Oxidation mechanism of elemental mercury by HCl over MnO₂ catalyst: Insights from first principles

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Catalytic oxidation of elemental mercury from flue gas is a promising way in the field of mercury pollution control. Among catalysts for Hg oxidation, MnO₂-based materials showed high catalytic activity. The oxidation mechanism of Hg on the MnO₂(110) surface was studied by periodic density functional theory calculations. The thermodynamic stability analysis suggests that the stoichiometric MnO₂(110) is the most stable surface. Hydroxylation and chlorination MnO₂ surfaces can exist under the SCR conditions. The reaction energy profiles of two possible routes (Hg → HgCl → HgCl₂ and Hg → HgCl₂) and the corresponding configurations were examined. The results show that HCl can undergo dissociative chemisorption to form a surface hydroxyl and manganese–chlorine complex. Hg oxidation reaction occurs through Langmuir–Hinshelwood mechanism in which adsorbed Hg reacts with adsorbed Cl from HCl dissociation. The HgCl₂ direct formation on MnO₂(Hg → HgCl₂) is hindered by high energy barrier of 98.25 or 101.97 kJ/mol. Hg can react with adsorbed Cl with a substantially lower barrier (40.12 or 43.59 kJ/mol) to form HgCl, and HgCl can react with adsorbed Cl with a low barrier (57.72 or 66.27 kJ/mol) to form HgCl₂. The calculated results suggest Hg oxidation by HCl over MnO₂ surface prefers the Hg → HgCl → HgCl₂ pathway rather than a pathway Hg → HgCl₂. The HgCl → HgCl₂ process is the rate-determining step for the overall oxidation reaction due to its high energy barrier.

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1. Introduction

Coal-fired power plants are considered to be the largest anthropogenic source of mercury (Hg) emissions [1]. On March, 2013, the US issued a new rule aimed at restricting mercury emission from coal-fired power plants in the Mercury and Air Toxics Standards (MATS) [2]. The MATS requires a maximum mercury emissions concentration between 1.4 and 4.1 μg/m³ (STP, dry) at 6 vol.% O₂ and as a 30-day average for existing power plants. Therefore, to bring coal-fired power plants into compliance with rules, effective technologies to govern mercury emission require to be developed.

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Mercury exists in three forms in coal-fired flue gases: elemental (Hg\textsuperscript{0}), oxidized (Hg\textsuperscript{2+}), and particulate (Hg\textsubscript{p}). Hg\textsuperscript{0} is easy to be captured in the electrostatic precipitator (ESP) and/or baghouse. Hg\textsuperscript{2+} is soluble in water and is easily removed with high efficiency by the wet flue gas desulfurization (WFGD) system \[4\]. Hg\textsuperscript{0}, however, is difficult to capture because of its insolubility and volatility. A promising technology for efficiently and economically controlling the Hg\textsuperscript{0} emission from flue gases is catalytic oxidation of Hg\textsuperscript{0} to its Hg\textsuperscript{2+} form that can be subsequently captured in downstream WFGD system. To date, selective catalytic reduction (SCR) catalysts \[5–7\], carbon-based catalysts \[8,9\], noble metals \[10,11\] and transition metal oxides catalysts \[12,13\] have been widely studied for Hg oxidation. Among these catalysts, MnO\textsubscript{2}-based catalysts have received lots of attention due to their high catalytic performance at low temperature for Hg removal \[14,15\].

In previous experimental studies \[14,16–21\], MnO\textsubscript{2}-based catalysts have shown impressive Hg oxidation activity. Qiao et al. \[20\] studied the catalytic activity of MnO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalysts for Hg\textsuperscript{0} removal in simulated flue gas. They found that the catalytic oxidation of Hg\textsuperscript{0} became dominant in the presence of HCl, and the removal efficiency of Hg\textsuperscript{0} is over 90%. In the subsequent paper \[14\], Hg\textsuperscript{2+} catalytic oxidation reaction on MnO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} was studied within 100–250 °C range, and the results showed that surface-bound chlorine should be available for Hg oxidation. Ji et al. \[21\] found MnO\textsubscript{2}/TiO\textsubscript{2} catalysts were effective for both Hg\textsuperscript{0} capture and low temperature SCR. Although many experimental studies have proven the removal efficiency of MnO\textsubscript{2} on Hg, the detailed reaction mechanisms are not well understood. It has been proposed three Hg oxidation mechanisms, i.e., Langmuir–Hinshelwood (L–H) mechanism, Eley–Rideal (E–R) mechanism, and Mars-Maessen mechanism. In L–H mechanism, Hg oxidation reaction occurs between two species (Hg and HCl) adsorbed to catalysts’ surface and forms adsorbed product HgCl\textsubscript{2}. In E–R mechanism, Hg oxidation reaction occurs between a catalyst-bound species and a gas-phase (or weakly bound) species. In Mars–Maessen mechanism, Hg would react with a lattice oxidant of catalyst that is replenished from the gas phase (either O\textsubscript{2} or Cl\textsubscript{2}) to form HgO or HgCl\textsubscript{2} directly. To date, there is no general agreement on the reaction mechanism of Hg oxidation over the MnO\textsubscript{2} catalysts.

