

A DENSITY FUNCTIONAL THEORY STUDY OF
MERCURY ADSORPTION ON PAPER WASTE
DERIVED SORBENTS

by

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ABSTRACT

For many years, researchers have been developing theoretical methods for investigating adsorption phenomena. Understanding adsorption of mercury species on dry sorbents is important for predicting the fate of mercury and its compounds in the environment, and in designing warm post-gasification gas clean-up systems for removing mercury from coal fired power plant flue gases.

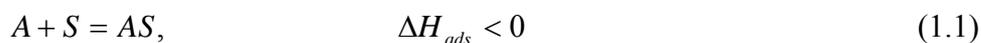
In this work, we focused on a newly developed sorbent, Paper Waste Derived Sorbent (PWDS), used in coal fired power plants for mercury adsorption and investigated the binding of mercury-containing species to the chemical surfaces making up portions of the sorbent using density functional theory (DFT) methods. Since CaO, Al₂O₃, and SiO₂ are the primary constituents of the PWDS, the adsorption of mercury-containing species on these substrates was investigated.

We studied the optimal clusters used in the calculations and optimized adsorption structures using the Harris and Perdew-Wang (PWC) local functionals with the Local Density Approximation (LDA) and the nonlocal Becke-Lee-Yang-Parr (BLYP) functional with the Generalized Gradient Approximation (GGA). The geometries obtained from different functionals were slightly different. However, adsorption energies of the mercury-containing species on each substrate surface were very different when calculated with different functionals. Besides obtaining structures and energies, the temperature effect on adsorption was investigated. The DFT

methods were subsequently used to uncover a method for estimating the adsorption of mercury-containing species on dry sorbents in the environment.

INTRODUCTION

The phenomenon of adsorption was discovered over two centuries ago (Toth & Toth, 2002). When a molecule approaches a surface, it encounters a net attractive potential that is similar to the potential between two molecules, and arises for the same reasons. The adsorption of a molecule on a solid surface is always an exothermic process. If we represent the gas molecule, the adsorbate, by A, and the adsorption site on the surface by S, the process of adsorption can be represented as a chemical reaction:



where ΔH_{ads} is the enthalpy change of adsorption process.

The solid is called the adsorbent, and the gas or vapor taken up on the surface is called the adsorbate. It is not possible to determine the surface areas of adsorbent materials by optical or electron microscopy because of the size and complexity of the pores and channels of the material (Toth & Toth, 2002), making study of adsorption phenomena experimentally difficult at direct measurement (Toth & Toth, 2002). The gas adsorption process, however, can be used to determine the accessible surface area of most adsorbents.

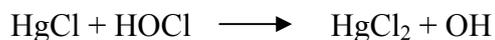
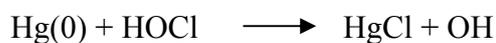
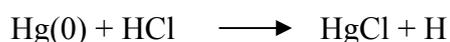
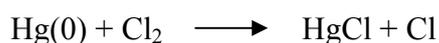
Gas adsorption is of practical consequence to engineers and chemists in many ways. Adsorption can provide a convenient, cheap and reusable method for purification of gas streams (Toth & Toth, 2002). For instance, gas masks used in World War I (and even in the present day) are an example of the utility of charcoal as an absorbent to remove nerve toxins from inhaled air (Toth & Toth, 2002). More significantly, perhaps, the phenomenon of surface adsorption has been used to modify the rates of product formation of chemical reactions through heterogeneous catalysis by adsorption followed by surface chemical reaction processes. For a catalyst to be useful, it must have a large surface area, bind the reactants quickly and effectively, stabilize the activated complex, and release the products of the reaction (Derzy, Lozovsky, & Cheskis, 1999).

Among practical gas adsorption processes, mercury adsorption in coal fired power plants is a typical and an important one. Mercury, as the most volatile trace metal in fossil fuels emitted to the atmosphere, is of great concern due to its toxic effects on the environment and its human health issues, as well as its role in the chemistry of the atmosphere (Pacyna & Pacyna, 2002). Mercury released from coal fired boilers accounts for the largest amount of anthropogenic mercury emissions in the U.S. based on the EPA Mercury Study Report (Johansen, 2003). Therefore, in this work we study mercury adsorption in coal fired boilers to investigate ways to reduce mercury emissions.

In flue gases, elemental mercury-Hg(0) is oxidized into mercurous-Hg(I), and mercuric-Hg(II) species in the form of HgCl and HgCl₂ (Niksa, Helble, & Fujiwara,

2001), mostly promoted by chlorine and atomic chlorine, as proposed by Sliger, et al. (Sliger, Kramlich, & Marinov, 2000). Thus, we mainly focus on these three mercury species.

The gas reaction submechanism includes the following reactions:



These reactions in coal fired power plants exhaust streams indicate that Cl-atoms first oxidize Hg(0) into HgCl and then oxidize the HgCl into HgCl₂. Here are the three Hg species we will consider in this work.

The EPA has set regulations on mercury emission concentrations of 0.1 ug/kg/day. In order to minimize the environmental damages and to meet the air quality standards, flue gases from coal burning power plants have to be treated to reduce mercury emissions. Cleanup technologies available to control mercury emissions include wet scrubbing (Nakazato, 1990) and adsorption on dry sorbents (Fouhy, 1992; Thielen, Thomas, & Seipenbusch, 1992). Processes based on adsorption on dry sorbents do not pose a problem for the treatment and transformation to inert waste liquid streams,

and therefore are very attractive, both for small and large combustors. Besides, elemental mercury ($\text{Hg}(0)$) vapor is insoluble and is not captured in wet scrubbers (E.P.A, 2006). Therefore, choosing appropriate dry sorbents to reduce Hg emissions is essential in meeting the regulations set by the U.S. EPA.

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 (Ghorishi, Singer, Jozewicz, Sedman, & Srivastava, 2002; Hocquel, Unterberger, & Hein, 2001; Jurng et al., 2002; Karatza, Lancia, Musmarra, Pepe, & Volpicelli, 1996b; Lancia, Karatza, Musmarra, & Pepe, 1996; Olson et al., 2003). However, the currently-used sorbents are expensive. The U.S. Department of Energy (DOE) estimated in the mid-1990s that annual costs could range between \$2 and \$6 billion per year (based primarily on tests using activated carbon, \$1000/ton (Srivastava, Staudt, & Jozewicz, 2005), as the standard process for removing mercury from the flue gases of coal combustion), and has already set a goal to develop mercury control technologies that can achieve 90 percent or greater capture at 50 to 75 percent of the cost of existing technologies and be available for commercial demonstration by 2010 (DOE, 2006). Therefore, 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 proved to be very effective in a bench scale Hg control system (Wendt, 2005). The components in PWDS are CaO 23%, $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ 29%, CaCO_3 41%, Inert 6%, and $\text{Ca}(\text{OH})_2$ 1%, on a molar basis (Wendt, 2005). Since CaO, and $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ are

primary constituents in this novel sorbent that could be used in coal fired power plants, adsorption phenomena of Hg, HgCl and HgCl₂ on the CaO, Al₂O₃ and SiO₂ surfaces were investigated so fundamental interactions between Hg-species and the sorbent can be explored.

There have been many experimental studies of adsorption of mercury on different sorbents (Gullett & Jozewicz, 1993; Karatza, Lancia, Musmarra, Pepe, & Volpicelli, 1996a; Karatza et al., 1996b; Krishnan, Gullett, & Jozewicz, 1994; Lancia, Musmarra, Pepe, & Volpicelli, 1993; Otani, Emi, Kanaoka, & Matsui, 1984; Otani, Kanaoka, & Emi, 1989; Tseng, Chang, & Sedman, 1990). From these results, it was found that: (I) the adsorption phenomena are strongly sensitive to temperature; (II) the lower the temperature, the higher the adsorption capacities; and (III) oxidized mercury is more easily adsorbed than elemental mercury.

It is very difficult to examine the adsorption mechanisms of Hg-containing species on surfaces experimentally (Niksa et al., 2001). Consequently, there have been no experimental studies to formulate mechanisms of adsorption of mercury species on most adsorbents and PWDS. On the other hand, the increase in computer speed and in the accuracy of the computational quantum chemistry methods leads them to be more useful for investigating surface phenomena (Zheng & Blowers, 2005).

