2 modified AC surface have been reported. Therefore, DFT calculations were conducted in this research to study the Hg^0 removal mechanism. A single-layer, zigzag graphene model was constructed to simulate the basic structure of AC adsorbents. The adsorption mechanism of mercury species was proposed from the analyses of stable geometries, adsorption energies, and electronic structures. Moreover, the oxidation pathway, energy barriers, and transition states were also obtained to investigate the Hg^0 oxidation mechanism. To better clarify the promotion effect of CeO_2 doping, a series of calculations was also performed on the plain AC surface as a comparison.

2. Models and Computational Details

2.1. AC and CeO_2 -AC Models

Experimental results have indicated that the surface structure of carbon-based adsorbents is mainly composed of 3–7 randomly associated benzene rings [24,25]. In terms of quantum chemical calculations, it has been reported that a carbonaceous species such as AC is generally represented by a single layer of graphene. The unsaturated edge can be the activated sites for adsorption because these carbon atoms have unpaired electrons that are easy to transfer [26,27]. Therefore, a zigzag-shaped graphene model which contained 6-fused benzene rings (C_{24}H_8) was applied in this paper as the basic framework. As for CeO_2 modification, a CeO_2 molecule was adsorbed on the middle edge of graphene to simulate the CeO_2 -AC surface. The sorbent surface model after geometry optimization is shown in Figures 1 and 2. Relevant geometric parameters are listed in Table 1.

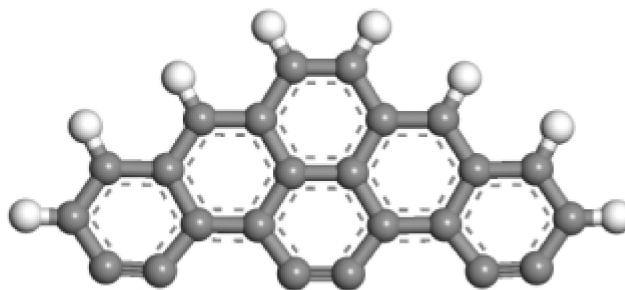


Figure 1. Conventional activated carbon (AC) surface model (the gray spheres represent C atoms, the white spheres represent H atoms, the same below).

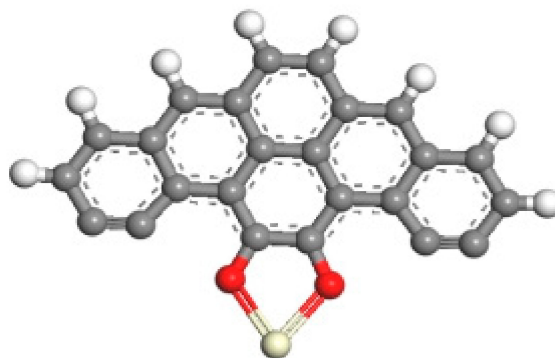


Figure 2. CeO₂-AC surface model (red spheres represent O atoms, light yellow spheres represent Ce atoms, the same below).

Table 1. Geometric parameters of activated carbon (AC) surface model.

Bond Type		C–C	C–H	C–O	C≡C	Ce–O
Bond Length (Å)	Conventional AC model	1.369–1.439	1.092	-	1.267	-
	CeO ₂ modified AC model	1.394–1.460	1.093	1.348	1.275	2.217

2.2. Computational Parameters

All DFT calculations were conducted by the DMol³ program in this research [28]. The GGA-PBE method was utilized to describe the exchange-correlation functional [29,30]. The core DFT semi-core pseudopotential (DSPP) method was used to set the core treatment of Hg and Ce, for C, H, Cl and O, the all-electron method was applied [31]. A real space orbital cutoff of 4.5 Å was conducted and a 0.005 Ha smearing was used to facilitate the self-consistent field (SCF) convergence. The double numerical basis set plus polarization (DNP method) with p-functions on all hydrogen atoms was applied for molecular orbitals in this research. The thresholds of energy, force, and displacement are 10^{−5} Hartree for energy change, 2 × 10^{−3} Ha/atom for the maximum force, and 5 × 10^{−3} Å for displacement. The adsorption energy on the AC surface (E_{ads}) is defined by Formula (1):

$$E_{ads} = E_{adsorbate-substrate} - E_{adsorbate} - E_{substrate} \quad (1)$$

where $E_{adsorbate-substrate}$ denotes the energy of adsorption configurations on the AC surface, $E_{adsorbate}$ and $E_{substrate}$ denote the energies of adsorbate and AC model, respectively. According to Formula (1), a negative value of E_{ads} indicates an exothermic reaction and high negative value indicates more heat release and a more stable product.

The reaction pathway is composed of intermediate (IM), transition state (TS), and final state (FS). The complete linear synchronous transit and quadratic synchronous transit (LST/QST) method was applied to obtain all transition states in this study [32]. Vibrational frequencies were also calculated for optimized configurations to identify stationary points (no imaginary frequency) and transition states (only one imaginary frequency). Reaction barriers were obtained by Formula (2):

$$E_{barrier} = E_{transition\ state} - E_{intermediate} \quad (2)$$

where $E_{transition\ state}$ and $E_{intermediate}$ represent the energies of transition states and intermediates, respectively.

