

# Theoretical Study of Mercury Species Adsorption on MgO(001) Surface

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**Abstract.** Traditional thermal power generation releases mercury, which will cause important environmental issues. As one of the main components of fly ash produced by coal-fired power generation, MgO can adsorb mercury in HCl atmosphere. Aiming to investigate the interaction mechanism of MgO with mercury in coal-fired flue gas in HCl atmosphere, density functional theory method is used to study the adsorption of mercury species on the fly ash component. The MgO(001) surface is built to study the stable adsorption configurations of  $\text{Hg}^0$ , HCl, HgCl and  $\text{HgCl}_2$  on all possible adsorption sites. Results show that  $\text{Hg}^0$ , HgCl and  $\text{HgCl}_2$  are all chemisorbed on MgO(001) surface weakly, while HCl is dissociatively adsorbed. HgCl cannot exist stably on the surface, so it has no obvious effect on the adsorption and oxidation of  $\text{Hg}^0$ .

## 1. Introduction

Mercury is an important pollutant in coal-fired flue gas, and its main existing forms are elemental mercury ( $\text{Hg}^0$ ), oxidized mercury ( $\text{Hg}^{2+}$ ) and particulate mercury ( $\text{Hg}^p$ ) [1,2]. The fly ash produced by coal-fired power generation can adsorb  $\text{Hg}^0$  which cannot dissolve in water and is difficult to be removed by existing pollution control devices, to a certain extent [3-5]. Since experimental research is difficult to explain the adsorption and oxidation of  $\text{Hg}^0$  on the surface of fly ash component in micro scale, the quantum chemical Density Functional Theory (DFT) calculation is used to create the conditions for revealing the adsorption and oxidation mechanism of  $\text{Hg}^0$ . On the basis of experimental research, many scholars have conducted deep studies using DFT method on the adsorption and oxidation mechanism of  $\text{Hg}^0$  on the surface of fly ash components including  $\text{Fe}_2\text{O}_3$ [6,7], CuO[8,9] and  $\text{MnO}_2$ [10,11]. However, theoretical studies on the adsorption mechanism of  $\text{Hg}^0$  by MgO are rare.

In this paper, the detailed mechanism of mercury species adsorption and dissociative adsorption of HCl on MgO(001) surface are studied by using first-principles calculations based on the density functional theory and the periodic slab models.

## 2. Computational details

### 2.1. Model

A four-layer MgO(001) slab is used with a  $2 \times 2$  ( $8.5088\text{\AA} \times 8.5088\text{\AA}$ ) unit cell, as is shown in Figure 1. The slabs are separated by a vacuum space of 12  $\text{\AA}$  to prevent interaction between periodic images. The positions of all atoms are allowed to relax with the exception of the bottom 2 layer kept fixed in their bulk positions throughout the calculations.



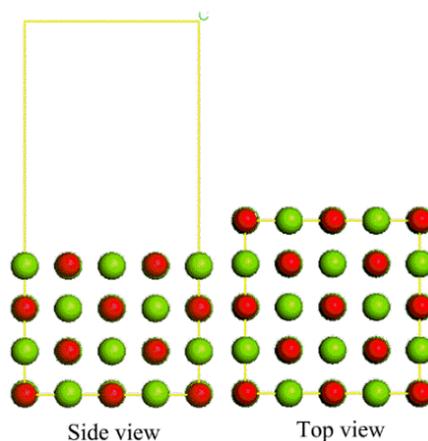
## 2.2. Computational methods

Structural optimizations are performed using DMol<sup>3</sup> package in Materials Studio software in this study. The Perdew–Burke–Erzerhoff generalized-gradient approximation (PBE, GGA) is used for the exchange–correlation functional. The double numerical basis set with polarization functions (DNP) and atomic orbital cutoff of 5.5 Å is used. The (3×3×1) k-points Monkhorst–Pack grid is used for bulk lattice optimization.

For the adsorption of mercury species on MgO(001) surface, the adsorption energy  $E_{ad}$  is defined as:

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

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.