Quantum chemical methods, in the form of density functional theory (DFT), have been applied to study the adsorption of Hg on different sorbents and the heterogeneous reactions of Hg on different catalysts \[15,22–24\]. We have presented theoretical studies of binding behavior of Hg on MnO\textsubscript{2} surface \[25\]. However, the detailed reaction mechanism of mercury oxidation by HCl over MnO\textsubscript{2} has not yet been investigated. Therefore, as a continuation of previous study, the interaction of HCl and the MnO\textsubscript{2} surface, and the detailed reaction mechanism of Hg oxidation by HCl over MnO\textsubscript{2} catalysts were investigated using the DFT method and periodic slab models. The energy profiles of Hg oxidation on MnO\textsubscript{2} surface was plotted. The configurations of involved transition states and intermediates along the reaction pathway of Hg oxidation on MnO\textsubscript{2} surface were located.

2. Computational method and models

2.1. Density functional theory calculations

DFT calculations were performed using the linear combination of atomic orbitals code Dmol\textsuperscript{3} package \[26\]. The electron exchange correlation functionals were modeled using the Perdew, Burke, and Ernzerhof (PBE) \[27\] approximation which was described using the generalized gradient approximation (GGA) scheme \[28\]. The spin polarization correction was addressed in the calculations. The double numerical basis set with polarization functions (DNP) and atomic orbital cutoff of 4.5 Å was used. The (4 × 4 × 7) k points Monkhorst–Pack grid were used for bulk lattice optimization. The structure of MnO\textsubscript{2} is of a tetragonal symmetry within P4\textsubscript{2}mmn space group. The optimized bulk lattice constants \(a = b = 4.4541 \text{ Å}, c = 2.9007 \text{ Å}\) are in good agreement with experimental values \(a = b = 4.4041 \text{ Å}, c = 2.8765 \text{ Å}\) \[29\]. The relative errors are within 1.1% and 0.8%, respectively, indicating that the calculations are reliable.

The MnO\textsubscript{2}(1 1 0) surface is the most thermodynamically stable one for all surfaces of MnO\textsubscript{2} \[30,31\]. At the MnO\textsubscript{2}(110) surface, there are fivefold, sixfold, twofold-coordinated and threefold-coordinated Mn\textsubscript{5}, Mn\textsubscript{6}, O\textsubscript{h}, and O\textsubscript{a} atoms, respectively, as shown in Fig. 1. A nine- layer (3 × 2 × 1) Monkhorst–Pack grids were used for the surface. The adsorption energy \(E_{\text{ads}}\) was calculated by:

\[
E_{\text{ads}} = E_{\text{adsorbate–substrate}} - (E_{\text{adsorbate}} + E_{\text{Substrate}})
\]

Here, \(E_{\text{adsorbate–substrate}}\), \(E_{\text{adsorbate}}\) and \(E_{\text{Substrate}}\) is the total energy of the adsorbate/substrate system, isolated adsorbate and the substrate, respectively. A negative \(E_{\text{ads}}\) value indicates a stable adsorbate–substrate system.

Transition states (TS) are determined using the linear synchronous transit/quadratic synchronous transit (LST/QST) combined with conjugate gradient (CG) method refinements method \[32,33\]. A maximum energy pathway is obtained by LST method along the path between the reactant and product, and TS approximation is constructed from the pathway by QST maximization. Then CG minimization is performed. The stationary point along this path is a real transition state, which is located by cycles of QST maximization with CG refinement until convergence is obtained or maximum number of allowed QST steps is reached. The energy barrier is defined as:

\[
E_{\text{Barrier}} = E_{\text{(transition state) – Intermediate}}
\]

where \(E_{\text{(transition state)}}\) and \(E_{\text{Intermediate}}\) represent the total energy of transition state and the intermediate, respectively.