3. Results and Discussion

3.1. Hg⁰ Adsorption Mechanism

The Hg⁰ adsorption mechanism was studied on the AC model and CeO₂-AC model first of all. All possible sites where the adsorption may occur were considered on the unsaturated edge, two stable

structures (1A, 1B and 1A*, 1B*, shown in Figure 3) were obtained on the CeO₂-AC and AC surface, respectively. The adsorption energies and related geometry parameters of 1A, 1B, 1A* and 1B* are shown in Table 2. In Figure 3 and Table 2, in terms of CeO₂-AC surface, the distance between the Ce and Hg atom is 3.431 Å in 1A and 3.508 Å in 1B. The adsorption energy is in the order of 1B < 1A (−42.05 kJ/mol vs. −46.94 kJ/mol). Generally, the adsorption energy of physisorption is usually about 0.1 eV (9.65 kJ/mol), while the adsorption energy of chemisorption usually ranges from 2 to 3 eV (192.97–289.46 kJ/mol) for molecular adsorption on solid surfaces [33]. Hence, the adsorption energies of Hg⁰ indicate a weak chemical adsorption. On the surface of AC, however, Hg⁰ adsorption energy in 1A* and 1B* is −119.92 kJ/mol and −146.01 kJ/mol, respectively. The distance between the Hg⁰ and AC surface is 2.511 Å for 1A* and 2.462/2.464 Å for the 1B* configuration. For the CeO₂-AC model, the Hg⁰ adsorption energy is lower than that on the AC surface. Therefore, it can be concluded that the doping of the CeO₂ molecule weakens the binding of Hg⁰ to some extent on the AC surface, but the adsorption manner of Hg⁰ still belongs to chemical adsorption.

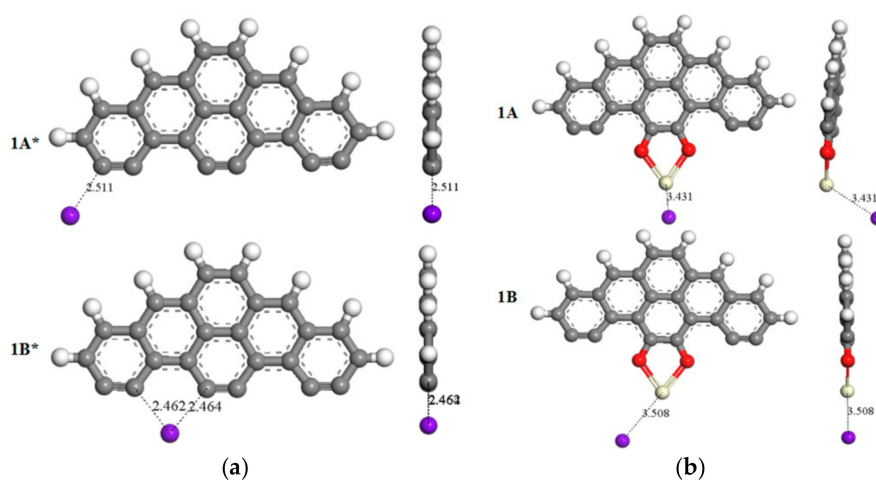


Figure 3. (a) Hg⁰ adsorption configurations on CeO₂-AC surface; (b) Hg⁰ adsorption configurations on AC surface. (The purple spheres represent Hg atoms, the same below. Both front view and side view are given.)

Table 2. Adsorption energies and configurations of Hg⁰ on AC surface.

CeO ₂ -AC Model			AC Model		
Configurations	R _{Hg-Ce} (Å)	E _{ads} (kJ/mol)	Configurations	R _{Hg-C} (Å)	E _{ads} (kJ/mol)
1A	3.431	−46.94	1A*	2.511	−119.92
1B	3.508	−42.05	1B*	2.462/2.464	−146.01

To further study the interaction between Hg⁰ and the AC surface during adsorption, the partial density of states (PDOS) analysis for Hg, Ce and C atoms were conducted for 1A and 1B*, which are the most stable configurations. The PDOS diagrams for Hg pre/post-adsorption, Ce pre/post-adsorption, and C pre/post-adsorption are depicted in Figure 4. In Figure 4a,b, the s and p orbital peaks of Hg are shifted to lower energy level after adsorption because of the electron transfer between Hg⁰ and the CeO₂-AC surface. At the same time, the intensity of the p-orbital is reduced, the peak of the Hg d-orbital at 16 eV disappears, and the peak at −3.1 eV also migrates to a lower energy level, which indicates that there is an intensive interplay between Hg⁰ and the CeO₂-AC surface. For Ce atoms, the energy band before Hg⁰ adsorption locates between −37 eV and 1.5 eV, all orbital peaks of the C atom on the AC surface only slightly change after adsorption while the peak of the d-orbital at 0.6 eV is slightly strengthened. The above analysis shows that Hg⁰ is strongly adsorbed and interacts with the Ce atoms on the surface, the electron orbitals of the Hg atom change significantly, while the

electronic structure of the Ce atoms on the CeO₂-AC surface does not change much, indicating the CeO₂-AC sorbent remained stable after adsorption.

The PDOS of C and Hg on the AC surface before and after adsorption are shown in Figure 4c,d. Similar to that on the CeO₂-AC surface, the s-orbital and p-orbital peaks of Hg after adsorption shift to lower energy level; the p-orbital intensity is reduced and retains several short peaks between -1.9 eV and 7.1 eV. The Hg d-orbital peak at 16 eV vanishes, the peak at -3.1 eV migrates to lower energy level, indicating an intensive interplay between Hg⁰ and the CeO₂-AC surface. The intensity of the p-orbital peak of the C atom on the surface slightly weakens, while the s-orbital peak does not show any significant change. According to the above analysis, it is known that the PDOS of Hg does not change much after CeO₂ doping, both adsorption sites on Ce and C atoms remain stable after Hg⁰ is strongly bound to the surface. Hence, it can be considered that although the doping of CeO₂ reduces the adsorption strength of Hg⁰ on AC sorbents to some extent, the adsorption mechanism remains the same and the capture of Hg⁰ in flue gas by AC sorbents is not significantly inhibited.