Molecular modeling methods have gained acceptance as practical tools in a variety of industries, such as bio-active materials like pharmaceuticals (Perus, Bischof, & Loo, 2005), electronic and photonic materials (Stirling & Pasquarello, 2005), homogeneous reactions and heterogeneous catalysis (Zheng & Blowers, 2005; Zheng & Blowers,

2006b), fuels and automotive chemicals (Zheng & Blowers, 2006a), and sorbents for gas separations (Zhang, Blowers, & Farrell, 2005; Zhang, Farrell, & Blowers, 2004). These computational methods are being adopted because they are proving their value over time. They are useful in developing hypotheses and a rational, strategic approach to problem solving, providing understanding and design rules, stimulating new ways of thinking, aiming for predictive results, rather than descriptive results, and most invaluable — steering experimental development while eliminating dead end research (Westmoreland, Kollman, & Chaka, 2002). Even though there is still much development needed in computational quantum chemistry methods, better and more accurate algorithms are continuously being explored. As more advanced software and hardware are developed, the molecular modeling methods become more attractive and successful applications become more common.

All in all, understanding the adsorbents' surface properties theoretically will help in choosing the best adsorbent for certain adsorbates. In this case, we are working on investigating the properties of Paper Waste Derived Sorbent and the adsorption properties of mercury-containing species toward PWDS. We would like to know the properties of PWDS using quantum chemical modeling methods, and mainly focus on the structure of PWDS, the active sites of PWDS, comparing the adsorption energy and studying the effect of temperature on the adsorption ability. There are many components in the PWDS and it is complicated to investigate them simultaneously. Therefore, each component will be investigated separately and will be discussed individually in the Appendix A, B and C.

Before describing in detail the approaches used here, a brief review of some of the different computational approaches for examining surface phenomena should be discussed in the background section.

BACKGROUND

There are two areas within computational chemistry devoted to the structure of molecules and their reactivity: molecular mechanics and quantum mechanics. The basic types of calculations they both perform include computing the energy, or properties related to the energy, of a particular molecular structure; performing geometry optimizations; and, computing the vibrational frequencies of molecules resulting from interatomic motion within the molecule (Foresman & Frisch, 1996). This chapter will explore these methods and their limitations to highlight the choices made for the methods employed in this research.

Molecular Mechanics

Molecular mechanics simulations apply the classical laws of physics to predict the structures and properties of molecules (Field, 1999). These methods are characterized by their particular force fields representing the interactions between atomic species. Molecular mechanics calculations are performed based on nuclei interactions and do not treat the electrons in a molecular system explicitly (Field, 1999). However, electron effects are included implicitly in the force fields through parameterizations.

The approximations in molecular mechanical calculations make the computations

quite inexpensive, which allows the methods to be used for very large systems containing thousands of atoms (Field, 1999). However, there are two major drawbacks of these methods. Firstly, each force field achieves good results only for a limited class of molecules for which the force field is parameterized. No force field can be used for all molecular systems. Secondly, molecular mechanics methods cannot treat chemical systems where electronic effects dominate because of the neglect of electrons. For example, they cannot describe processes involving bond formation or bond breaking, like adsorption processes.

Quantum Mechanics

Electronic structure theory based on quantum mechanics is one of the most fundamental tools for molecular and material modeling, and applies the laws of quantum mechanics rather than classical physics as the basis for the calculations (Shankar, 1994). The energies and structures of molecules are obtained through the solution of the Schrödinger equation, which can be written as:

$$\hat{H}(r, R)\Psi(r; R) = E(R)\Psi(r; R) \quad (2.1)$$

$E(R)$ in the Schrödinger equation stands for the energy of the system, which is also the eigenvalue solution of the equation. $\Psi(r; R)$ is the wave function that determines the electron density and various properties, such as dipole moments and electrostatic potentials. $H(r, R)$ in the Schrödinger equation is named the Hamiltonian, and it represents the sum of the total potential and kinetic energies of the system (Levine, 2000). These terms can be written as:

$$H = -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) + \sum_{i < j} \sum \left(\frac{e_i e_j}{r_{ij}} \right) \quad (2.2)$$

The first term in equation (2.2) accounts for the kinetic energies, and the second term accounts for the potential energies, including attractions or repulsions between particles. Equations (2.1) and (2.2) are the time-independent Schrödinger equation because time-derivatives and time-dependent terms have been eliminated. The time-dependent form is usually used when one is concerned with transient phenomena such as rapidly oscillating electric fields or scattering (Levine, 2000). This research does not concern these phenomena so Equations (2.1) and (2.2) are acceptable here.

For any but the smallest systems, however, exact solutions to the Schrödinger equation cannot be computed (Teter, Payne, & Allan, 1989). Various approximate methods for solving the Schrödinger equation are available, from molecular modeling, to semi-empirical molecular orbital (MO) methods, to ab initio MO methods, and density functional theory (DFT) methods.

Semi-Empirical Molecular Orbital (MO) Methods

Semi-empirical MO methods neglect most of the two-electron integrals in solving the Schrödinger equation and use experimental results (parameters) to adjust integrals to obtain accurate results at very low cost. Some of the methods used in modeling, especially for large biological molecules, are MNDO/d (Thiel, 1996), AM1 (Dewar, Zoebisch, Healy, & Stewart, 1985) and PM3 (Stewart, 1989). These approaches, with parameters readjusted especially for absorption spectra, are powerful tools for excited states of large molecular systems and molecules containing transition metals. These inexpensive methods have been used to calculate nonlinear optical properties of large molecules, in particular for industrial applications (Westmoreland et al., 2002).

Some of the recent developments for semi-empirical methods are intended for applications to even larger molecules. The MOZYME method (Stewart, 1989) performs direct calculations of electron density and energy without diagonalizing the semi-empirical SCF matrix and can be used for geometry optimizations of large molecules. Applications so far include polypeptides consisting of 248 amino acid residues. Some applications consist of 1960 atoms with 140 residues. These new methods are likely to be used in the near future for industrial applications for systems like these.

Summarizing semi-empirical MO methods, their largest merit is definitely low computational cost. They are more expensive than the molecular mechanics (MM) methods, but they allow breaking of bonds and take electronic effects explicitly into account, which MM cannot do. Important shortcomings of semi-empirical methods are low reliability (qualitative at best, and particularly poor for transition states) for the energetic results and the lack of reliable parameters for transition metals (Foresman & Frisch, 1996; Frank, 1999; Leach, 1998; Levine, 2000), like mercury in this work. Therefore, these approaches are not applicable to most homogeneous and heterogeneous catalysis or adsorption modeling efforts. In the near future, the semi-empirical approach will remain a quick and inexpensive alternative to *ab initio* calculations in industrial and biomolecular applications, but will not be useful for adsorption of chemicals on transition metal surfaces.

Ab initio MO Methods

In the *ab initio* MO methods, the Schrödinger equation is solved “from the

beginning” (which is not “from first principles”, as *ab initio* is frequently translated) (Westmoreland et al., 2002). These methods usually express the molecular orbitals as linear combinations of a finite number of basis functions:

$$\varphi_i = \sum_{r=1}^{Nbasi} C_{ir} \chi_r \quad (2.3)$$

where φ_i is the wave functions of the molecular orbitals, C_{ir} is the expansion factor and χ_r is one-electron spin orbital.

The basis set can start as small as “minimal” (one basis function per valence shell), but can be improved systematically by moving to “double zeta” (two per valence shell), to “double zeta plus polarization”, to “triple zeta plus double polarization plus higher angular momentum plus diffuse functions” (Yamaguchi, Gaw, & Schaefer, 1983), eventually approaching the complete basis set. The total electronic wave function is expressed as a linear combination of Slater determinants (SDs) (Olsen, Roos, Jorgensen, & Jensen, 1988):

$$\Psi = \sum_I D_I \Phi_I, \Phi_I = (N!)^{-1/2} \sum_P P(-1)^P \{\varphi_{1s_1}(1)\varphi_{2s_2}(2)\varphi_{3s_3}(3)\dots\varphi_{Ns_N}(N)\} \quad (2.4)$$

The simplest form of the total wave function is a single SD, which is called the Hartree-Fock (HF) approximation. To include “electron correlation,” one has to use more than one SD (Olsen et al., 1988). Extensive studies in the last 20 years have established that, with an increasing order of sophistication and accuracy, Møller-Plesset 2nd order perturbation (MP2) and coupled cluster single and double with perturbative triple excitation (CCSD(T)) methods, among others, have been found to be reasonable approximations of a full configuration interaction (Full CI) calculation (Westmoreland et al., 2002). The CCSD(T) calculation with a very large

basis function, or an extrapolation scheme such as G2, G3 or CBS methods to reach this target calculation, have been found to provide energetics (atomization, ionization, and others) within a few kcal/mol compared to experimental results (Yarkony et al., 1995).