2.2. Ab initio thermodynamic calculations

The ab initio thermodynamic method has been successfully applied in many catalytic systems \[15,34\], and in this work ab initio thermodynamic calculations were used to identify the lowest-energy structure of different terminated MnO\textsubscript{2}(110) surfaces for a given condition of thermodynamic reservoirs as a function of temperature (T) and pressure (P). The thermodynamic
stability of oxygen-vacancy, protonation, hydroxylation, and chlorination of MnO$_2$ surfaces were analyzed by ab initio thermodynamic calculations. As suggested by Scheffler and Reuter [35], the stability of a given surface can be determined by the surface free energy $\gamma(T, p_i)$ within the general scheme:

$$\gamma(T, p_i) = \frac{1}{2A} \left[ G - \sum_i N_i \mu_i(T, p_i) \right]$$

(3)

Here $G$ is the Gibbs free energy of a periodic surface, $A$ is the surface area of the surface, $\mu_i(T, p_i)$ is the chemical potential of the species $i$, and $N_i$ represents the atom numbers of the corresponding element. For the MnO$_2$ surface, the above equation can be rewritten as:

$$\gamma(T, p_i) = \frac{1}{2A} \left[ G_{\text{slab}} - N_{\text{Mn}} \mu_{\text{Mn}}(T, p_i) - N_0 \mu_O(T, p_i) \right]$$

(4)

$G_{\text{slab}}$ is the Gibbs free energy of a solid MnO$_2$ slab, $E_{\text{slab}}$, which is obtained from the DFT total energy of the surface at 0 K. $\mu_{\text{Mn}}$ and $\mu_O$ are the chemical potentials of Mn and O. In a general sense, the bulk MnO$_2$ and its components satisfy the following relation:

$$\mu_{\text{Mn}} + 2\mu_O = G_{\text{MnO}_2}^{\text{bulk}}$$

(5)

$G_{\text{MnO}_2}^{\text{bulk}}$ is the Gibbs free energy of the per formula unit MnO$_2$. Thus, for the MnO$_2$ system, the Eq. (4) can be rewritten as:

$$\gamma(T, p_i) = \frac{1}{2A} \left[ E_{\text{slab}} - N_{\text{Mn}} G_{\text{MnO}_2}^{\text{bulk}}(T, p_i) + (2N_{\text{Mn}} - N_0) \mu_O(T, p_i) \right]$$

(6)

For the gas phase reservoirs, O$_2$, H$_2$O and HCl are considered in this work. And the species chemical potential can be written as follows:

$$\mu_i = \frac{1}{2} \mu_i^{\text{gas}}$$

(7)

$$\mu_O + 2\mu_H = \mu_{\text{H}_2\text{O}}^{\text{gas}}$$

(8)

$$\mu_O + \mu_{\text{H}} = \mu_{\text{HCl}}^{\text{gas}}$$

(9)

The gas phase species $\mu_i$ (O$_2$, H$_2$O and HCl) chemical potential can be related with the temperature and pressure as follows:

$$\mu_i(T, p) = E_{i}^{\text{total}}(\text{DFT}) + E_{i}^{\text{ZPE}} + \mu_i(T, p^0) + k_B T \ln \left( \frac{p}{p^0} \right)$$

(10)

$E_{i}^{\text{total}}$ is the DFT total energy of the isolated gas phase molecule. $\mu_i(T, p^0)$ can be obtained from the NIST-JANAF thermodynamic stable [36]. $k_B$ is the Boltzmann constant.

From Eqs. (5, 7 and 8), $\mu_O$ varies under different gas phases. Thus, $\mu_O$ is constrained in a suitable range. First, if $\mu_O$ is too low, MnO$_2$ will not steadily exist, and decompose into metal Mn and O atoms. Thus

$$\min(\mu_O(T, p)) = \frac{1}{2} \{ G_{\text{CeO}_2}^{\text{bulk}}(0, 0) - G_{\text{Ce}}^{\text{bulk}}(0, 0) \}$$

(11)

For the gas phase oxygen atom condensed. So the high limit of the $\mu_O$ is:
If we defined the relative chemical potential of oxygen to be 

$$\Delta \mu_0 = \mu_0 - \frac{1}{2} C^\text{gas}_2,$$

the range of the $\Delta \mu_0$ is:

$$\frac{1}{2} (G^\text{bulk}_{\text{MnO}_2} - G^\text{bulk}_{\text{Mn}} - G^\text{gas}_2) < \Delta \mu_0 < 0$$