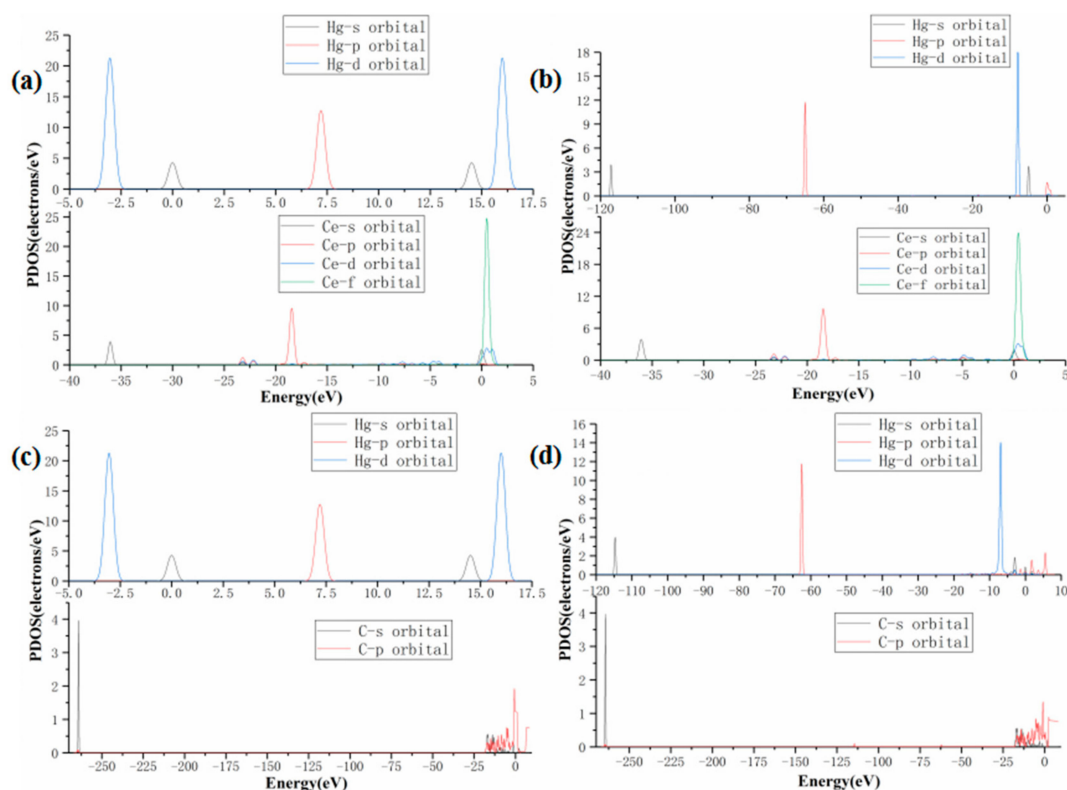


Figure 4. (a) Hg⁰ pre-adsorption partial density of states (PDOS) on CeO₂-AC; (b) Hg⁰ post-adsorption PDOS on CeO₂-AC; (c) Hg⁰ pre-adsorption PDOS on AC; (d) Hg⁰ post-adsorption PDOS on AC.

3.2. HCl Adsorption Mechanism

Previous studies have shown that HCl is a crucial compound in the Hg⁰ oxidation process, because the Hg species in flue gas mainly exists as HgCl₂ after Hg⁰ oxidation [34]. Therefore, it is necessary to explore the adsorption manner of HCl, HgCl₂ and intermediate HgCl to reveal the oxidation mechanism of Hg⁰ in flue gas. DFT calculations were applied to investigate all possible adsorption configurations of HCl molecules on the surface of CeO₂-AC and AC. A stable configuration and adsorption energy were obtained and are shown in Figure 5 and Table 3.

As is seen in Figure 5, the adsorption mode of HCl molecules can be divided into two categories. (1) The HCl molecule dissociates on the AC surface, as shown by configurations 2A–2B, 2A*–2C*, which have relatively high adsorption energies (-149.38 kJ/mol and -371.63 kJ/mol), the binding of HCl molecules to the surface is relatively intense. (2) No dissociation occurs on the sorbents,

as depicted in configuration 2C–2E and 2D*–2E*, the adsorption energies range from -41.20 kJ/mol to -55.79 kJ/mol, suggesting a weak chemical adsorption. In these configurations, HCl exists on the surface as HCl molecules, the geometric parameters and adsorption energies are close, only the orientation of the HCl molecule and adsorption site are slightly different. By comparing the adsorption configuration and adsorption energy of HCl on the two AC surfaces, it can be concluded that after CeO_2 doping, the adsorption energy of the HCl molecules increases, and the adsorption capacity for HCl is enhanced.