Ab initio quantum chemistry has long been applied as a major tool for investigating the structure, stability, reaction kinetics and mechanisms of different molecular systems (Jursic, 1997; Lynch & Truhlar, 2001; Saeys, Reyniers, Marin, Van Speybroeck, & Waroquier, 2003; Truong, 2000; Truong & Truong, 1999; Wong, Pross, & Radom, 1994; Wong & Radom, 1995, 1998; Xiao, Longo, Hieshima, & Hill, 1997; Zheng & Blowers, 2005). *Ab initio* calculations are based on the laws of quantum mechanics only and on the values of a small number of physical constants like the speed of light, the masses and charges of electrons and nuclei, Planck's constant, etc. These methods compute solutions to the Schrödinger equation through a series of rigorous mathematical approximations.

The difference between semi-empirical and *ab initio* methods lies in the trade-off between computational cost and the accuracy of results (Westmoreland et al., 2002). With the availability of good parameters, semi-empirical calculations are relatively inexpensive and provide fairly accurate energies and structures. *Ab initio* methods, in contrast, provide highly accurate predictions for a broad range of systems (Frank, 1999). However, the chemical systems of interest are restricted to up to a few hundred atoms because of the high computational cost (Foresman & Frisch, 1996). In summary, *ab initio* methods are the ultimate theoretical methods for electronic

structure calculations, applicable to any atoms or molecules in both ground and excited states. The approximations can be systematically improved using better basis sets and better wave functions. The results can be very accurate, with an average error of ± 2 kcal/mol, close to the expected experimental error (Westmoreland et al., 2002). The disadvantage of *ab initio* methods is their computational cost, much more demanding than semi-empirical and DFT methods (HeadGordon, 1996). Especially discouraging is the high-order power dependency on the size of the system, up to M^7 or M^8 , where M is the molecular size (HeadGordon, 1996). As a consequence, for example, CCSD(T) with a large basis set is routinely applicable only to molecules having at most several non-H atoms. The *ab initio* methods have been, and will be, used in industrial applications when the accuracy is needed or when inexpensive alternative methods, such as semi-empirical MO or DFT, do not work. A comparison of different computational methods is summarized in Figure 2-1 below.

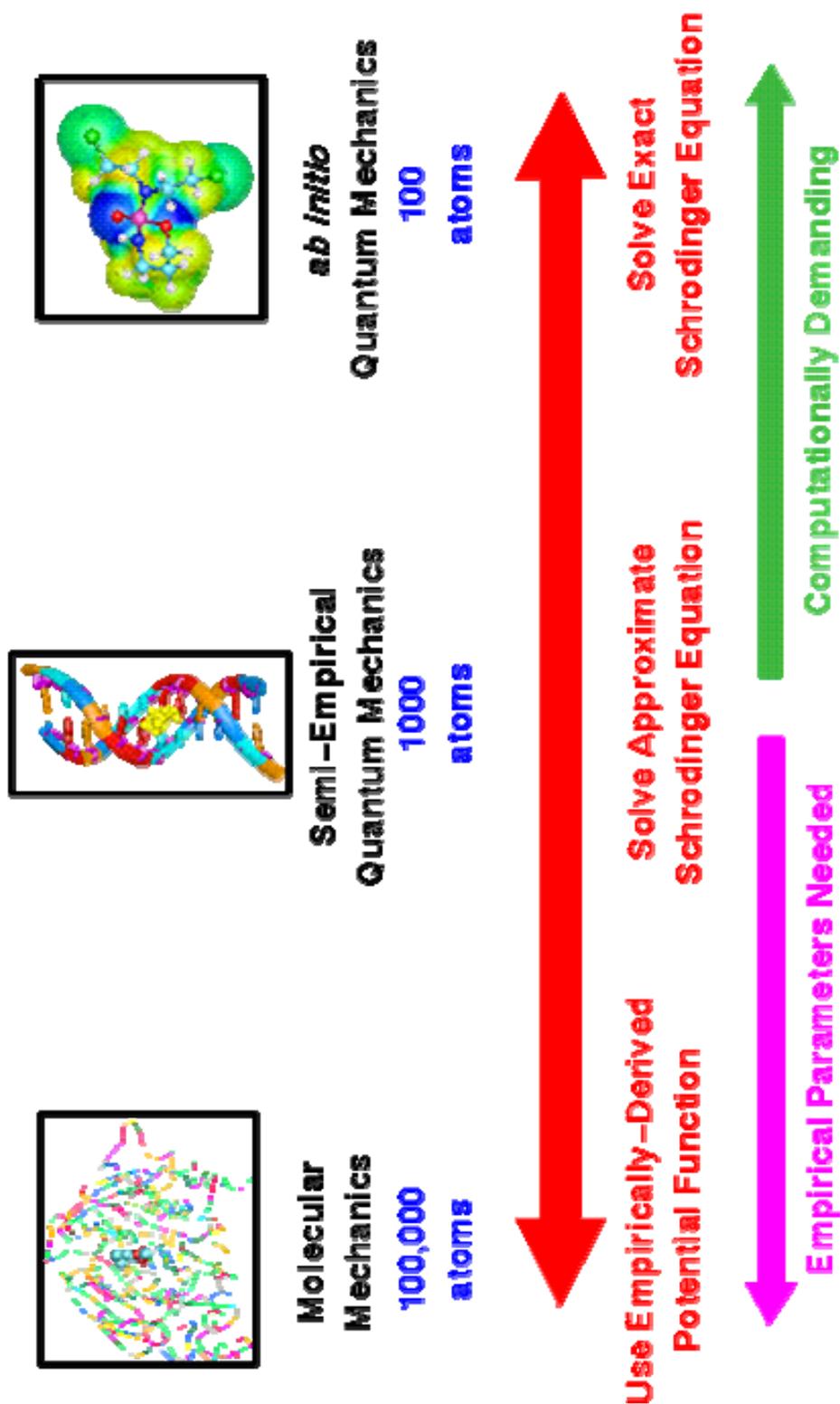


Figure 2-1. Comparison of computational methods

Source: Adapted from, Zheng, X. 2006, "A Computational Investigation of Hydrocarbon Cracking: Gas Phase and Heterogeneous Catalytic Reaction on Zeolites", Ph.D. Dissertaion.

Density Functional Theory Methods

Density functional theory (DFT) calculations of the geometry optimization, single point energy and other properties of molecules are based on the fact that the properties of a molecule in a ground electronic state are determined by the ground state electron density (Westmoreland et al., 2002). At a very basic level, density functional methods are similar to some *ab initio* methods in many ways. DFT calculations have the same computational cost as Hartree-Fock theory, the least expensive *ab initio* method, but include the effects of electron correlation, which is the fact that electrons react to each other's motion (Zheng, 2006).