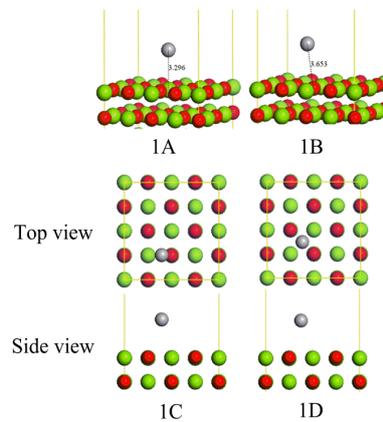


**Figure 1.** MgO(001) surface. Green and red balls represent Mg and O atoms, respectively.

## 3. Results and discussion

### 3.1. $Hg^0$ adsorption on MgO(100) surface

There are four possible adsorption sites for  $Hg^0$  on MgO(001) surface, Mg 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 energies results show that the stability of  $Hg^0$  adsorption is in the order of 1A < 1D < 1C < 1B. All of the adsorption energy values are negative with less absolute value, which indicates the  $Hg^0$  adsorption is weak chemisorption. The adsorption energy of  $Hg^0$  adsorption on Mg site is relatively lower, and  $Hg^0$  is closer to the surface with a distance of 3.296 Å, indicating that  $Hg^0$  is more likely to be bound to the surface Mg atoms. The above results show that  $Hg^0$  cannot be absorbed directly on MgO(001) surface.



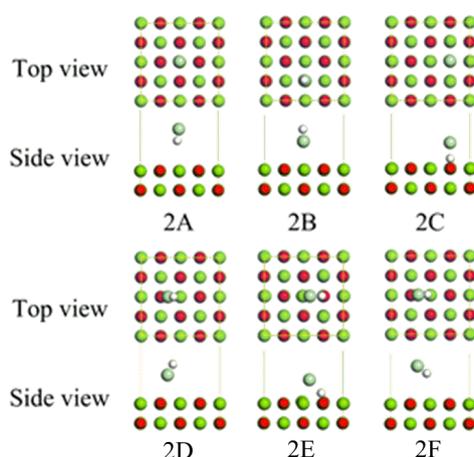
**Figure 2.** Optimized configurations of  $\text{Hg}^0$  adsorption on  $\text{MgO}(001)$  surface. Grey balls represent Hg atoms.

**Table 1.** The adsorption energies and geometric parameters of  $\text{Hg}^0$  adsorption on  $\text{MgO}(001)$  surface.

| No.       | Hg-O ( $\text{\AA}$ ) | Hg-Mg ( $\text{\AA}$ ) | Eads(kJ/mol) |
|-----------|-----------------------|------------------------|--------------|
| <b>1A</b> | -                     | 3.296                  | -11.087      |
| <b>1B</b> | 3.653                 | -                      | -8.690       |
| <b>1C</b> | 3.446                 | 3.591                  | -9.266       |
| <b>1D</b> | 3.616                 | 3.649                  | -9.438       |

### 3.2. HCl adsorption on $\text{MgO}(001)$ surface

HCl in coal-fired flu gas can act as the oxidative agent of the  $\text{Hg}^0$  catalytic oxidation reaction, while the mechanism of HCl affecting the  $\text{Hg}^0$  oxidation on the fly ash composition is still not clear. All possible adsorption sites and initial configuration of HCl are considered. 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  $2\text{E} < 2\text{C} < 2\text{D} < 2\text{B} < 2\text{F} < 2\text{A}$ . All of the adsorption energy values are negative, among which the absolute value of adsorption energy of 2A, 2B, 2D and 2F are relatively low, indicating they are weak chemisorption, while that of 2C and 2E are relatively high. In 2C, the adsorption energy is  $-94.749$  kJ/mol, the distance of H-Cl elongates from  $1.293$   $\text{\AA}$  to  $1.715$   $\text{\AA}$ . H atom of HCl interacts with surface O and the length of new-formed H-O bond is  $1.073$   $\text{\AA}$ . 2E is strong chemisorption with an adsorption energy of  $-94.749$  kJ/mol, in which dissociative adsorption of HCl take place and the H-Cl bond breaks, the distance of H-Cl elongates to  $1.923$   $\text{\AA}$ , H atom interacts with surface O and the length of H-O bond is  $1.022$   $\text{\AA}$ . After the dissociative adsorption of HCl, the Cl radical doesn't adsorb on the surface but releases to the gas phase, which shows that Cl radical may combine with Hg in the gas phase to form  $\text{HgCl}$ , an intermediate of oxidation reaction.



