

Theoretical Study of Mercury Species Adsorption on CaO(100) Surface

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Abstract. As an important air pollutant, mercury produced by power generation can be captured by CaO in coal-fired fly ash. In order to understand the interaction mechanism of CaO with mercury in HCl atmosphere, the density functional theory method is utilized to investigate the adsorption of mercury species on the fly ash components. The CaO(100) surface is built to study the stable adsorption configurations of Hg^0 , HCl, HgCl and HgCl_2 on all possible adsorption sites. The results show that CaO(100) surface cannot absorb Hg^0 directly, but the intermediate HgCl can be adsorbed on the surface stably, and then continue to combine with a Cl radical to produce HgCl_2 , which is easy to be removed.

1. Introduction

Mercury in coal-fired flue gas from power generation can cause global air pollution [1]. Previous studies showed that fly ash from the combustion of fossil fuel had a certain adsorption and oxidation ability to mercury [2-4]. Typically, fly ash is consisted of unburned carbon, CaO, MgO, Fe_2O_3 , CuO, MnO_2 , Al_2O_3 and SiO_2 and their metal salts [5]. The mechanism of heterogeneous interaction between fly ash and mercury is very complex. The difficulty of mercury removal in coal-fired flue gas is the elimination of elemental mercury which is insoluble in water and difficult to be captured by existing pollution control devices [6]. Previous studies have found that the unburned carbon in fly ash and activated inorganic components are the keys of adsorption and oxidation of Hg^0 [7]. Some researchers regarded fly ash as a whole to study the mechanism of the oxidation of Hg^0 and found that the oxidation of Hg^0 by fly ash followed the Mars-Maessen mechanism, and the lattice oxygen in the fly ash played the role of the oxidant [8-10]. But up to now, there is no identical conclusion on the adsorption and oxidation mechanism of Hg^0 on the chemical composition of fly ash.

In order to investigate the detailed mechanism of Hg^0 adsorption on CaO(100) surface, first-principles calculations based on the density functional theory and the periodic slab models are used to study the adsorption of mercury species as well as the adsorption and dissociation of HCl.

2. Computational details

2.1. Model

The CaO(100) surface is selected as it is the most stable low-index facet which can well represent the property of CaO. A four-layer CaO(100) slab is cleaved from the perfect crystal with the topmost two layers fully relaxed and the bottom two layers fixed to model the CaO(100) surface. A 2×2 super cell of the unit cell is performed containing 8 Ca cations and 8 O anions for each surface layer. 12 Å



vacuum layer is built above the surface to eliminate the interference of the imaging CaO(100) surface, as is shown in Figure 1.

2.2. Computational methods

All DFT calculations are carried out using DMol³ package in Materials Studio software in this study. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerh of (PBE) functional is selected for calculating exchange and correlation functional. The molecular orbitals are expanded by double numerical basis set with polarization functions (DNP). All electrons are treated with DFT Semi-core Pseudopots (DSPP). 5.5 Å atomic radius cutoff is selected with a smearing value of 0.005 Ha to accelerate convergence. 3×3×1 Monkhorst–Pack k-point sampling is selected for Brillouin zone integration during geometric optimization calculation.

For the adsorption of mercury species on CaO(100) surface, the adsorption energy E_{ad} is defined as:

$$E_{ad} = E_{sys} - E_{ads} - E_{sur} \quad (1)$$

Where E_{sys} is the system total electronic energy after adsorption; E_{ads} is the electronic energy of adsorbate; E_{sur} is the electronic energy of the surface.