The electron density in this formalism is defined as:

$$\rho(r) = \rho(x, y, z) = N \int \psi^*(1,2,\dots,N) \psi(1,2,\dots,N) dx_1 dx_2 \dots dx_N \quad (2.5)$$

where the ψ is the wave function of a molecule. The electron density is a function of position only, that is, of just three variables, while the wave function of an N-electron molecule is a function of 4N variables. No matter how large the molecule is, the electron density is still a function of only three variables, while the complexity of the wave functions for the *ab initio* methods just described in the previous section increases with the number of electrons to powers up to 7 or 8. Therefore, DFT is less computationally expensive and more accessible than wave function computational methods with similar accuracy, especially for larger systems. The DFT ground state energy of a molecule, which is a function of the ground state electron density, can be expressed as (Frank, 1999):

$$E[\rho(\mathbf{r})] = -\sum_{A=1}^M \int \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \rho(\mathbf{r}) d\mathbf{r} + \sum_{i=1}^N \int \psi_i(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \psi_i(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[\rho(\mathbf{r})] \quad (2.6)$$

The first term is the potential energy due to the nuclei-electron attraction; the second term is the non-interaction electronic kinetic energy; the third term is the classical repulsion energy term; the fourth term is defined as the remainder after subtraction of the non-interaction kinetic energy, attraction energy and repulsion energy from the real total energy that includes the terms needed for an exact energy (Zheng, 2006). Unlike the Hartree-Fock approximate energy, Eq (2.6) is the exact energy of the system. Once we know the density function $\rho(\vec{r})$ and the exchange-correlation energy function $E_{xc}[\rho(\vec{r})]$, we can obtain the exact energy. The density function $\rho(\vec{r})$ can be calculated using Eq. (2.7) where the wave function can be obtained by solving the Kohn-Sham (KS) equation:

$$\left[-\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{Ai}} + \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V^{xc} \right] \psi_i = \varepsilon_i \psi_i \quad (2.7)$$

where the ψ is the KS spatial orbital function, ε_i the KS energy level and V^{xc} is the exchange correlation potential which is defined as the functional derivative of $E_{xc}[\rho(\vec{r})]$ with respect to $\rho(\vec{r})$:

$$V^{xc}(r) = \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta \rho(\vec{r})} \quad (2.8)$$

The exchange-correlation energy $E_{xc}[\rho(\vec{r})]$ is a function of $\rho(\vec{r})$. The various approximations of $E_{xc}[\rho(\vec{r})]$ separate the different DFT methods from each other. These approximations will be discussed next before the inherent trade-offs of how they can be applied most effectively are examined in this work.

Local density approximation (LDA)

The simplest approximation to $E_{xc}[\rho(\vec{r})]$ is the local density approximation,

which assumes the system is a homogeneous electron gas and $E_{xc}[\rho(\vec{r})]$ depends only on the local value of the electron density (Sahni, 2004). $E_{xc}[\rho(\vec{r})]$ can be written in a simple form:

$$E_{xc}^{LDA}(\rho) = \int \rho(\vec{r}) \varepsilon_{xc}(\rho(\vec{r})) d\vec{r} \quad (2.9)$$

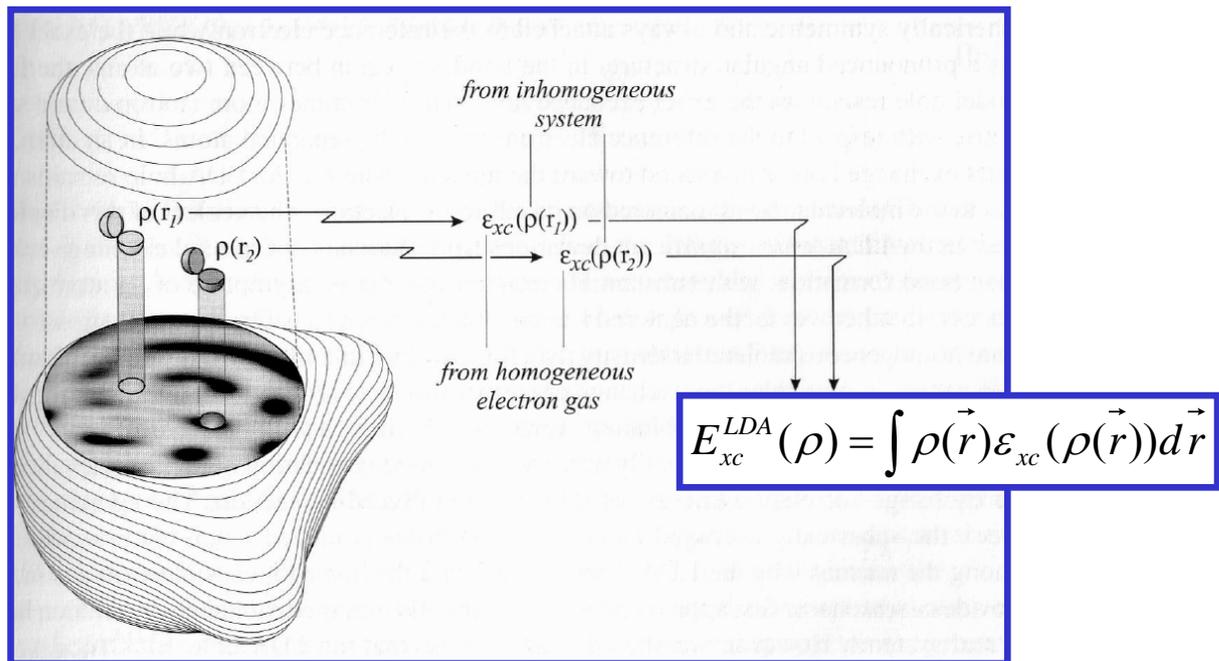


Figure 2-2. Illustration of LDA

where $\varepsilon_{xc}(\rho(\vec{r}))$ is the exchange-correlation energy per particle of a uniform electron gas of density $\rho(\vec{r})$. $\varepsilon_{xc}(\rho(\vec{r}))$ is composed of two parts:

$$\varepsilon_{xc}(\rho(\vec{r})) = \varepsilon_x(\rho(\vec{r})) + \varepsilon_c(\rho(\vec{r})) \quad (2.10)$$

The correlation part was studied by various authors based on sophisticated interpolation schemes. For instance, the most popular $\varepsilon_{xc}(\rho(\vec{r}))$ functional was developed by Vosko, Wilk and Nusair (Vosko, Wilk, & Nusair, 1980), and the more recent and probably the most accurate expression of $\varepsilon_{xc}(\rho(\vec{r}))$ was the one given by

Perdew and Wang (PWC) (Perdew & Wang, 1992).

Because of the inclusion of the exchange-correlation term, LDA approximations are more accurate than HF approximations with similar computational costs (Zheng, 2006). Experience has shown the LDA can successfully determine the optimized geometries (Andzelm & Wimmer, 1992; Dickson & Becke, 1993) and harmonic frequencies (Johnson, Gill, & Pople, 1993; Zhou, Wheelless, & Liu, 1996) for investigated systems (Sahni, 2004).

However, the energies calculated with the LDA functional are rather poor due to the assumption of a homogenous electron gas in the system (Sahni, 2004). Due to some of these limitations, the LDA methods were not explored further in this work other than their ability to reproduce geometries well, even if their energetic predictions are not accurate.

Generalized gradient approximation (GGA)

The electron density in a real molecule varies greatly from place to place (Sahni, 2004). To get a more accurate approximation of the exchange-correlation energy, functionals which include not only the electron density but also the gradient of the electron density were developed (Sahni, 2004). Usually, E_{xc}^{GGA} is calculated by the sum of the exchange and correlation parts, and is equal to:

$$E_{xc}^{GGA} = E_{xc}^{LDA} + \sum_{\sigma} \int C_{xc}^{\sigma}(\rho(\vec{r})) \frac{\nabla \rho}{\rho^{4/3}} d\vec{r} \quad (2.11)$$

The most widely used exchange functional was developed by Becke (Becke, 1993), and was designed to recover the exchange energy density asymptotically far from a finite system. Other exchange energy functionals include FT97 (Filatov & Thiel,

1997) and PW91 (Wang & Perdew, 1991). One of the most popular correlation functionals is the LYP functional (Lee, Yang, & Parr, 1988). The other most used choice is the P86 functional (Perdew, 1986).

Previous studies demonstrated that, for the main group element systems, the GGA calculations generally provide better approximations for energetic properties than the LDA functional, but do not lead to improvements in molecular geometries (Koch & M.C., 2001). However, for transition metal systems which are limited to carbonyl complexes, GGA usually gives more accurate answers than LDA methods for both geometries and energies (Zhang et al., 2005). Since it is not possible to use the HF and MP methods to accurately model transition metal systems, and DFT methods usually give better results than HF and MP methods for investigated systems (Zheng, 2006), GGA methods are applied more for transition metal systems than the other methods (Zheng, 2006).

All in all, the greatest advantage of DFT is low cost (Westmoreland et al., 2002). On one hand, DFT methods could be as accurate as MP2 if the proper functionals are used. The methods have a smaller M (molecular size) dependency than the comparable *ab initio* methods, and they are applicable to very large molecules, and electronic properties calculated with DFT are also reasonably reliable. However, DFT methods fail without clear reasons in some cases (Gutsev, Rao, & Jena, 2000; Rao & Jena, 2002; Westmoreland et al., 2002) and there is no systematic way of improving the approximations (Westmoreland et al., 2002). It is desirable to confirm DFT predictions by comparing them with known experimental results and high-level

ab initio methods, if possible, and if they are computationally tractable.