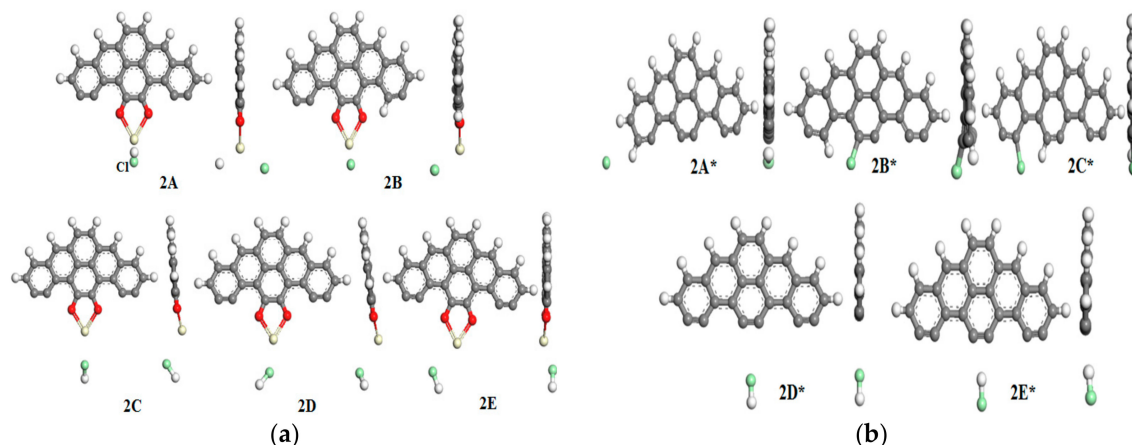


Figure 5. (a) Adsorption configurations of HCl on CeO_2 -AC model; (b) Adsorption configurations of HCl on AC model. (Green spheres represent Cl atoms, the same below. Front view and side view of configurations are all given.)

Table 3. Adsorption energies/configurations of HCl on CeO_2 -AC surface and AC surface.

CeO ₂ -AC Surface				AC Surface			
Configurations	R _{X-Ce} (Å) *	R _{H-Cl} (Å)	E _{ads} (kJ/mol)	Configurations	R _{X-C} (Å) *	R _{H-Cl} (Å)	E _{ads} (kJ/mol)
2A	2.633/2.157	4.036	−174.27	2A*	1.095	2.707	−149.38
2B	2.623	5.291	−371.63	2B*	2.373	1.089	−254.78
2C	3.088	1.361	−54.85	2C*	2.257	1.088	−255.40
2D	3.071	1.362	−54.97	2D*	3.496/3.501	1.291	−41.20
2E	3.226	1.343	−52.63	2E*	2.411/2.385	1.304	−55.79

* X denotes H or Cl atoms.

3.3. HgCl Adsorption Mechanism

HgCl is an important intermediate for Hg^0 oxidation and can be further oxidized to HgCl_2 . The stable adsorption configuration and adsorption energy of HgCl on the active site of AC sorbent are shown in Figures 6 and 7 and Table 4. The adsorption manner of HgCl on the AC surface can also be divided into two kinds, dissociative adsorption and non-dissociative adsorption. In configuration 3A and 3B, dissociation occurs for the HCl molecule and the Hg–Cl bond is cracked. The distance between the Cl radical and the Ce atom on the adsorbent surface is 2.623 Å/ 2.625 Å and the adsorption energies of the two configurations are -281.58 kJ/mol and -294.50 kJ/mol, respectively. In terms of 3C and 3D, the Hg–Cl bond is not broken, the bond lengths are 2.556 Å, 2.580 Å, and the adsorption energy of HgCl molecules on the AC surface are -153.09 kJ/mol and -139.80 kJ/mol, respectively. Both kinds of adsorption belong to intense chemical adsorption, suggesting that the combination of HgCl on the sorbents is relatively stable, which is beneficial to the conversion of the intermediate HgCl to the final product HgCl_2 .

The adsorption mechanism of HgCl on AC is similar to that on the CeO_2 -AC surface. In the 3A* and 3B* configurations, the Hg atom of HgCl is bound to a C atom on the AC surface, the adsorption energies are -258.70 kJ/mol and -259.47 kJ/mol, respectively. In the 3C* configuration, HgCl molecules are cracked, the Hg atom and Cl radical are separately combined with two carbon

atoms on the graphene edge, the adsorption energy is -301.32 kJ/mol. It can be seen that the doping of CeO_2 lowers the adsorption energy of HgCl slightly, while the adsorption mechanism remains the same.

Table 4. Adsorption energies/configurations of HCl on CeO_2 -AC model and AC model.

CeO_2 -AC Surface				AC Surface			
Configurations	$R_{\text{X-Ce}}$ (Å) *	$R_{\text{Hg-Cl}}$ (Å)	E_{ads} (kJ/mol)	Configurations	$R_{\text{Hg-C}}$ (Å) *	$R_{\text{Hg-Cl}}$ (Å)	E_{ads} (kJ/mol)
3A	2.623	7.191	-281.58	3A*	2.149	2.391	-258.70
3B	2.625	5.219	-294.50	3B*	2.156	2.393	-259.47
3C	3.177	2.556	-153.09	3C*	2.323/2.427	3.689	-301.32
3D	3.275	2.580	-139.80	-	-	-	-

* X denotes Hg or Cl atoms.