3. Results and discussion

3.1. Structure and stability of the MnO₂(110) surfaces

In Hg oxidation reaction, surface-oxygen of catalyst is an important active site [15]. While the formation of oxygen vacancies over surface and diffusion of oxygen from bulk to surface play important role during the whole Hg oxidation cycle. Thus, it is important to analyze the stability of the stoichiometric and oxygen-vacancy MnO₂(110) surfaces under flue gas conditions as a function of the oxygen partial pressure and temperature to determine their impact on MnO₂(110) surfaces. The thermodynamic stabilities of stoichiometric and oxygen-vacancy surfaces of the MnO₂(110) are shown in Fig. 2. As shown in Fig. 2, under the SCR flue gas conditions ($500 \text{ K} < T < 700 \text{ K}, p_{O_2} \approx 0.05 \text{ atm}$), the value of oxygen chemical potential is around $-1 \text{ eV}$ and the stoichiometric MnO₂(110) surface is the most stable one with the lowest free energy. In other words, the stoichiometric surface is more stable than the Obr-half vacancies, Obr-all vacancies or Ocus surfaces under SCR conditions. These results are supported by scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) experimental results from Loomer et al. [37], who suggest that the oxidation state of manganese atom in natural manganese minerals is 4.0.

H₂O is an important component in the flue gases. The structure of MnO₂ may be modified by the flue gases and temperature. Therefore, the thermodynamic stability of protonated and hydroxylated surfaces of MnO₂ was studied and shown in Fig. 3. In the oxygen-rich region (ORR) of Fig. 3, the H₂O adsorbed (H₂O on Mn) and H₂O dissociated (HO on Mn and H on Obr) surfaces are much lower in free energy, suggesting they are more stable than other surfaces. The main reason causing stable hydroxylated surfaces is the hydrogen bonds between surface hydroxyl groups. Therefore, the presence of H₂O in the flue gas may modify the composition and the reactivity of the MnO₂ surface by hydroxylation.

HCl plays a key role in Hg catalytic oxidation reaction and the presence of HCl may lead to surface chlorination. Therefore, it is necessary to study the structure and stability of the MnO₂ surfaces as a function of HCl partial pressure and temperature to understand the function of MnO₂ as a catalyst for mercury oxidation. The thermodynamic stability of two chlorinated surfaces are shown in Fig. 4. It can be seen that the surface of Cl on Mn and H on Obr 1/6 ML is lower in free energy for the chemical potential...
of HCl ranging from −3.0 to 2 eV. The stability of chlorinated MnO$_2$(110) surface increases with the concentrations of HCl. In addition, high coverage of chlorinated MnO$_2$(110) surface will decrease the stability of chlorinated structures.

3.2. Hg$^0$ and HCl adsorption on the MnO$_2$(110) surface

Hg atom was placed on the different adsorption sites of the surface: Mn top, O$_3$ top, O$_{br}$ top, and O$_{br}$ bridge. The adsorption energy of Hg on MnO$_2$(110) is ranging from −63.51 to −78.32 kJ/mol, and the stability of Hg adsorption on MnO$_2$(110) surface is in the order of O$_3$ top < Mn$_3$ top < O$_{br}$ top < O$_{br}$ bridge. It was found that Hg adsorption on MnO$_2$(110) is chemisorption, which is in good agreement with XPS experiment reporting that a HgMnO$_x$ mixed phase is formed after Hg$^0$ adsorption [20]. More detailed discussion has been reported in our previous work [25].

HCl is the most important reactant for HgCl$_2$ formation due to the large HCl concentration compared to Cl$_2$ in the flue gas [38]. The overall reaction of Hg$^0$ oxidation is generally agreed by the following equation:

$$\text{Hg}^0 + 2\text{HCl} + 1/2\text{O}_2 \rightarrow \text{HgCl}_2 + \text{H}_2\text{O}$$

(14)

The adsorption and dissociation of HCl were examined to understand the reactivity of the surface and the whole oxidation reaction. The stable adsorption configurations of HCl on MnO$_2$(110) surface are shown in Fig. 5, and the adsorption energies and geometric parameters are given in Table 1. The most stable structure for HCl
Adsorption on MnO$_2$ (110) surface is 1C with an adsorption energy of −181.50 kJ/mol, showing a chemical adsorption. In 1C, the H–Cl bond is stretched from 1.290 Å (gaseous HCl) to 2.261 Å, and the bond lengths of H–O and Cl–Mn are 0.993 and 2.251 Å, respectively, which suggests that the H–Cl bond is broken after HCl adsorption on MnO$_2$ (110) surface. The other stable configuration for HCl (1B) is similar in geometric structure to that of 1C.