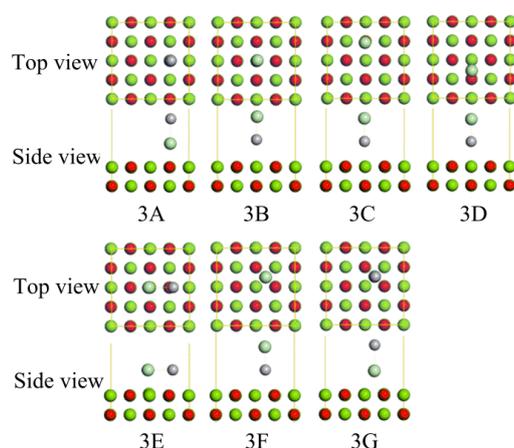
**Figure 3.** Optimized configurations of HCl adsorption on MgO(001) surface. White and grey-green balls represent H and Cl atoms respectively.

**Table 2.** The adsorption energies and geometric parameters of HCl adsorption on MgO(001) surface.

| No.       | H-O<br>(Å) | H-Mg<br>(Å) | Cl-O<br>(Å) | Cl-Mg<br>(Å) | H-Cl<br>(Å) | $E_{\text{ads}}$ (kJ/mol) |
|-----------|------------|-------------|-------------|--------------|-------------|---------------------------|
| <b>2A</b> | -          | 3.353       | -           | -            | 1.293       | -10.125                   |
| <b>2B</b> | -          | -           | 3.021       | -            | 1.295       | -14.496                   |
| <b>2C</b> | 1.073      | -           | -           | -            | 1.715       | -94.749                   |
| <b>2D</b> | -          | -           | 3.144       | 3.366        | 1.295       | -15.267                   |
| <b>2E</b> | 1.022      | -           | -           | 2.51         | 1.923       | -118.092                  |
| <b>2F</b> | 3.415      | -           | 4.2         | -            | 1.291       | -10.540                   |

### 3.3. HgCl adsorption on MgO(001) surface

HgCl is a possible intermediate of oxidation reaction of  $\text{Hg}^0$ . So, it is necessary to study the adsorption of HgCl on MgO(001) surface. All possible adsorption sites and initial configuration of HgCl are considered. 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  $3\text{E} < 3\text{G} < 3\text{A} < 3\text{C} < 3\text{D} < 3\text{F} < 3\text{B}$ . All of the adsorption energy values are negative, but their absolute values are all less than 80 kJ/mol, showing they are relatively weak chemisorption. In addition, the difference of adsorption energy between various configurations is not large. Except for 3E, the absolute values of adsorption energies of other configurations are less than 50 kJ/mol, and all of them are vertical adsorption. The most stable structure for HgCl adsorption on the surface is 3E, in which HgCl adsorbs on the surface horizontally, and Hg atom is close to the surface O atom, Cl atom is close to the adjacent surface Mg atom, the distance between Hg and O is 2.768 Å, the distance between Cl and Mg is 2.614 Å, and Hg-Cl bond elongates slightly from 2.495 Å to 2.700 Å. All these results show that HgCl cannot be absorbed stably on MgO(001) surface, i.e., the intermediate of  $\text{Hg}^0\text{-Hg}^{2+}$  oxidation cannot be formed on the surface.



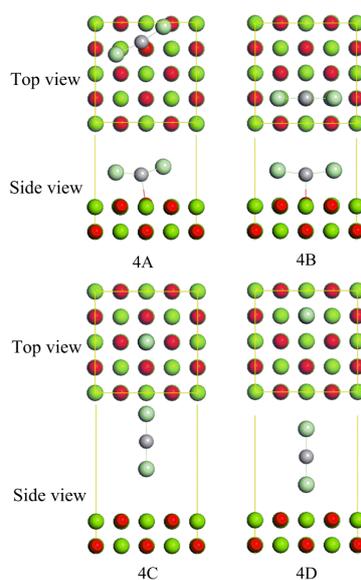
**Figure 4.** Optimized configurations of HgCl adsorption on MgO(001) surface.