Hybrid functionals

Recently, Becke has formulated functionals which include a mixture of Hartree-Fock and DFT exchange along with DFT correlations in order to get more accurate modeling results (Becke & Johnson, 2005; Johnson & Becke, 2005). It makes sense to combine the best features of various levels and approaches. The results of this combination are the hybrid methods. The exchange-correlation energy function E_{XC} is defined as:

$$E_{XC,hybrid} = c_{HF} E_{X,HF} + c_{DFT} E_{XC,DFT} \quad (2.12)$$

where the c 's are constants (Foresman & Frisch, 1996).

The hybrid methods include several categories (Westmoreland et al., 2002). There are methods that are hybrid in a temporal sense, mixing electronic structure calculations with molecular dynamics methods. For example, the Car-Parrinello molecular dynamics (CPMD) method (Car & Parrinello, 1985), combining molecular dynamics with DFT calculations under a periodic boundary condition with the orbitals expanded in the plane wave. This method and its various modifications have been very successful and popular for materials modeling (Hutter & Iannuzzi, 2005). This approach is also being used more often for calculations of heterogeneous and some homogeneous catalysis systems in industrial applications (Hutter & Iannuzzi, 2005; Westmoreland et al., 2002).

Another set of methods includes approaches that are spatially hybrid, applying different methods in different physical regions of a molecular or computational

domain. One should be able to combine a “more accurate, more expensive” method for the active part and a “less accurate, less expensive” method for the rest of the molecule. For example, the QM/MM methods (Warshel & Karplus, 1972), have been applied mainly to biological problems such as enzyme reactions and reactions in solution (Friesner & Beachy, 1998), but have also been applied to adsorption phenomena as well (Jung, Choi, & Gordon, 2001). Very recently a DFT/MM method has been developed (Cui & Karplus, 2000) which is expected to apply for an adsorption system with a large number of molecules.

PRESENT STUDY

The Approaches in Using Molecular Modeling for Surfaces

In any surface calculation with density functional or *ab initio* methods, it is impossible to completely model the entire surface, even with robust computer codes and highly efficient super computers (Neurock, 2003). Instead, there are three approaches commonly used for handling the surface when an adsorbate is present. They are known as the cluster, embedding-cluster, and periodic methods.

Cluster Approaches

A method for representing surfaces is to use a smaller cluster (Hoeft et al., 2001; Serrano-Andres & Merchan, 2005) of atoms to represent the surface, often terminating unfilled valencies with hydrogen atoms or hydroxyl groups to mimic a continuous surface. The basic premise behind the approach is that reactions and adsorption are local phenomena, primarily affected by the nearby surface structure. The clusters can adopt different sizes and configurations depending on the specific system being examined and the accuracy of the desired results (Apai, Hamilton, Stohr, & Thompson, 1979).

The advantage of the cluster approach is that the active site is described explicitly by the interactions between the local molecular orbitals of the adsorbate and the

adsorbent. This enables one to probe bonding and reactivity and to formulate structure property relationships easily (Westmoreland et al., 2002). On the other hand, the disadvantage is the incomplete representation of the electronic system provided by the small size and the discrete nature of the cluster employed (van Santen & Neurock, 1995; Whitten & Yang, 1996). Two possible underlying problems with the small clusters are their failure to describe the electronic band properties and in not converging properly (Hoeft et al., 2001). By carefully optimizing the adsorbate-cluster interactions, the lowest energy structures and electronic states can be calculated and used to predict reliable energetic data (Westmoreland et al., 2002). These cluster approaches normally allow one to use higher levels of theory and larger basis sets so one is able to obtain more accurate energetic results (Neurock, 2003).

The cluster approach has been used in the literature to model zeolites (van Santen & Kramer, 1995), metal oxides (Hermann, Witko, & Michalak, 1999; Hoeft et al., 2001; Pelmeshnikov et al., 2000; Pelmeshnikov et al., 1996; Rivanenkov, Nasluzov, Shor, Neyman, & Rosch, 2003), metal sulfides (Neurock & van Santen, 1994), and some other catalysts (Hermann, Michalak, & Witko, 1996). Based on this discussion, the cluster approach is the primary one adopted in this work. Before discussing results on each surface, though, a more complete discussion of the competing methods should be done to highlight why they were not used.

Embedded-cluster Approaches

The embedded-cluster approach is simply an extension of the cluster model (Neurock, 2003). In this method, a QM method is used to model the local region

about the active site. This primary cluster is then embedded in a much larger system in order to simulate the external electronic environment. The outer model employs a much simpler quantum mechanical treatment to simulate the external environment. Mostly, the molecular mechanics methods (MM) are used, therefore the embedded-cluster method is commonly known as the QM/MM method (Raimondi et al., 2001).

The difficulties with this method involve accurately matching the electronic structure at the interface between the inner-cluster and the external model (Greatbanks, Hillier, Burton, & Sherwood, 1996). The newest methods treat the core region with DFT and the outer shell with MM, and can be carried out on systems that contain thousands to tens of thousands of atoms (Westmoreland et al., 2002). These approaches have been successfully applied in modeling drugs, proteins and other biological systems (Friesner & Beachy, 1998). This method has the potential to be applicable for systems with large number of molecules.

Periodic Quantum Mechanical Calculations

Another method for handling surfaces is to use a periodic model to describe the surface where periodic boundary (McCarthy & Hess, 1992; Neurock, 2003; Poshusta, Tseng, Hess, & McCarthy, 1993) conditions are used to enable the code to rapidly calculate interactions. One generally picks a cell unit size for the surface, which would include several layers of surface atoms and a vacuum space above the surface. The smaller the unit cell size is, the faster the calculation. Modeling chemisorption at higher coverages is therefore typically easier than modeling the low coverage

situations where larger surfaces with only a few adsorbates would appear (Westmoreland et al., 2002). The vacuum space needs to be set high enough to prevent the adsorbate from interacting with the periodic lower bound of the surface that would appear above the vacuum (Gross, 2002).

The advantage of the periodic approach is that a much more complete electronic structure can be included. The disadvantage is that only systems with highly periodic structures can currently be examined within reasonable computational times (Zeigler, Prahofer, & Kim, 2000). Industrial systems, however, in reality are often ill-defined supported particles, which are difficult to model using the periodic approach (Westmoreland et al., 2002). Besides, very large CPU times are required for the calculations. Many of the current methods use ultrasoft pseudopotentials that cut down computational times by a factor of two or three (Vanderbilt, 1990), but this will only help so much in making the calculations feasible. Due to these reasons, the periodic approach will only be used with the CaO surface since it is the most periodic.

All three approaches just discussed have all played important roles in understanding model chemistries over time. The method of choice for a particular problem clearly requires a careful consideration of the advantages and disadvantages of each method and their impact on results. These trade-offs were used to develop the approaches used in this work that are described next.

The Modeling Approach used on PWDS

DFT methods were used in this work, which have already been proved to be fairly robust (Gross, 2002; van Santen & Kramer, 1995; van Santen & Neurock, 1995) at

low cost, and can be used to calculate structural properties that are typically within 0.05 Å and 1-2° of experiment, while overall adsorption and reaction energies are typically within 5-7 kcal/mol of experimental values, and spectroscopic analyses are within a few percent of experimental data (van Santen & Kramer, 1995; van Santen & Neurock, 1995).

Among the three modeling methods, cluster models have proved to be successful for simulating metal-oxide surfaces, like the oxides in this work (Hoeft et al., 2001; Pelmenschikov et al., 2000; Pelmenschikov et al., 1996; Rivanenkov et al., 2003). In this work, then, the cluster method was predominantly used to simulate the surface of each component of the PWDS while a few tests were run with periodic methods for comparison for some of the appropriate system. Also, one of the main advantages of the cluster approach is that it is inherently local in nature and can be easily applied not only to bulk crystals, but also to amorphous materials (Mukhopadhyay, Sushko, Stoneham, & Shluger, 2004, 2005), surfaces (Sushko, Gavartin, & Shluger, 2002; Sushko, Shluger, & Catlow, 2000) and complex interfaces (Johnson, Stefanovich, & Truong, 1998). The Al₂O₃ and SiO₂ in PWDS exist in an amorphous form, which is another reason we employed cluster models in this research.

