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Density functional theory study of mercury adsorption and oxidation on CuO(1 1 1) surface

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HIGHLIGHTS

- The adsorption mechanism of mercury on CuO(1 1 1) surface is investigated.
- Hg^0 is physically adsorbed on CuO(1 1 1) surface.
- HCl rather than Cl_2 is responsible for the oxidation of Hg^0 on CuO(1 1 1) surface.

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ABSTRACT

The structures and electronic properties of Hg, HgCl, and $HgCl_2$ adsorption on CuO(1 1 1) surface have been determined using density functional theory with the generalized gradient approximation. After optimization, a small adsorption energy of 27.4 kJ mol^{-1} is found when the Hg atom on the CuO(1 1 1) surface, which infers Hg^0 is weakly physisorbed at the surface of the CuO. The adsorption configurations of HgCl, Cl_2 and HCl are the dissociative modes, but $HgCl_2$ with the molecular modes. The mercury oxidation reaction of Hg^0 on CuO(1 1 1) surface via Cl_2 and HCl are examined and the activation barrier are 14.44 and 2.57 kJ mol^{-1}, respectively. It is indicated that the oxidation reaction of Hg^0 via HCl on the CuO(1 1 1) surface is likely the dominant interaction pathway.

1. Introduction

Mercury (Hg) is a major atmospheric pollutant from coal combustion industries [1,2]. Mercury can exist in the elemental (Hg^0), oxidized (Hg^{2+}), or particulate (Hg_p) forms in the flue gas depending upon combustion conditions, the coal's chlorine content, and amount of hydrogen chloride. Hg_p and Hg^{2+} can be captured by particulate matter control devices and wet flue gas desulfurization systems, respectively [3]. However, Hg^0 is difficult to be captured because of its high volatility and low solubility in water. Thus, the development of an efficient method for the removal of Hg^0 is an urgent concern.

Various sorbents or catalysts may be used in the combustion flue gas environment to capture and/or oxidize elemental Hg (Hg^0), including activated carbon [4–6], metal oxides [7,8], metal sulfides [9], and pure metals [10,11]. CuO is usually present in the fly ashes of combusted coals and ores through coal gasification. This compound is of scientific and technological importance as catalysts [12]. Among these sorbents and catalysts, CuO exhibited significant catalytic activity in the surface-mediated oxidation of Hg^0 in the presence of HCl. It was presumed that Hg oxidation is preceded by the Deacon process, where Cl_2 is produced via the catalytic oxidation of HCl on the CuO surface [13].

During the oxidation reaction of Hg^0, experimental information is not always sufficient. Quantum chemistry methods based on density functional theory have been increasingly used to evaluating the mechanisms involved in elemental mercury adsorption and oxidation on solid surfaces. Meanwhile, understanding the adsorbents' surface properties theoretically will help us to choose the best adsorbent for certain adsorbates. Zhang studied the mercury oxidation mechanism on Pd(1 0 0) surface which occurs through a Langmuir–Hinshelwood mechanism [14]. Guo studied the roles of perfect and defective γ-Fe_2O_3 surface in fly ash for mercury removal, and found that the capacity of γ-Fe_2O_3 for elemental mercury removal is sensitive to the structure of solid materials [15]. Tao found that the Eley–Rideal mechanism with Hg^0 adsorption on H_2S/α-Fe_2O_3 surface is the most probable reaction process

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[16]. Steckel characterized the interaction of mercury with copper, nickel, palladium, platinum, silver, and gold surfaces [17]. To our knowledge, the adsorption mechanism of elemental mercury on CuO surface has been reported [18]. However, correlations between Hg-containing species and CuO(1 1 1) surface have not been well established. Little is known at the molecular level about the mercury oxidation mechanism on CuO surface.

In this paper, the structure of Hg, HgCl and $HgCl_2$ adsorption on CuO(1 1 1) surface have been determined using density functional theory with the generalized gradient approximation. The possible oxidation mechanism of Hg^0 on CuO(1 1 1) surface via HCl or Cl_2 have been investigated.

2. Computational model and method

2.1. Computational model

CuO has a monoclinic structure with space group C2/c1 (a = 4.690 Å, b = 3.420 Å, c = 5.131 Å, and β = 99.540) [19]. Each atom has four nearest neighbors of the other kind: Cu atom is surrounded by a square of oxygen atoms, while each oxygen atom is surrounded by a distorted tetrahedron of copper atoms [18,20]. It is found that CuO(1 1 1) have the lowest surface free energies and hence should be the most preferential facets of CuO [21]. In addition, being an important crystal face, CuO(1 1 1) surface is modeled by using the supercell approach, where periodic boundary condition is applied to the central supercell so that it is reproduced periodically throughout space. Fig. 1 displays the side view and the top view of CuO(1 1 1) surface configurations. The CuO(1 1 1) surface includes eight different types of surface adsorption sites, including "Cu_{suf}", "Cu_{sub}", "O_{suf}", "O_{sub}", "Cu_{sub}-Cu_{sub} bridge", "O_{sub}–O_{sub} bridge", "O_{suf}–O_{suf} bridge", "Cu_{suf}–Cu_{suf} bridge" sites, which are denoted as I, II, III, IV, V, VI, VII and VIII, respectively.