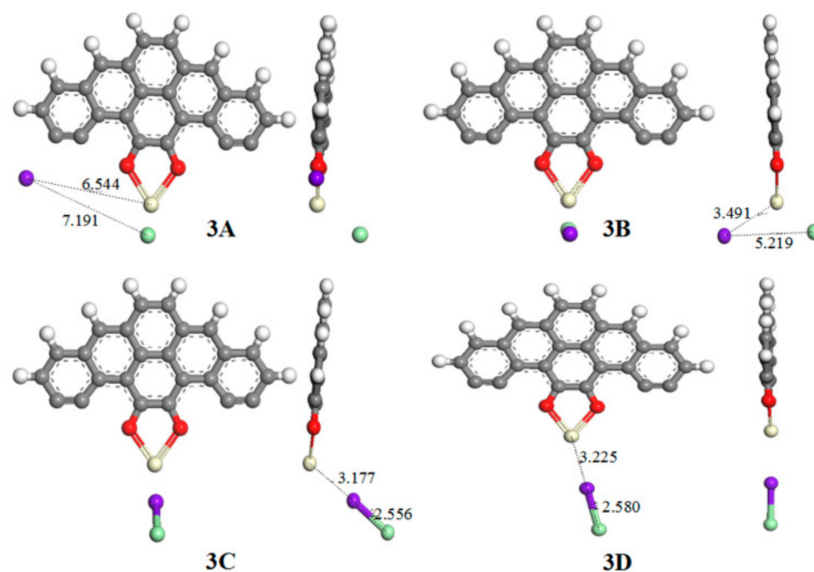


Figure 6. Adsorption configurations of HgCl on CeO_2 -AC model.

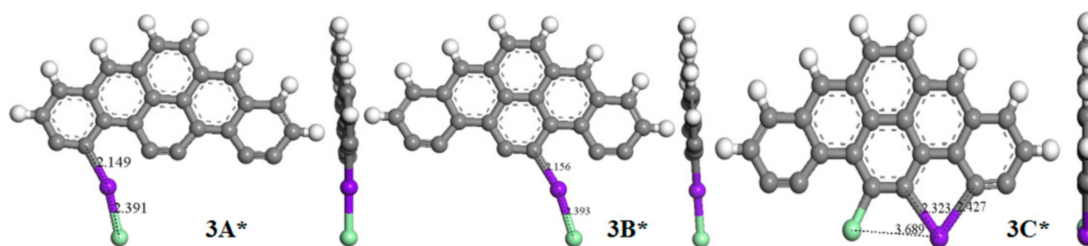


Figure 7. Adsorption configurations of HgCl on AC model.

3.4. HgCl_2 Adsorption Mechanism

When HCl exists in flue gas, HgCl_2 is the final product from Hg^0 oxidation. All possible sites on the edge of graphene have been considered, configurations and adsorption energies are depicted in Figures 8 and 9 and Table 5. For 4A configuration on the CeO_2 -AC surface, HgCl_2 dissociated into an HgCl radical and a Cl radical, which is bound to the CeO_2 -AC surface by chemisorption, the adsorption energy for this process is -202.70 kJ/mol. For configuration 4B, the HgCl_2 molecule also dissociates into an HgCl radical and a Cl radical, which are all bound to the CeO_2 -AC surface with -287.46 kJ/mol adsorption energy. In configuration 4C, two Hg-Cl bonds of the HgCl_2 molecule are all broken, forming one weakly adsorbed Hg atom on the edge of the CeO_2 -AC and two Cl radicals bonded to the Ce atom supported on the CeO_2 -AC surface. Since HgCl_2 is completely dissociated, the adsorption energy of the configuration 4C is the largest, i.e., -399.03 kJ/mol. Based on the above

results, after the HgCl_2 molecule is captured by the CeO_2 -AC sorbent, it may exist on the AC sorbent in the manner of dissociative adsorption, and the value of the adsorption energies suggests that the bonding is considerably strong. Moreover, it is noteworthy that the adsorption energy in 4C is the largest, and the adsorption energy of the 4B configuration is the second largest when the Cl radical and Hg atoms are adsorbed on the surface, when only one Cl radical is bonded in 4A, is the adsorption energy minimal. Hence, it can be inferred that the adsorption energy of Hg^0 is smaller than that of the Cl radical on the surface; the adsorption can be stronger when the Cl end of the HgCl_2 molecule is bonded on the adsorbent.

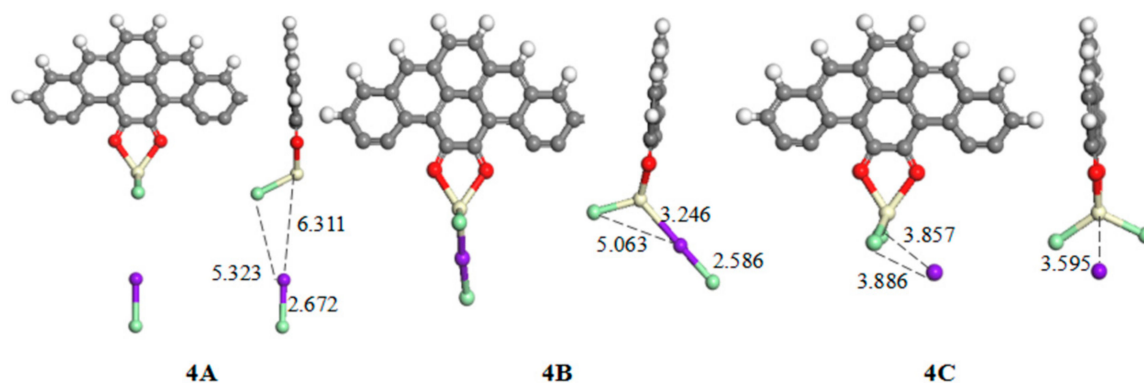


Figure 8. Adsorption configurations of HgCl_2 on CeO_2 -AC model.