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APPENDIX A

A DENSITY FUNCTIONAL THEORY STUDY OF
MERCURY-CONTAINING
SPECIES ADSORPTION ON CALCIUM OXIDE

Xinxin Li and Paul Blowers

Abstract

Understanding adsorption of mercury species on CaO surfaces is important for predicting the fate of mercury and its compounds in the environment, and in designing warm post-gasification gas clean-up systems for removing mercury from coal fired power plant flue gases. This research investigated the binding of Hg, HgCl and HgCl₂ to the CaO(001) surface using density functional theory (DFT) methods. The CaO surface was modeled with a 3x3x2 cluster, 4x4x2 cluster, 5x5x2 cluster, and a periodic system. Comparison of calculated Ca-O, Hg(I)-O, Hg(II)-O and Cl-Ca bond distances, and adsorption energies indicated that the 4x4x2 cluster was able to adequately simulate the CaO structure with the least computational time. Structures optimized using the Harris and Perdew-Wang (PWC) local functionals with LDA were slightly different from structures optimized using the nonlocal

Becke-Lee-Yang-Parr (BLYP) functional with GGA. Adsorption energies of the Hg-containing species on the terrace site of the CaO surface were calculated with the local density approximation PWC functional and the gradient corrected BLYP functional. Besides obtaining structures and energies, the temperature effect on adsorption was investigated. The DFT methods were subsequently used to uncover a method for estimating the adsorption of Hg-containing species on a CaO sorbent in the environment.

Keywords: Mercury, Calcium Oxide, Paper Waste Derived Sorbents

Introduction

Mercury released from coal fired boilers accounts for the largest amount of mercury emission in the U.S. based on the EPA Mercury Study Report (Johansen, 2003; Renner, 2004). In flue gases, elemental mercury-Hg(0) is oxidized into mercurous-Hg(I), and mercuric-Hg(II) species in the form of HgCl and HgCl₂ (Niksa et al., 2001), mostly promoted by chlorine and atomic chlorine, as proposed by Sliger, et al. (Galbreath & Zygarlicke, 1996; Sliger et al., 2000). The EPA has set regulations on mercury emission concentrations of 0.1 µg/kg/day, and choosing appropriate sorbents to reduce Hg emissions is an essential key in meeting this regulation. While 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 (Chang & Ghorishi, 2003; Ghorishi et al., 2002; Hocquel et al., 2001; Jurng et al., 2002; Karatza et al., 1996b; Krishnan et al., 1994; Lancia et al., 1996; Olson et al., 2003; Otani, Emi, Kanaoka, Uchijima, & Nishino, 1988; Otani, Kanaoka, Usui, Matsui, & Emi, 1986; Scala, 2001a, 2001b), 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 (Wendt, 2005). The components in PWDS are CaO 23%, Al₂O₃·SiO₂ 29%, CaCO₃ 41%, inert 6%, and Ca(OH)₂ 1%. 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, HgCl and HgCl₂ on the CaO surface was investigated so the fundamental interactions between Hg-species and the sorbent can be explored.

It is very difficult to examine the adsorption mechanisms of Hg-containing species on surfaces experimentally (Niksa et al., 2001). On the other hand, the increase in computer speed and in the accuracy of the computational 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. Before describing in detail the approaches used here, a brief review of some of the different computational approaches for examining surface phenomena should be discussed.

In any surface calculation with density functional or ab initio methods, it is impossible to completely model the entire surface, even with robust computer codes and highly efficient super computers (Neurock, 2003). Instead, there are three approaches commonly used for handling the surface when an adsorbate is present. One method is to use a periodic model to describe the surface where periodic boundary (McCarthy & Hess, 1992; Neurock, 2003; Poshusta et al., 1993) conditions are used to enable the code to rapidly calculate interactions. One generally picks a cell unit size for the surface, which would include several layers of surface atoms and a vacuum space above the surface. The vacuum space needs to be set high enough to prevent the adsorbate from interacting with the periodic lower bound of the surface that would appear above the vacuum (Gross, 2002). As one includes more atoms in

the cluster, one needs more computer memory, and the calculations take longer to complete.

Another method for representing surfaces is to use a smaller cluster(Hoeft et al., 2001; Serrano-Andres & Merchan, 2005) of atoms to represent the surface, often terminating unfilled valencies with hydrogen atoms to mimic a continuous surface. These cluster approaches normally allow one to use higher levels of theory and larger basis sets so one is able to obtain more accurate energetic results(Neurock, 2003); however, two possible underlying problems with the small clusters are their failure to describe the electronic band properties and in not converging properly(Hoeft et al., 2001). The final method of handling surface-adsorbate interactions is to perform QM/MM calculations(Raimondi et al., 2001) where quantum mechanical calculations are used to describe a small subset of the atomic system where highly accurate interactions are needed, such as at the site of adsorption, while molecular mechanical methods are used to handle all other interactions. Among the three methods, cluster models have proved to be successful for simulating metal-oxide surfaces(Hoeft et al., 2001; Pelmeshnikov et al., 2000; Pelmeshnikov et al., 1996; Rivanenkov et al., 2003). In this work, then, the cluster method was predominantly used to simulate the CaO(001) surface while a few tests were run with periodic methods for comparison. The adsorption of Hg-containing species with other components of PWDS will appear in subsequent papers.

We studied Hg, HgCl and HgCl₂ adsorption on the CaO(001) surface by performing DFT calculations(Zhang et al., 2005) using LDA/PWC and GGA/BLYP functionals

on cluster models, as well as using a periodic model in this work. DFT has already been proved to be fairly robust (Gross, 2002) and can be used to calculate structural properties that are typically within 0.05 Å and 1-2° of experiment, while overall adsorption and reaction energies are typically within 5-7 kcal/mol of experimental values, and spectroscopic analyses are within a few percent of experimental data (Vansanten & Kramer, 1995; Vansanten & Neurock, 1995). However, it should be pointed out that the accuracy of DFT in treating the Hg transition metal system does have limitations since the system possesses spin multiplet structures that are energetically close to each other (Gutsev et al., 2000; Rao & Jena, 2002). In this work, we used both the LDA and GGA functionals to obtain the geometries, adsorption energies and frequencies. The goal of the research is to investigate which functional gives more reliable answers compared to available data, and also to introduce the use of computational chemistry methods for predicting Hg species adsorption on CaO, which has never been studied before with theoretical calculations. Finally, we were interested in understanding the role of temperature on the adsorption ability.

The number of published papers employing CaO cluster models is quite limited, but some publications have appeared (Bawa & Panas, 2001; Di Valentin, Figini, & Pacchioni, 2004; Karlsen, Nygren, & Pettersson, 2002; Pacchioni, Ricart, & Illas, 1994). Recent work on a similar cluster looked at NO_x and other species being adsorbed on a relatively small CaO cluster that was allowed to relax during the geometry optimization (Karlsen, Nygren, & Pettersson, 2003). Other researchers

used a fixed cluster approach as we have here (Di Valentin et al., 2004; Karlsen et al., 2002; Pacchioni et al., 1994). There are a few other calculations on CaO surfaces, which are for much smaller adsorbates where more elaborate methods can be applied (Di Valentin et al., 2004; Jensen, Pettersson, Swang, & Olsbye, 2005; Karlsen et al., 2002; Pacchioni et al., 1994). It is already generally accepted that cluster models and DFT calculations, as employed in the present work, offer a useful description for the thermodynamic properties of adsorption on metal-oxides (Hoeft et al., 2001; Rivanenkov et al., 2003).

Methods

Calculations were done using density functional theory (DFT) with the DMol³ (Delley, 1990) package in the Accelrys Materials Studio[®] (2001). All simulations used double-numeric with polarization (DNP) basis sets (Delley, 1996), and the nuclei and core electrons were described with DFT semi-local pseudopotentials (Delley, 2002). The local density approximation (LDA) (Perdew & Wang, 1992) to the exchange-correlation functional was used to obtain one-electron energies of the cluster models, as was the generalized gradient approximations (GGA) (Becke, 1988a, 1988b; Lee et al., 1988). In addition, the Harris approximation (Harris, 1984) was used in combination with LDA to see if geometry optimizations could be done more efficiently to reduce computational cost, while the PWC functional (Perdew & Wang, 1992) was combined with the LDA method, and the BLYP correlation functional (Becke, 1988a; Lee et al., 1988) was combined with the GGA method. To summarize, for geometry optimization and

energy calculations, the results reported here combined the LDA/PWC with the Harris approximation or used the GGA/BLYP combination.