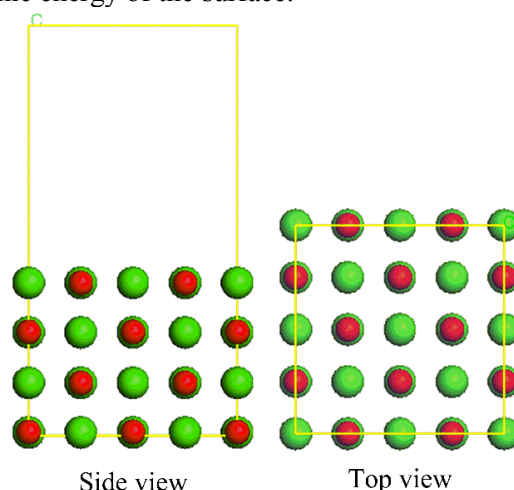


Figure 1. CaO(100) surface. Green and red balls represent Ca and O atoms, respectively.

3. Results and discussion

3.1. Hg^0 adsorption on CaO(100) surface

Adsorption of Hg^0 is the premise of its oxidation on CaO(100) surface. There are four possible adsorption sites for Hg^0 on the surface, Ca site (1A), O site (1B), bridge site (1C) and hollow site (1D), respectively. The optimized configurations of Hg^0 adsorption on each site are shown in Figure 2. The adsorption energies and geometric parameters are given in Table 1. The adsorption energy results show that the stability of Hg^0 adsorption is in the order of $1B < 1C < 1D < 1A$. The adsorption energy of Hg^0 adsorption on O site is relatively lower, and Hg^0 is closer to the surface with a distance of 3.017 Å, indicating that Hg^0 is more likely to be bound to the surface O atoms. However, the adsorption energy of each configuration is positive, that is, Hg^0 adsorption on CaO(100) surface is physisorption, which shows that Hg^0 cannot be adsorbed directly by CaO(100) surface.

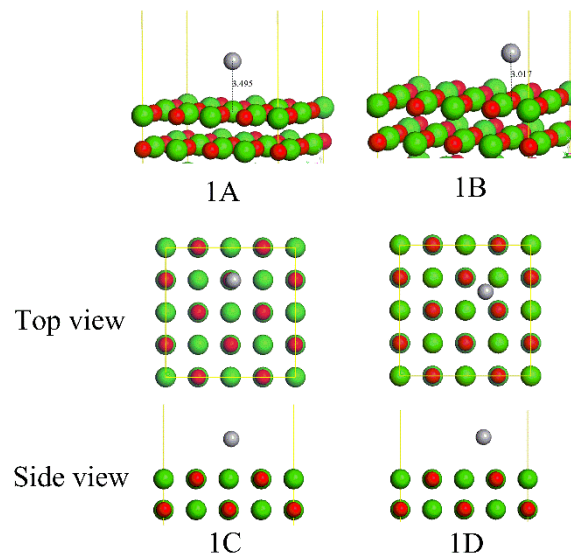


Figure 2. Optimized configurations of Hg^0 adsorption on $\text{CaO}(100)$ surface. (The grey balls represent Hg atoms. The same below.)

Table 1. The adsorption energies and geometric parameters of Hg^0 adsorption on $\text{CaO}(100)$ surface.

No.	Hg-O (Å)	Hg-Ca (Å)	E_{ads} (kJ/mol)
1A	-	3.495	23.192
1B	3.017	-	20.666
1C	3.045	3.794	20.776
1D	3.549	3.668	22.280

3.2. HCl adsorption on $\text{CaO}(100)$ surface

HCl in coal-fired flu gas can take part in the Hg^0 catalytic oxidation reaction, while whether HCl can affect the Hg^0 oxidation on the fly ash composition is still not clear. The optimized configurations of HCl adsorption on each site are shown in Figure 3. The adsorption energies and geometric parameters for HCl adsorption on the surface are given in Table 2. The adsorption energy results show that the stability of HCl adsorption is in the order of $2B < 2C < 2A$. The adsorption energy of 2A and 2C is positive, and the HCl molecule doesn't interact with the surface, indicating that these two configurations are physisorption only. The most stable structure for HCl adsorption on the surface is 2B with an adsorption energy of -46.50 kJ/mol. In 2B, H atom of HCl interacts with surface O and the bond length of H-Cl elongates from 1.291 Å to 1.980 Å. The length of new-formed H-O bond is 0.999 Å, and the distance between Cl and Ca is 2.974 Å. After the dissociative adsorption of HCl, the Cl radical doesn't adsorb on the surface, instead, it releases to the gas phase, which can be concluded that Cl radical may combine with Hg in the gas phase to form HgCl , an intermediate of oxidation reaction.