On the surface of the plain AC surface without CeO_2 , however, the adsorption of HgCl_2 includes two types, dissociative adsorption and non-dissociative adsorption. In terms of 4A*, one Hg–Cl bond of the HgCl_2 molecule is broken, the generated Cl radical is bound to the AC surface and the Hg end of another part of the HgCl radical is also bound to the adjacent carbon atom on the plain AC surface, the adsorption energy of 4A* is -369.19 kJ/mol. In configuration 4B* where non-dissociative adsorption occurs, the Hg–Cl bonds are slightly elongated but not broken compared to that of the HgCl_2 molecule (2.345 Å) in the gas phase, and the linear molecule configuration remains steady. The adsorption energy on the plain AC surface is -101.54 kJ/mol. In the 4C* configuration, the bond angle $\angle\text{Cl-Hg-Cl}$ is slightly reduced compared with the HgCl_2 molecule in the gas phase (180°), the Hg–Cl bond length is slightly elongated, the HgCl_2 molecule is adsorbed on the AC model in parallel, the adsorption energy is -110.80 kJ/mol. For configuration 4D* the HgCl_2 molecule is distorted, the Hg–Cl bond elongates slightly and the angle of the $\angle\text{Cl-Hg-Cl}$ is reduced to 92.65° with a -186.98 kJ/mol adsorption energy. Compared with the dissociative adsorption configurations on the CeO_2 -AC surface, the adsorption energy on the conventional AC surface is more positive, indicating that the HgCl_2 molecule is preferred to be dissociatively adsorbed on the AC after CeO_2 doping, the HgCl_2 molecule is more tightly bound on the CeO_2 -AC surface, so it has a better removal performance for HgCl_2 in coal-fired flue gas.

Table 5. Adsorption energies and configurations of HgCl_2 on CeO_2 -AC surface and AC surface.

CeO ₂ -AC Surface				AC Surface				
Configurations	R _{X-Ce} (Å)	R _{Hg-Cl} (Å)	E _{ads} (kJ/mol)	Configurations	R _{Hg-C} (Å)	R _{Hg-Cl} (Å)	∠Cl-Hg-Cl (°)	E _{ads} (kJ/mol)
4A	2.599	5.323/2.672	−202.70	4A*	2.121	2.368/3.468	–	−369.19
4B	2.616	5.063/2.586	−287.46	4B*	6.043/6.119	2.356/2.362	179.82	−101.54
4C	2.640/2.643	3.886/3.857	−399.03	4C*	3.202/3.258	2.367/2.368	171.63	−110.80
–	–	–	–	4D*	2.271/2.309	2.546/2.515	92.65	−186.98

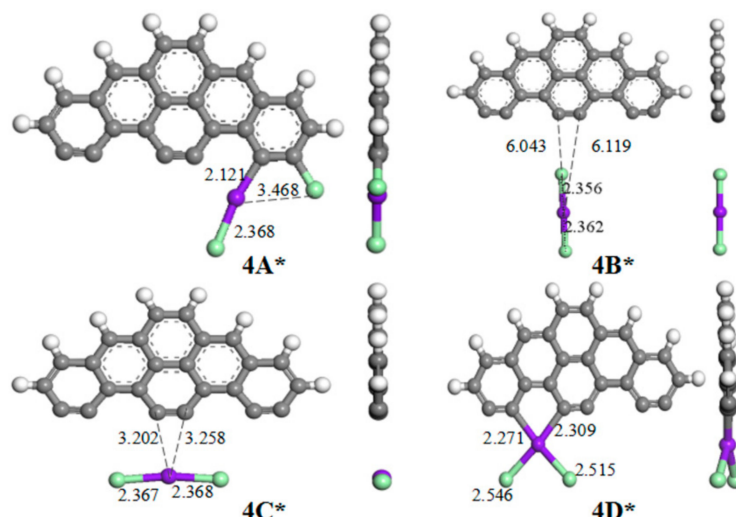


Figure 9. Adsorption configurations of HgCl_2 on AC model.

3.5. Hg^0 Oxidation Mechanism

Based on the Hg^0 , HCl , HgCl , and HgCl_2 adsorption mechanism discussed above, the oxidation mechanisms of Hg^0 on the CeO_2 -AC and AC surface were further studied, the reaction energy barriers and relative geometries in the oxidation route were calculated. The potential energy diagram of the reaction pathways are illustrated in Figure 10, and the relative configurations for reactants, products, and transition states involved in the paths are shown in Figure 11.

