

ADSORPTION ENERGIES OF MERCURY CONTAINING SPECIES ON THE SURFACE OF CALCIUM OXIDE (0 0 1) PREDICTED BY DENSITY FUNCTIONAL THEORY

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Abstract— In this work, the use of computational chemistry methods for predicting Hg and HgCl₂ adsorption on CaO was introduced, which has never been studied before with theoretical calculations. The GGA functionals was used to obtain the optimized geometries and adsorption energies of proposed periodic and adsorption site structures. Also, the goal of the research is to investigate if GGA functionals gives reliable answers compared to available experimental datas.

Index Terms— Adsorption Energy, Calcium Oxide, Density Functional Theory, Mercurous Hg(I) Species, Mercuric-Hg(II) Species

1 INTRODUCTION

As flue gases are released from coal fired boilers, elemental mercury-Hg(0) is oxidized into mercurous Hg(I), and mercuric-Hg(II) species in the form of HgCl and HgCl₂ [1], mostly promoted by chlorine and atomic chlorine, as proposed by Slinger, et al. [2], [3]. However, only the mercuric-Hg (II) form (HgCl₂) exists in the flue gases because HgCl is directly oxidized to HgCl₂. The Environmental Protection Agency (EPA) has set regulations on mercury emission concentrations of 0.1 µg Hg / 1 kg coal / day, and choosing appropriate sorbents to reduce Hg emissions is an essential key in meeting this regulation. There are many experimental papers on Hg reduction and various kinds of sorbents being used in coal fired power plants, such as activated carbon, calcium-based sorbents, fly ash and zeolites [4], [5]. Finding and exploring the properties of effective and inexpensive sorbents is the current challenge. Paper Waste Derived Sorbent (PWDS) is a newly developed sorbent and was proved to be very effective in a bench scale Hg control system [6]. The components in PWDS are CaO 23 wt%, Al₂O₃ • SiO₂ 29 wt%, CaCO₃ 41 wt%, inert 6 wt% and Ca(OH)₂ 1 wt%. Since CaO is one of the primary constituents in this novel sorbent that could be used in coal fired power plants, the adsorption of Hg and HgCl₂ on the CaO surface were investigated so the fundamental interactions between Hg-species and the sorbent could be explored.

It is very difficult to examine the adsorption mechanisms of Hg-containing species on surfaces experimentally [7]. On the other hand, theoretical methods can be employed to investigate how Hg-containing species are adsorbed on the sorbent. The increase in computer speed and the accuracy of computa-

tional quantum chemistry methods leads them to be applied to the study of surface chemistry more frequently. Meanwhile, understanding the adsorbents' surface properties theoretically will help us to choose the best adsorbent for certain adsorbates. We studied Hg and HgCl₂ adsorption on the CaO (0 0 1) surface by performing Density Functional Theory (DFT) calculations using Generalized Gradient Approximation (GGA/BLYP) functionals on periodic model in this work.

2 METHODOLOGY

DFT with the DMol³ [8] package in the Accelrys Materials Studio 2001 (Accelrys Inc.) was used for this study. All simulations for periodic CaO models used the AE (all electron) method and DNP (double-numeric) basis set. The GGA was combined with the Becke-Lee-Yang-Parr (BLYP) correlation functional [9], [10], [11]. The higher-level calculations of the GGA/BLYP method used the fully optimized geometries to obtain the adsorption energies. Mulliken and Hirshfeld population analyses were computed, not only to calculate atomic charges for Hg and HgCl₂ adsorption models on CaO periodic slabs, but also to investigate how the mercury-containing species interact with the model CaO surfaces.

Spin unrestricted calculations on the periodic slab were also conducted because spin polarization could have an affect on the adsorption energies. Spin-orbit coupling effects are neglected in this scalar relativistic approach based on prior research with other mercury calculations [12]. The numerical basis functions of DMol³ are more complete functions than Gaussian functions, and are expected to have small BSSE (the basis set superposition error) contributions while ab initio methods use BSSE calculations to estimate the errors associat-