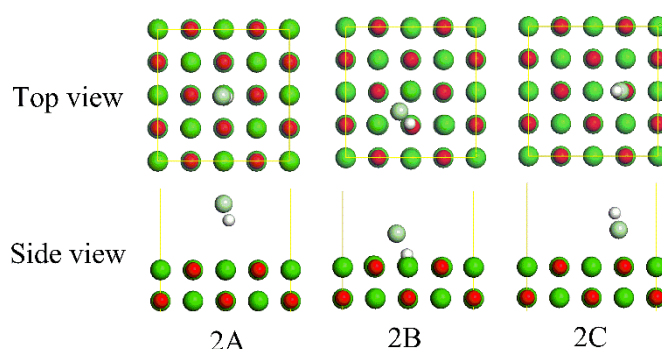


Figure 3. Optimized configurations of HCl adsorption on CaO(100) surface. (The white and grey-green balls represent H and Cl atoms respectively. The same below.)

Table 2. The adsorption energies and geometric parameters of HCl adsorption on CaO(100) surface.

No.	H-O (Å)	H-Ca (Å)	Cl-O (Å)	Cl-Ca (Å)	H-Cl (Å)	E_{ads} (kJ/mol)
2A	-	3.776	-	-	1.292	26.157
2B	0.999	2.609	-	2.974	1.980	-181.126
2C	-	4.452	2.868	-	1.306	12.807

3.3. HgCl adsorption on CaO(100) surface

HgCl is a possible intermediate of oxidation reaction of Hg^0 . So, it is necessary to calculate the adsorption of HgCl on CaO(100) surface. The optimized configurations of HgCl adsorption on each site are shown in Figure 4. The adsorption energies and geometric parameters for HgCl adsorption on the surface are given in Table 3. The adsorption energy results show that the stability of HgCl adsorption is in the order of $3\text{B} < 3\text{C} < 3\text{A}$. The adsorption energies of these three configurations are negative, indicating that HgCl is chemically adsorbed on CaO(100) surface. The most stable structure for HgCl adsorption on the surface is 3B with an adsorption energy of -108.905 kJ/mol. In 3B, HgCl adsorbs on the surface horizontally, and Hg atom is close to the surface O atom, Cl atom is close to the surface Ca atom, Hg-Cl bond elongates from 2.495 Å to 2.948 Å, and the distance between Hg and O is 3.002 Å, the distance between Cl and Ca is 2.768 Å. The chemisorption of HgCl on CaO(100) surface provides the possibility for the combination of Cl and HgCl to form HgCl_2 . However, in 3C, the Hg-Cl bond breaks, the distance of Hg and Cl elongates from 2.495 Å to 3.315 Å, Cl atom approaches to the surface, which indicates there is possibility for HgCl dissociation and Hg^0 re-release to the gas phase.

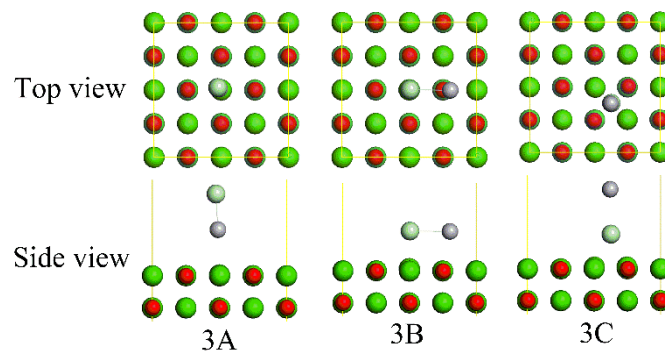


Figure 4.Optimized configurations of HgCl adsorption on CaO(100) surface.