The (001) surface of CaO was chosen and has been used by other theoretical investigators (Bawa & Panas, 2001; Di Valentin et al., 2004; Karlsen et al., 2002; Pacchioni et al., 1994) as a surface of interest. In this work, the surface was modeled by a 3x3x2 cluster, 4x4x2 cluster, 5x5x2 cluster, and a periodic structure. A two atom layer of metal-oxide surface atoms was used which proved to be sufficient to investigate adsorbate surface interactions in prior research (Xu, Zhang, Lu, & Li, 2004). It should be noted that the CaO (001) structure was fixed with a bond length of 2.405 Angstroms between every Ca-O pair to enable more rapid computations to investigate this surface. This bond length is the experimentally determined one that is the default for the CaO (001) cleaved surface in DMol³. No terminal atoms were added to fill the valencies of the edge atoms (Jensen et al., 2005) as that would have made the computations more expensive and the electrons should be distributed well if the cluster is large enough (Lv, Xu, Wang, & Zhang, 1998). The strengths and weaknesses of each cluster model used in this work will now be examined.

The DFT adsorption energy was calculated as:

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

where ΔE_{ads} is the adsorption energy, $E_{Hg-species+surface}$ represents the energy of the adsorbate-surface species, $E_{Hg-species}$ is the energy of the gas phase mercury-containing species, and $E_{surface}$ is the energy of the isolated cluster in kcal/mol.

Results and Discussion

Hg species adsorption on CaO 3x3x2 cluster

As mentioned earlier, computational demand is increased as one moves from smaller clusters to larger ones. In this work, the 3x3x2 cluster is the smallest one that can symmetrically represent the overall CaO (001) surface, as described in Figure 1(a), provided that the Hg-containing species interacts with the O atom. If the adsorbate interacts with the Ca atoms, then one would have edge effects(Lv et al., 1998) and this cluster would not be large enough to handle the adsorbate, unless one used a Ca-centered 3x3x2 cluster.

The Hg-O distance for the optimized adsorbed structure of Hg leads to a bond length of 3.144 Angstroms between the mercury and oxygen atoms at the GGA level. This can be compared to the gas phase Hg-O bond length predicted to be 2.132 Å at the same level of theory. The predicted adsorption energy is 20.0 kcal/mol. For HgCl, the Hg-O distance is 2.827 Å, while the Cl moves to overlap with the Ca atoms with a distance of 3.121 Å. The heat of adsorption is 49.9 kcal/mol. Finally, HgCl₂ has a bond length of 2.632 Å between Hg-O, 3.194 Å between Cl(1)-Ca and 3.194 Å between Cl(2)-Ca and the heat of adsorption is 47.5 kcal/mol. The structure becomes bent as the adsorption occurs, which may be why there is a slight decrease in adsorption energy for the fully oxidized form of mercury; there is an energy cost of 5.6 kcal/mol to bend the HgCl₂ molecule from its lowest energy linear form in the gas phase.

Hg species adsorption on CaO 4x4x2 cluster

One is able to have interactions among a wider range of surface atoms with less interference of edge effects if the cluster is larger than $3 \times 3 \times 2$. Figure 1(b) shows a $4 \times 4 \times 2$ cluster pulled out from the CaO bulk system.

The simulations on the $4 \times 4 \times 2$ surface showed the $3 \times 3 \times 2$ oxygen-centered cluster was the correct one after a mercury atom was placed above the $4 \times 4 \times 2$ surface on the terrace site and a geometry optimization was done. The results of the calculation showed that Hg gravitated to an atop site over oxygen instead of moving into bridge, hollow, or atop-calcium sites. Geometry parameters for adsorption of the three Hg-containing species on the $4 \times 4 \times 2$ CaO cluster obtained by both LDA and GGA functionals are reported in Table 1.

The Hg-O distance for adsorption is 3.034 \AA at the LDA level and 3.144 \AA at the GGA level. The bond length difference between the two functionals is tolerable compared with the bond length differences obtained in other research compared to experimental values, which typically have differences of $0.03\text{-}0.27 \text{ \AA}$ (Zhang et al., 2005).

The Hg-O distance for the HgCl species is 2.543 and 2.517 \AA at the LDA and GGA levels, respectively. This shorter distance suggests that HgCl is more strongly bound by the surface and the heat of adsorption at the LDA and GGA levels demonstrates this with energies of adsorption of 49.4 and 35.3 kcal/mol . The geometry parameters for the Ca-Cl distance are 2.933 \AA and 2.943 \AA . For this species, we see that the LDA and GGA methods, then, give geometries that are very similar to each other.

For HgCl_2 adsorption, the Hg-O distance is 2.406 Å at the LDA level and 2.666 Å at the GGA level, again showing a larger difference between the two approximations. The Ca-Cl distances are 3.001 and 3.048 Å at the LDA level and 3.215 and 3.294 Å at the GGA level. The heats of adsorption are slightly smaller than for HgCl with values of 46.6 and 28.7 kcal/mol at the LDA and GGA levels.

Hg species adsorption on CaO 5x5x2 cluster

The optimized structure for HgCl_2 adsorption on the CaO 5x5x2 cluster is shown in Figure 1(c). Again, we see that mercury moved to the atop-O site instead of moving into other possible sites for adsorption, which demonstrates that mercury-oxygen interactions are more favorable than mercury-calcium interactions.

For Hg(0) adsorbed on the 5x5x2 cluster, the optimized distance between the Hg atom and O atom in the cluster obtained from LDA was 3.039 Å and GGA was 3.194 Angstroms, as shown in Table 1. Comparing this with the Hg-O bond length of 2.132 Å in the gas phase from calculation at the GGA level, we see the Hg atom adsorption on the 5x5x2 cluster is probably not close enough to form a chemical bond between the Hg and O atoms. Instead, the interaction tends towards longer range physical adsorption between Hg(0) and the CaO surface. This is supported by weaker adsorption energies of 20.3 and 6.5 kcal/mol at the LDA and GGA levels.

As was seen for the 4x4x2 cluster, we see that the Hg atom moves closer to the surface as one moves from mercury atom to HgCl. However, the trend is not the same for the LDA and GGA results as Hg-O moves closer with LDA but farther away for the higher level GGA calculations. Regardless of the geometry information,

Table 2 shows that the heats of adsorption get stronger as one moves from Hg(0) to HgCl, with an energy of 33.4 kcal/mol with GGA, and then to 26.1 kcal/mol for GGA for HgCl₂.

Hg species adsorption on a CaO periodic system

Figure 1(d) shows the periodic system used to investigate mercury adsorption with an HgCl₂ molecule adsorbed on the surface. This structure was optimized at the GGA/BLYP level. The cluster here has a vacuum layer of 10 Angstroms. 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 shown unit cell. For the single point energy calculation for interactions between Hg-containing species and the CaO structures, we find the computational cost for the periodic calculation was 45% more time consuming than the 5x5x2 non-periodic system, a significant increase in cost.

Mercury-containing species were placed in atop, hollow, and bridge atom sites on the terrace of the periodic CaO surface. The geometry optimizations for all species led to the mercury adsorbate being above the oxygen atom, while chlorine atoms, if they were present, primarily moved to overlap with Ca-atoms, as shown in Figure 1(d). Here, we see the HgCl₂ structure becomes bent, with the chlorine atoms moving farther away from the surface. It should be noted that the HgCl₂ remains a linear species other than bending in the z-direction to take advantage of orbital overlap for all three atoms. This shows the importance of allowing the adsorbate

structure to optimize even if the overall cluster is held in a fixed configuration to reduce computational costs(Xu et al., 2004).

Time cost for performing a single point energy

We did single point energy calculation with LDA for the interaction of Hg with the optimized structure for each cluster and the periodic system. Using the 4x4x2 cluster, computational time is increased over that needed for the 3x3x2 cluster-11.1 minutes by a factor of almost 3, reaching 32.5 mins and time for the 5x5x2 cluster was almost six times that of the 3x3x2 cluster and double that of the 4x4x2 cluster, reaching 50.6 mins. The calculation time for periodic structure is the longest, which is 70.4 mins. Clearly, one would like to find the minimum cluster size that can represent the interactions between mercury and the surface to be able to perform more estimates with higher calculational levels.