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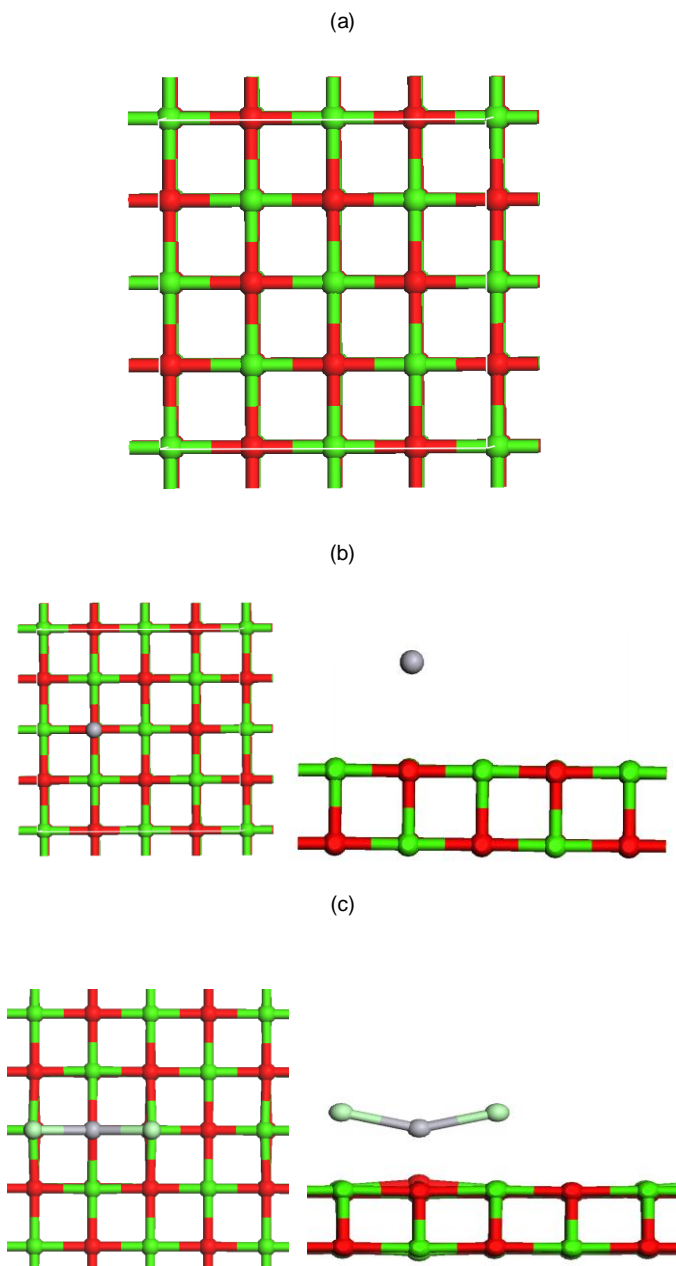


Fig.1. Optimized geometry of Structure of Hg and HgCl₂ adsorption on CaO (a) the infinite CaO (0 0 1), (b) Hg consistently adsorbed on an atop site over the oxygen atoms on the surface of the CaO (0 0 1), (c), HgCl₂ adsorbed on the CaO (0 0 1) wherein each chlorine atom gravitated to calcium sites. Green color depicts calcium atoms; light green is Chlorine, red is Oxygen, and gray is Mercury.

ed with their incomplete basis sets [13]. A small BSSE contribution due to the basis sets of DMol³ was verified by calculating water dimer with a larger basis set. The interaction energy was changed by less than 0.5 kcal/mol in these calculations [14], [15]. They, indirectly, proved that further basis set extensions have a small BSSE effect on interaction energies.

The surface of CaO (0 0 1) that has been used by other theoretical researchers [16] was investigated. It should be noted

that the 3×3×2 cluster model had edge effects but 5×5×2 cluster models succeeded in size convergence [17]. The 5×5×2 cluster models are large enough to handle the adsorbates studied here. In this work, the clean perfect surface was modeled by a 5×5×2 periodic structure. The Hg coverages for the periodic slab is 4.0% since the surface was designed with a 5×5 unit cell. These low coverages were used to approximate pure component adsorption on fresh adsorbates, which would overestimate the results for aged systems. Two surface layers of metal-oxide were employed to investigate interactions between the adsorbate and surface [18]. For some calculations, all CaO (0 0 1) structures were fixed with a bond length of 2.4 Å between every distance for the Ca–O pairs for rapid investigation of mercury adsorption. This bond length is the default for the CaO (0 0 1) cleaved surface in DMol³. The periodic system studied has a vacuum thickness of 10 Å. This distance was chosen to eliminate spurious interactions between the adsorbate and the periodic image of the bottom layer of the surface, which would appear on the top of the 5×5 unit cell. Also, the k-point was set to the 2×2×1 mesh by Monkhorst-Pack scheme [19] in this calculation on the periodic slab.

3 RESULTS AND DISCUSSIONS

3.1. Structure of Hg and HgCl₂ adsorption on CaO

Hg consistently adsorbed on an atop site over the oxygen atoms on the surfaces, and each chlorine atom gravitated to calcium sites according to the optimized geometries, as shown in Figure 1. Bond lengths for each species indicate which species are more strongly adsorbed to the surface. The distances between mercury and oxygen on the 5×5×2 surface are 3.535 Å for Hg(0) and 2.344 Å for Hg(+2) at the present calculation levels. The chlorine atom has a bond length of 3.258 Å to the surface with calcium. In Figure 1.c the movement of the oxygen out of the flat surface makes it more favorable for strong interactions with mercury so that the Hg is much closer to the surface at 2.344 Å. the relaxation effect is not essential for the Hg adsorption model, the relaxation effect plays an important role in the HgCl₂ adsorption model to move the adsorption energy into the chemisorption range as discussed in the next section.