Table 3.The adsorption energies and geometric parameters of HgCl adsorption on CaO(100) surface.

No.	Hg-O (Å)	Hg-Ca (Å)	Cl-O (Å)	Cl-Ca (Å)	Hg-Cl (Å)	E _{ads} (kJ/mol)
3A	-	3.316	-	-	2.621	-50.833
3B	3.002	-	3.92	2.768	2.948	-108.905
3C	-	-	3.219	2.950	3.315	-99.878

3.4. HgCl_2 adsorption on CaO(100) surface

The oxidation of Hg^0 is to transform Hg^0 to Hg^{2+} which is easy to remove. In the Hg^0 oxidation process with HCl, HgCl_2 is the final product of the reaction. The optimized configurations of HgCl_2 adsorption on each site are shown in Figure 5. The adsorption energies and geometric parameters for HgCl_2 adsorption on CaO(100) surface are given in Table 4. The adsorption energy results show that the stability of HgCl_2 adsorption is in the order of $4A < 4C < 4B$. The adsorption energy of 4B is positive, showing it is physisorption. The HgCl_2 adsorption in 4C is very weak chemical adsorption with an adsorption energy of -5.729 kJ/mol. In 4A, the angle of Cl-Hg-Cl changes greatly from 180° to 147.476° , Hg atom interacts with the surface O atom forming a 2.288 Å Hg-O bond, while the Cl-Hg bonds have no significant elongation. The adsorption energy of 4A is -81.812 kJ/mol, much greater than that of 4C, but it is still a weak chemical adsorption. These results suggest that HgCl_2 can desorb from CaO(100) surface and then be captured and removed by the downstream WFGD system. But at the same time, it is still possible for HgCl_2 to stay on the surface and be captured by the dust removal devices together with fly ash.

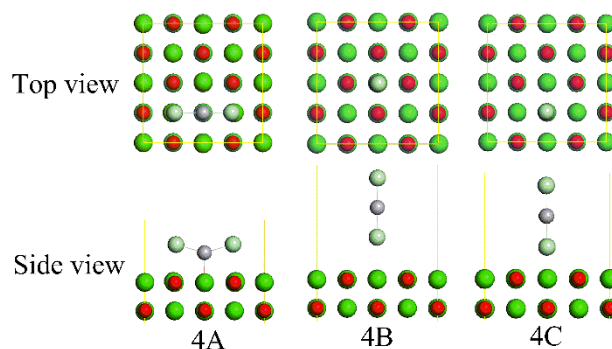


Figure 5.Optimized configurations of HgCl_2 adsorption on CaO(100) surface.

Table 4. The adsorption energies and geometric parameters of HgCl₂ adsorption on CaO(100) surface.

No.	Hg-O (Å)	Hg-Ca (Å)	Cl-O (Å)	Cl-Ca (Å)	Hg-Cl (Å)	Cl-Hg-Cl (°)	E _{ads} (kJ/mol)
4A	2.288	-	-	3.049	2.450	147.476	-81.812
4B	-	-	-	3.415	2.423	179.703	7.821
4C	-	-	2.559	-	2.432	179.903	-5.729

4. Conclusions

The detailed adsorption mechanism of Hg on CaO(100) surface is investigated by a systematic density functional theory study and the periodic slab model. Hg⁰ is physically adsorbed on CaO(100) surface, while HCl is dissociatively absorbed, and HgCl and HgCl₂ is chemically adsorbed. After the dissociation adsorption of HCl, the Cl radical releases to the gas phase, which indicates that Cl radical may combine with Hg in the gas phase to form HgCl, and then HgCl may continue to combine with a Cl free radical to form HgCl₂. HgCl₂ can either desorb from CaO(100) surface or stay on the surface and can be removed by the downstream pollutant control devices under both conditions, hence to realize the removal of Hg⁰.

5. Acknowledgments

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6. References

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