**Table 3.** The adsorption energies and geometric parameters of HgCl adsorption on MgO(001) surface.

| No.       | Hg-O<br>(Å) | Hg-Mg<br>(Å) | Cl-O<br>(Å) | Cl-Mg<br>(Å) | Hg-Cl<br>(Å) | $E_{\text{ads}}$ (kJ/mol) |
|-----------|-------------|--------------|-------------|--------------|--------------|---------------------------|
| <b>3A</b> | -           | -            | 2.701       | -            | 2.756        | -49.927                   |
| <b>3B</b> | -           | 3.009        | -           | -            | 2.528        | -43.035                   |
| <b>3C</b> | 2.709       | -            | -           | -            | 2.526        | -45.938                   |
| <b>3D</b> | 2.935       | 3.014        | -           | -            | 2.510        | -45.277                   |
| <b>3E</b> | 2.768       | -            | -           | 2.614        | 2.700        | -72.103                   |
| <b>3F</b> | 3.145       | 3.201        | -           | -            | 2.519        | -44.963                   |
| <b>3G</b> | -           | -            | 3.064       | 2.963        | 2.822        | -51.748                   |

### 3.4. $\text{HgCl}_2$ adsorption on MgO(001) surface

In the  $\text{Hg}^0$  oxidation reaction with HCl,  $\text{HgCl}_2$  is the final product of the reaction. All possible adsorption sites and initial configurations of  $\text{HgCl}_2$  are considered. The optimized configurations of  $\text{HgCl}_2$  adsorption on each site are shown in Figure 5. The adsorption energies and geometric parameters for  $\text{HgCl}_2$  adsorption on MgO(001) surface are given in Table 4. The adsorption energies results show that the stability of  $\text{HgCl}_2$  adsorption is in the order of  $4\text{B} < 4\text{A} < 4\text{C} < 4\text{D}$ . The most stable structure for  $\text{HgCl}_2$  adsorption on the surface is 4B, in which  $\text{HgCl}_2$  adsorbs on the surface horizontally, and Hg atom is close to the surface O atom, Cl atoms are close to 2 adjacent surface O atoms, The Hg-Cl bond has no significant elongation, but the Cl-Hg-Cl angle is reduced to  $163.399^\circ$ . Similar to HgCl, the adsorption of  $\text{HgCl}_2$  on the surface is also a very weak chemisorption. Based on the adsorption of HgCl on MgO(001) surface, it can be inferred that MgO(001) surface has no obvious effect on the adsorption and oxidation of  $\text{Hg}^0$ .



**Figure 5.** Optimized configurations of  $\text{HgCl}_2$  adsorption on  $\text{MgO}(001)$  surface.

**Table 4.** The adsorption energies and geometric parameters of  $\text{HgCl}_2$  adsorption on  $\text{MgO}(001)$  surface.

| No. | Hg-O<br>(Å) | Hg-Mg<br>(Å) | Cl-O<br>(Å) | Cl-Mg<br>(Å) | Hg-Cl<br>(Å) | Cl-Hg-Cl<br>(°) | $E_{\text{ads}}$<br>(kJ/mol) |
|-----|-------------|--------------|-------------|--------------|--------------|-----------------|------------------------------|
| 4A  | 2.629       | 3.889        | -           | -            | 2.379        | 157.442         | -31.195                      |
| 4B  | 2.502       | -            | -           | -            | 2.377        | 163.399         | -51.625                      |
| 4C  | -           | -            | -           | 4.455        | 2.339        | 179.809         | -12.955                      |
| 4D  | -           | -            | 2.933       | -            | 2.342        | 179.953         | -12.923                      |

#### 4. Conclusions

The detailed adsorption mechanism of Hg on  $\text{MgO}(001)$  surface is investigated by a systematic density functional theory study and the periodic slab model.  $\text{Hg}^0$ ,  $\text{HgCl}$  and  $\text{HgCl}_2$  are all chemically absorbed on  $\text{MgO}(001)$  surface weakly, while  $\text{HCl}$  is dissociatively absorbed. Since  $\text{HgCl}$  cannot exist stably on the surface, the intermediate of  $\text{Hg}^0\text{-Hg}^{2+}$  oxidation cannot be formed. As a result, on  $\text{MgO}(001)$  surface, the adsorption and oxidation of  $\text{Hg}^0$  cannot be obviously promoted.

#### 5. Acknowledgments

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