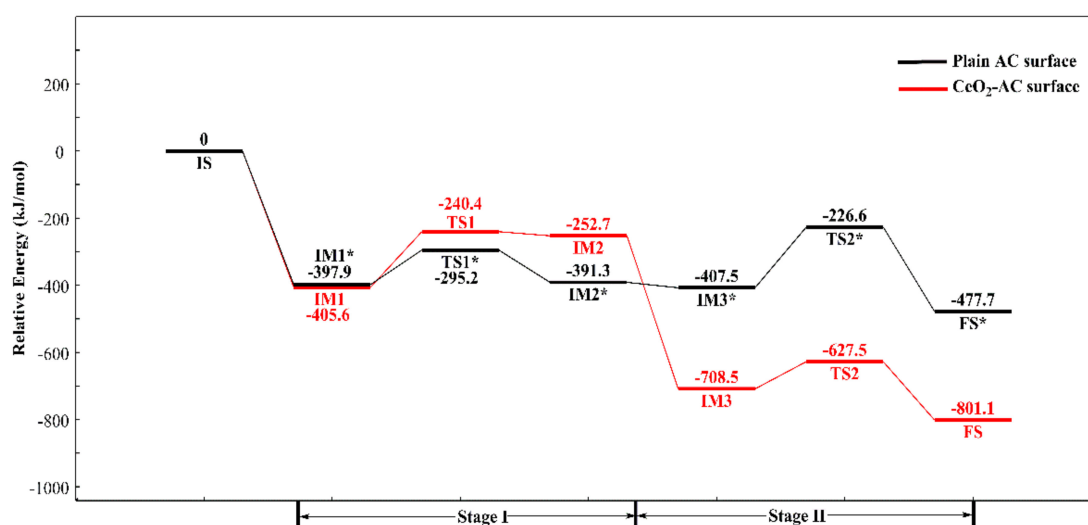


Figure 10. Potential energy diagram of Hg^0 oxidation pathways on CeO_2 -AC surface and plain AC surface.

The red line in Figure 10 represents the oxidation pathway of Hg^0 on the CeO_2 -AC surface. Depending on the different products, the oxidation path can be divided into two phases. In the first phase, the HCl molecule is first combined with the sorbent surface by dissociative adsorption. Then an H radical and a Cl radical are adsorbed on the Ce atom on the CeO_2 -AC surface, releasing 405.6 kJ/mol to form a stable IM1 configuration. Subsequently, the Hg^0 atom and Cl radical migrate toward each other forming the transition state TS1 , a 2.689 Å Hg-Cl bond is formed and finally stabilized at 2.572 Å in IM2 . In this process, an HgCl molecule is formed with a reaction barrier of 165.3 kJ/mol and 152.9 kJ/mol adsorption energy. After the HgCl is formed, the oxidation reaction in the second stage is carried out according to the path of $\text{IM2} \rightarrow \text{IM3} \rightarrow \text{TS2} \rightarrow \text{FS}$. Firstly, the IM2 configuration combines

with another HCl molecule to form a stable configuration, IM3, which is exothermic by 450.8 kJ/mol. In IM3, another adsorbed HCl molecule is cracked. After dissociation, the Hg–Cl bond is formed between the Cl radical and HgCl to form a bent HgCl₂ molecule, while the H radical moves close to the C atom at the edge of AC surface, forming the transition state TS2, with an 81.0 kJ/mol energy barrier for this process. Consequently, in the transition state TS2, a linear HgCl₂ molecule further desorbs from the CeO₂-AC surface to form the final state FS. The distance between the Hg and Ce atom on the AC surface in FS is expanded from 3.212 Å to 6.470 Å; the process generating HgCl₂ requires an exotherm of 92.5 kJ/mol. It can be seen that the two-step oxidation of Hg⁰ and HCl follows the Langmuir–Hinshelwood mechanism [35,36], and the rate-determining step is the first stage, i.e., the formation of the HgCl molecule. The energy barrier of the entire pathway is 165.3 kJ/mol.

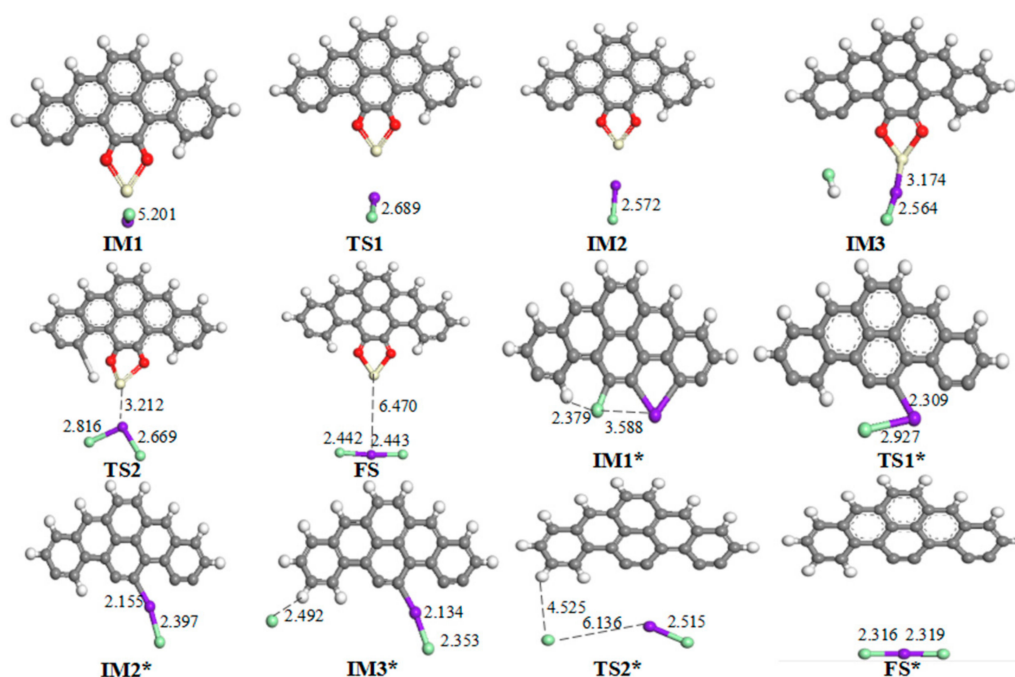


Figure 11. Relative configurations of reactions, products, and intermediate states involved in Hg⁰ oxidation route.