A six-layer slab with a (3 × 2) unit cell is used to model the 1/6 monolayer (ML) coverage. Adsorbate and the top tree atomic layers of the substrate are allowed to relax in all of the geometry optimization calculations [22]. The vacuum region between slabs is 10 Å to eliminate spurious interactions between the adsorbate and the periodic image of the bottom layer of the surface [18].

2.2. Computational method

The geometric and electronic aspects of the structures are investigated in the framework of density functional theory (DFT) using the $Dmol^3$ program package in Materials Studio 7.1 [23,24], and the main calculations here are conducted with the generalized gradient approximation with a PW91 functional, which can give very much better results for the adsorption energies than the local density approximation, though it still does not give full chemical accuracy [25–27]. The DFT calculations coupled with a van der Waals-inclusive correction (DFT-D) are carried out to improve the calculations [28]. The inner electrons of Cu atoms and Hg atoms are kept frozen and replaced by an effective core potential (ECP) [29], and other atoms in this study are treated with an all electron basis set.

A Monkhorst–Pack mesh k-points grid of 3 × 2 × 2 is used to simplify the Brillouin zone and the real space cutoff radius is maintained as 5.0 Å. The parameters criteria for the tolerances of energy, force, displacement, and SCF convergence criteria are 1.0×10^{-5} Ha, 0.002 Ha $Å^{-1}$, 0.005 Å, and 1.0×10^{-6}, respectively. A Methfessel–Paxton smearing of 0.005 Ha is used to improve calculation performance. Meanwhile, transition state (TS) search is performed at the same theoretical level with the complete linear synchronous transit and quadratic synchronous transit (LST/QST) method [30]. In this method, the LST method performs a singly interpolation to a maximum energy, and the QST method alternates searches for an energy maximum with constrained minimizations in order to refine the transition states to a high degree [31,32].

In this work, the bond lengths of HgCl and $HgCl_2$ molecules are calculated to be 2.508 Å and 2.318 Å, respectively, which agree with the experimental values of 2.36–2.50 Å and 2.25–2.44 Å [33].

The adsorption energy is computed by subtracting the energies of the gas phase species and the surface from the energy of the adsorbed system as follow:

$$E_{ads} = E_{adsorbate} + E_{CuO(1\ 1\ 1)} - E_{adsorbate/CuO(1\ 1\ 1)} \quad (1)$$

where E_{ads} is the adsorption energy, $E_{adsorbate/CuO(1\,1\,1)}$ is the total energy of the adsorbed molecule on the CuO(1 1 1) surface, $E_{adsorbate}$ is the energy of isolate adsorbed molecule in the vacuum, and $E_{CuO(1\,1\,1)}$ is the energy of the CuO(1 1 1) surface. With this definition, a positive adsorption energy corresponds to a stable adsorption.

3. Results and discussion

3.1. Hg^0 adsorption on the CuO(1 1 1) surface

The adsorption mechanism of Hg^0 is firstly investigated with eight adsorption sites on the CuO(1 1 1) surface. During a full geometry optimization, four stable adsorption configurations are obtained, as presented in Fig. 2. The modes of the Hg bonded to I, IV, VI and VII sites are all converted to the mode of Hg bonded to the II site. The calculated adsorption energies and Mulliken charges are listed in Table 1.

Comparison of the adsorption energies shows that Hg(a) mode is the most stable configuration, which indicates that the Hg atom is more preferable to bond with the Cu_{sub} site. The adsorption

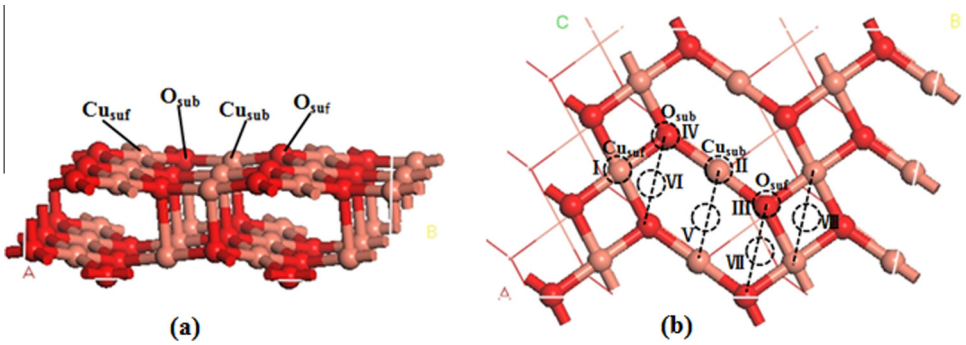

Fig. 1. The slab model of the CuO(1 1 1) surface. (a) side view; (b) top view. The orange and red spheres represent the Cu and O atoms, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)