3.2. Electronic properties of Hg and HgCl₂ adsorption on CaO

The adsorption energies of mercury-containing species on the modeled structures, investigated with GGA/BLYP methods were calculated through the following equation:

$$\Delta E_{\text{ads}} = E_{\text{Hg-species+surface}} - E_{\text{Hg-species}} - E_{\text{surface}} \quad (1)$$

where ΔE_{ads} is the adsorption energy, $E_{\text{Hg-species+surface}}$ represents the energy of the adsorbate species–surface, $E_{\text{Hg-species}}$ is the energy of the gas phase mercury-containing species, and E_{surface} is the energy of the isolated periodic model, in kcal/mol and the results indicate a –4.84 kcal/mol for Hg(0) and –30.28 kcal/mol for HgCl₂. These show the trends as the adsorption strength is changed for the different oxidation states. Metallic

mercury, which is not reactive, has a weak adsorption on the $5 \times 5 \times 2$ periodic slab. The adsorption of elemental mercury on the periodic structure is attributed to be physical adsorption according to the fact that the adsorption energy of Hg(0) from the GGA/BLYP calculations falls into the physical adsorption range of about 6 kcal/mol [20]. The oxidized mercury in the form of HgCl₂ over metallic Hg has a stronger adsorption energy value on the $5 \times 5 \times 2$ periodic slab. These results suggest that CaO will be a stronger adsorbent for the reactive oxidized mercury species. The adsorption energies of HgCl₂ on the CaO surfaces is chemisorption [17]. The chlorine atoms released from HCl or Cl₂ in the coal combustion flue gas system greatly enhance the adsorption capability of the CaO according to these predicted results. The fact that fluoro-, bromo-, and chloro-carbons are destructively adsorbed on the CaO surfaces and that calcium oxides can be effective in removing halogenated carbons as shown by Decker, et al. [21] is consistent with the results.

Charge analyses results depend on the methods used and show how electron density is partitioned. In order to understand the trends in atomic charge transfer, atomic charges with two different methods including the Mulliken and the Hirshfeld population analyses are compared. The Mulliken method is the most commonly used population method and the Hirshfeld population analysis is based on the deformation density on the free atom electron density. The atomic charges for a fixed clean periodic CaO slab and CaO slabs reacted with Hg and HgCl₂ were used to obtain the final Mulliken and Hirshfeld charges. The Mulliken charges of the mercury atoms in Hg and HgCl₂ on the surfaces are changed by -0.041 and -0.069, respectively and the chlorine is negatively charged to -0.145. On the CaO surface, the final atomic charges of the nearby calcium atoms were almost the same after CaO-Hg adsorption while all charges on nearby oxygen atoms were changed positively after CaO-mercury species were formed. The adsorption of CaO-HgCl₂ receives more charge transfer between HgCl₂ and the CaO surface compared with the mercury adsorptions. This is intuitive because the adsorption of HgCl₂ is stronger because bonding occurs, as described earlier. The trends in the Hirshfeld charges are similar to the Mulliken charge analysis; the Hirshfeld charges of the nearby calcium atoms were changed on the average by -0.03 for Hg adsorption and -0.03, -0.03, -0.07 and -0.07 for HgCl₂. This is consistent with the Mulliken charge analysis as the same calcium atoms of the surface interact with mercury adsorbates. Again, when the mercury is oxidized, mercury is charged more negatively. This result is in good agreement with the fact that adsorption becomes stronger when a larger charge transfers occur. The comparison of results of adsorption energies is in accordance with the results of the charge transfer calculations.

4 CONCLUSIONS

The adsorption energies of Hg, HgCl and HgCl₂ adsorption on CaO surfaces were calculated by GGA/BLYP methods. Ele-

mental mercury adsorption on the CaO (0 0 1) surface is physisorption in nature. Additionally, HgCl₂ on the calcium oxide surface are at chemisorption. Stronger adsorption occurs when mercury is oxidized. The oxidized mercury has an active interaction with the surface according to the Mulliken and Hirshfeld charge analyses. This research paper is the first in a series of investigating the mechanism of mercury adsorption on PWDS. Since flue gases are generally released at high temperatures, the CaO component of PWDS might not be a very strong adsorbant itself to remove mercury. Future work may examine more chemical arrangements that include CaO components as a part of a more complex sorbent environment.

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