The oxidation pathway of Hg⁰ on the AC surface is depicted as the black portion in Figure 10, and the entire reaction is still divided into two phases. The first phase is the formation process of HgCl. First of all, one Hg atom and one HCl molecule are adsorbed on the AC surface to form IM1* and release 397.9 kJ/mol of heat, the HCl molecule dissociates into one Cl radical and one H radical respectively combining with two C atoms on the AC surface. Subsequently, the Cl radical migrates to the Hg atom adsorbed on the adjacent C site, forming a transition state TS1* and overcoming a 102.7 kJ/mol barrier. In TS1*, the Cl radical further moves closely to Hg⁰, the distance between the Cl radical and Hg⁰ in IM2* is shortened from 2.927 Å to 2.397 Å, the obtained HgCl molecule is continuously adsorbed on the AC surface. In the second phase, the IM2* configuration captures another HCl molecule and releases 16.2 kJ/mol of heat converting to the configuration IM3*, the Hg–Cl bond length in IM3* is 2.353 Å. Subsequently, HCl in the transition state TS2* dissociates again on the AC surface, the distance between the H radical and Cl radical increases from 2.492 Å to 4.525 Å, the distance between the Cl radical and Hg atoms is 6.136 Å, and the energy barrier to form transition state TS2* is 180.9 kJ/mol. In configuration TS2*, the dissociated Cl radical continues to migrate to the HgCl molecule, eventually forming HgCl₂ in FS* which is exothermic by 70.2 kJ/mol to form HgCl₂. The reaction between the Hg⁰ and HCl molecule in the conventional AC model also follows the Langmuir–Hinshelwood mechanism. However, due to the high energy barrier in the second phase of oxidation, unlike the CeO₂-AC surface, the rate-determining step is the formation of HgCl₂.

Based on the above discussion, the adsorption energy of Hg^0 and HgCl on the AC sorbents is reduced after CeO_2 modification, the interplay between Hg^0 and the AC sorbent is relatively weak, resulting in a relatively high energy barrier in the formation of HgCl in the first stage of Hg^0 oxidation. On the other hand, the modification of CeO_2 increases the adsorption energy of HCl and HgCl_2 on the AC sorbent, which is beneficial to the further oxidation of the intermediate HgCl to form HgCl_2 , making the reaction energy barrier relatively low. Therefore, on the CeO_2 -AC surface, the energy barrier of the HgCl formation process is relatively high, which is the rate-determining step of Hg^0 oxidation, whereas, on the plain AC model, the rate-determining step is the HgCl_2 formation process. Comparing the energy barriers on these two AC sorbents, the modification of CeO_2 reduces the reaction energy barrier of Hg^0 oxidation to some extent (165.3 kJ/mol vs. 180.9 kJ/mol). Ultimately, the catalytic oxidation capacity of AC sorbents is enhanced for removing mercury species in coal-fired flue gas.

Moreover, adsorption energies of HCl and HgCl_2 demonstrate that the adsorption of HCl and HgCl_2 on CeO_2 is stronger than that on the C atoms on the plain AC surface. Therefore, although reducing the adsorption strength of Hg^0 on the AC surface to some extent, the doped CeO_2 forms some adsorption sites which are easier for HCl and HgCl_2 to be adsorbed. In addition, for heterogeneous oxidation of mercury, the route involves two steps, i.e., the formation of HgCl and HgCl_2 , and the latter is usually regarded as the rate-determining step due to the relatively high energy barrier. Whereas, with regard to the CeO_2 -AC sorbents, the energy barrier of HgCl_2 formation is reduced on the CeO_2 site, hence promoting the oxidation procedure of Hg^0 and improving the ability to capture mercury species.

4. Conclusions

DFT calculations were implemented in this paper to study the Hg^0 adsorption and oxidation mechanism in coal-fired flue gas on a plain AC surface and CeO_2 -AC surface. The adsorption energies were calculated, as well as the energy barriers of the Hg^0 oxidation pathways. The effect of CeO_2 doping was estimated by comparison of the removal mechanism on the plain AC surface and CeO_2 -AC surface.

The calculation results demonstrate that the adsorption modes of Hg^0 , HCl , HgCl and HgCl_2 are chemisorption, indicating they are tightly bound on the AC sorbent. PDOS analysis of the Hg^0 adsorption shows that Hg^0 is intensely adsorbed on the adsorbent, strong interaction and charge transfer occur between Hg^0 and the AC surface, the orbital peaks in the PDOS figure change significantly after adsorption. HCl , HgCl and HgCl_2 can all be dissociated and adsorbed on the AC surface, after dissociation of HCl molecules, the Cl radical does not bond with the surface. Hg and HgCl in the gas phase may combine with a Cl radical and generate the intermediate HgCl or the final product HgCl_2 . The adsorption energies of HgCl and HgCl_2 are relatively high, indicating that CeO_2 doping enhances the ability to capture HgCl and HgCl_2 . What is more, the AC sorbent has a certain catalytic effect on the oxidation of Hg^0 , the rate-determining step of Hg^0 oxidation on the plain AC surface is the formation of HgCl_2 . The doping of CeO_2 reduces the reaction energy barrier and enhances the catalytic oxidation ability to remove Hg^0 . The rate-determining step is the generation of HgCl . On the plain AC surface and CeO_2 -AC surface, the oxidation of Hg^0 follows the Langmuir–Hinshelwood mechanism.

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