The partial density of states (PDOS) of the surface atoms was investigated to provide further insight into the binding mechanism of HCl on the MnO$_2$ (110) surface, as shown in Fig. 6 and Fig. 7. In Fig. 6, the H s- and p-orbitals for gaseous HCl are strongly hybridized with the Cl s- and p-orbitals, suggesting a strong interaction between H and Cl. After adsorption, all orbitals of H and Cl atoms shift downward and lower in energy, and PDOS of H and Cl have no hybridization peaks at all. Meanwhile, in Fig. 7, the H s- and p-orbitals are hybridized with the O s- and p-orbitals approximately at −19.0 and −6.5 eV. And the Cl s- and p-orbitals are hybridized with Mn s-orbital approximately at −18.0, −2.1 and 1.2 eV. The PDOS analyses suggest that H–Cl bond is totally broken and a surface hydroxyl and manganese–chlorine complex are formed on MnO$_2$ (110) surface. On the basis of above analyses, it can be inferred that HCl undergoes dissociative chemisorption on MnO$_2$ (110) surface and transformed into surface hydroxyl and manganese–chlorine complex, which verifies the experimental predictions [14,20].

### 3.3. Reaction mechanism of Hg oxidation by HCl over MnO$_2$ surface

From the above results, chlorinated MnO$_2$ (110) surface is stable under SCR conditions, Hg is chemically adsorbed on MnO$_2$ (110) surface and HCl dissociates on MnO$_2$ (110) surface. It can be concluded that Hg oxidation follows L–H mechanism, where Hg oxidation reaction starts with the interaction of adsorbed Hg$^0$ with the active chlorinated sites on MnO$_2$ (110) surface. This conclusion
was validated by a recent experimental study by Scala et al. [39]. They found that the presence of HCl promotes Hg oxidation and both HCl and Hg are adsorbed on the surface of MnO2/Al2O3. In addition, kinetics model based on L–H mechanism well describes the Hg oxidation reaction between Hg and ozone molecule over MnO2/Al2O3 [40], which suggests that Hg and oxidizing agent tend to be co-adsorbed on the adjacent active sites and L–H mechanism may apply to describe Hg oxidation reaction on MnO2-based catalysts.

For Hg oxidation pathway analyses, the most stable adsorption configurations of atomic Hg, Cl and H atoms (IM1 and IM1'), as shown in Fig. 8, are taken as the initial configurations of the Hg oxidation species on MnO2(110) surface. Two pathways for Hg oxidation on MnO2 surface via IM1 and IM1' were studied and shown in Fig. 8. The pathway 1 goes through two steps: (1) Hg → HgCl and (2) HgCl → HgCl2. The pathway 2 goes through one step: Hg → HgCl2. The energies of the optimized intermediate (IM), transition state (TS) and final state (FS) are relative to the initial adsorption configuration. The structures of intermediates, transition states and final states in Hg oxidation pathways on MnO2(110) surface are shown in Fig. 9. The energy barriers of two pathways for Hg oxidation are listed in Table 2.

In the case of Hg oxidation reaction via IM1, the pathway 1 for Hg oxidation is via IM1 → TS1 → IM2 → TS2 → FS1 including two steps: (1) Hg → HgCl and (2) HgCl → HgCl2. The Hg → HgCl reaction is exothermic by 28.06 kJ/mol with an energy barrier of 40.12 kJ/mol. At IM1, the Hg is adsorbed on Obr site and Cl is on Mn site. Then, the Cl atom approaches the Hg, forming a transition state TS1. Over TS1, a intermediate, IM2, the MnHgCl complex is formed on the MnO2(110) surface with Hg–Cl bond length 2.403 Å, indicating the formation of HgCl. At the same time, the distance between Hg and O increases gradually: 2.639 Å in IM1, 2.993 Å in TS1, and 3.652 Å in IM2. The second step is HgCl → HgCl2 via the IM2 → TS2 → FS1. This step is endothermic by 6.64 kJ/mol. The energy barrier for this step is 57.72 kJ/mol higher than that in the first step, suggesting the rate-limiting step for the Hg oxidation reaction. Finally, a HgCl2 molecule is formed with Hg bound to Mn-top site and two Cl atoms turned upward. During this step, the distance between Cl and Hg decreases gradually: 2.649/2.403 Å in IM2, 2.440/2.432 Å in TS2, and 2.378/2.377 Å in FS1, indicating the formation of HgCl2. Pathway 2 (Hg → HgCl2) is via IM1 → TS3 → FS1. The energy barrier for this pathway is as high as 98.25 kJ/mol, suggesting an unfavorable oxidation pathway. The whole reaction is exothermic by 21.42 kJ/mol.

In the case of Hg oxidation reaction via IM1', the pathways of Hg oxidation is similar to that in the case via IM1. For pathway 1, the first step is exothermic by 25.89 kJ/mol with an energy barrier of 43.59 kJ/mol. The second step is exothermic by 15.84 kJ/mol with an energy barrier of 66.27 kJ/mol, suggesting the rate-limiting step. For the pathway 2 directly oxidizing Hg to HgCl2, the energy barrier is as high as 101.97 kJ/mol, suggesting an unfavorable oxidation pathway. The whole reaction is exothermic by 41.73 kJ/mol.

Comparing the oxidation pathways in the two cases, Hg oxidation prefers the pathway: Hg → HgCl → HgCl2, rather than a pathway directly oxidizing Hg to HgCl2. The rate-limiting step is the second step HgCl → HgCl2, i.e., the formation of HgCl2.

Furthermore, it’s interesting to compare Hg oxidation on MnO2 to that on other catalyst surfaces. The Hg oxidation reaction on Au(1 1 1) [10], Pd(100) [33] and V2O5/TiO2(001) [32] has been calculated using DFT method. Meanwhile, the experimental studies have proven that Au, Pd and V2O5/TiO2 catalysts are very effective for the oxidation of Hg0 to Hg2+ [41,42]. It was found that Hg oxidation over Au surface occurs via a L–H mechanism and the Hg oxidation pathway tends to Hg → HgCl → HgCl2, rather than HgCl → HgCl2 [10], which is similar to our conclusion. Hg oxidation on Pd surface also follows the L–H mechanism. Further comparing MnO2 with V2O5/TiO2, we found that Hg oxidation reaction on V2O5/TiO2 undergoes by E–R mechanism because Hg is physically adsorb on V2O5/TiO2. But HgCl2 formation reaction is the rate-determining step for all of them due to its high barrier. Specifically, barriers of HgCl2 formation on MnO2(110) surface is either 57.72 or 66.27 kJ/mol, Au(1 1 1) surface is from 33 to 55 kJ/mol, Pd(100) surface is 67.53 kJ/mol, and V2O5/TiO2(001) surface is 91.53 kJ/mol. We found that barrier of rate-determining step on MnO2 is higher than that on Au(1 1 1), but lower than that on Pd(100) and V2O5/TiO2(001), which implies that MnO2 will be an attractive alternative for Hg oxidation in current SCR catalysts.

![Fig. 8. The reaction pathways and energy profiles of Hg oxidation on MnO2(110) surface via (a) IM1 and (b) IM1'.](image-url)
4. Conclusion

The detailed Hg oxidation mechanism by HCl over MnO$_2$(110) surface was firstly investigated by a systematic density functional theory study and the periodic slab model. The ab initio thermodynamic studies suggest that the oxygen-vacancy surfaces of MnO$_2$(110) cannot stably exist under flue gas conditions. Hydroxylation MnO$_2$(110) surfaces take place at low oxygen partial pressures, and chlorination MnO$_2$(110) surfaces can stably exist under low HCl concentrations. Details of the electronic properties of HCl adsorption on MnO$_2$(110) show that HCl undergoes dissociative chemisorption on MnO$_2$(110) surface to form a hydroxyl and manganese–chlorine complex. The Hg oxidation on MnO$_2$(110) surface follows a Langmuir–Hinshelwood mechanism in which adsorbed Hg$^0$ reacts with manganese–chlorine complex via the Hg$^+$HgCl$^-$HgCl$_2$ pathway. In the whole Hg oxidation reaction, the formation of HgCl$_2$ is the rate-determining step because of its high energy barrier. Further investigations will be carried out to examine the reaction rate equation by experimental studies and quantum chemistry.

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