Adsorption energies and temperature effects on equilibrium constants

The adsorption energy of each Hg-containing species on various model structures calculated with LDA and GGA methods was computed with Equation (1) and the results are shown in Table 2. The trends in energies are shown for each surface and species in Figure 2.

Figure 2 shows that the 3x3x2 cluster has much stronger adsorption energies than any of the other clusters, probably being too small and having edge effects, and this cluster will not be considered further in this work. On the other hand, there are smaller differences between the energies for the 4x4x2, 5x5x2, and periodic structures. This suggests that one may use the 4x4x2 cluster for future mercury-CaO calculations

while keeping computational costs to a minimum. As discussed, we see the time used for a single point energy calculation on the 4x4x2 cluster is 1/3 less than the time consumed for a 5x5x2 cluster calculation, and less than half of the running time on the periodic structure.

We have talked about the adsorption of Hg(0) on the CaO 5x5x2 cluster, which we suggest is physical adsorption. From Table 2, we see the adsorption energy of Hg(0) from GGA calculations falls into the physical adsorption range, which is about 6 kcal/mol (Adamson, 1997). On the other hand, the adsorption energy of Hg(0) from LDA calculations is much larger and could indicate chemisorption is happening. This disagrees with our previously discussed bond lengths which are nearly 50% longer than for the gas phase Hg-O species. Based on these two parallel lines of reasoning, we believe the GGA/BLYP functional should be more accurate for Hg interactions with this sorbate using DFT calculations. There is no experimental data to compare to at this point.

Figure 2 shows trends in adsorption strength as the oxidation state of mercury is changed. Metallic mercury has the weakest adsorption, with a value of 7.1 kcal/mol on the 4x4x2 cluster with GGA calculations, which falls into the physical adsorption range (Adamson, 1997). Addition of one chlorine to increase the oxidation state of mercury to +1 leads to an increase of heat of adsorption to 35.3 kcal/mol. Further oxidation to +2 by forming HgCl₂ leads to a value of 28.7 kcal/mol, which is somewhat weaker. These results suggest that CaO will act as a stronger adsorbent for the oxidized species, although metallic Hg will also adsorb.

The Cl atoms released from HCl or Cl₂ in the coal combustion flue gas system greatly enhance the adsorption capability of the CaO, forming chemical bonds with the substrate surface and reducing the temperature at which the adsorption occurs. From the energies calculated in this work, it is suggested that the HgCl and HgCl₂ adsorption on the CaO(001) surface is chemisorption(Adamson, 1997).

As discussed above, the geometry properties from the most feasible cluster - 4x4x2 cluster are shown in Table 1 and reveal some interesting information when compared to Figure 2. One would expect that, as the adsorption became stronger, the species would move closer to the surface since the interactions are driving a more favorable bonding scheme. In this case, we see that the Hg-O distance shortens from 3.144 Angstroms for Hg to 2.517 Angstroms for HgCl, which has the largest adsorption energy, then extends to 2.666 Angstroms for HgCl₂. On the other hand, the Ca-Cl distance gets longer for HgCl₂ compared to HgCl. The HgCl molecule moves closest to the CaO surface for the three Hg-containing species, which indicates stronger bonding. These results indicate there is significant overlap in orbitals for the Hg-O interaction and the Ca-Cl interactions. It is the cumulative effect of strong interactions among each adsorbate-surface atom pair that may be driving the stronger adsorption, as opposed to charge transfer within the adsorbate that is affecting electrostatic attractions only. Future work with Natural Bond Order (NBO) calculations(Glendening & Weinhold, 1998) may shed more light on these phenomena, but are outside the scope of this work.

The effect of temperature on the equilibrium constant for the adsorption of Hg on CaO was preliminarily examined with both LDA and GGA calculations, and the results are shown in Figure 3. The temperature range is 250-600K. This figure was generated by using the computed enthalpy and entropy from the quantum calculations to obtain the Gibbs free energy, followed by calculating the equilibrium constant.

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

$$K = \exp(-\Delta G / RT) \quad (3)$$

where the ΔG is the change of Gibbs free energy for the adsorption process, ΔH is the change of enthalpy, and ΔS is the change of entropy of the adsorption. T is temperature and R is 0.001986 kcal/mol·K. From the figure, we can see the equilibrium constant decreases as the temperature increases, as one expects for exothermic systems(Lancia et al., 1996). We believe the adsorption of HgCl and HgCl₂ will show the same trend with the Hg atom adsorption on the CaO surface and future work will examine these trends.

Comparison between the functionals

A comparison of the bond lengths obtained from the LDA and GGA functionals in Table 1 shows the geometry optimization is insignificantly different but lead to LDA having slightly shorter bonds. The bond length difference between the two functionals is about 0.01-0.26 Angstroms, which is tolerable compared with the bond length differences obtained from other work and those experimental values, which are typically differences of 0.03-0.27Å(Zhang et al., 2005). Thus, the LDA methods could be applied to obtain geometry optimizations when computational time is limited.

This could be followed by a single point GGA energy calculation which seems to be more accurate based on this work. From Table 2, we see the energies from LDA are too large and not as reasonable compared to GGA, as we mentioned before.

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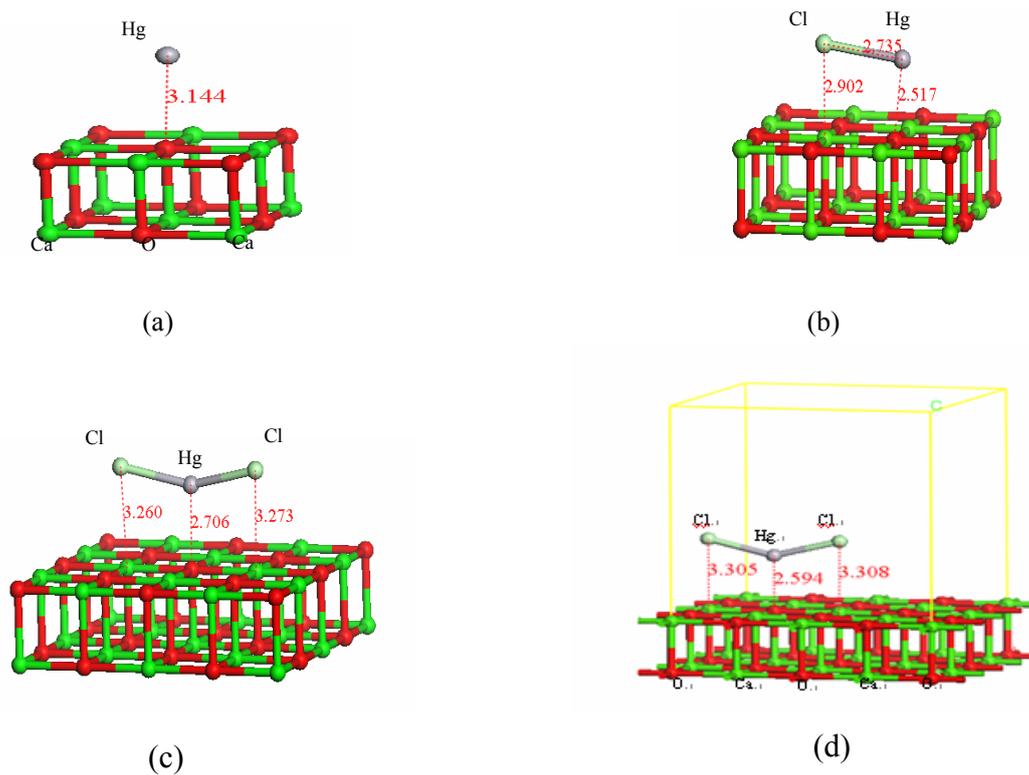


Figure 1. The Ca-O distance in the clusters is 2.405 Å. (a) Hg atom adsorption on a 3x3x2 cluster calculated by LDA/PWC. (b) HgCl adsorption on a CaO 4x4x2 cluster calculated by GGA/BLYP. (c) HgCl₂ adsorption on a CaO 5x5x2 cluster calculated by GGA/BLYP. (d) HgCl₂ optimized structure for adsorption on a periodic system calculated by GGA/BLYP. The distance of Hg-O is 2.594Å and Ca-Cl is about 3.305Å.

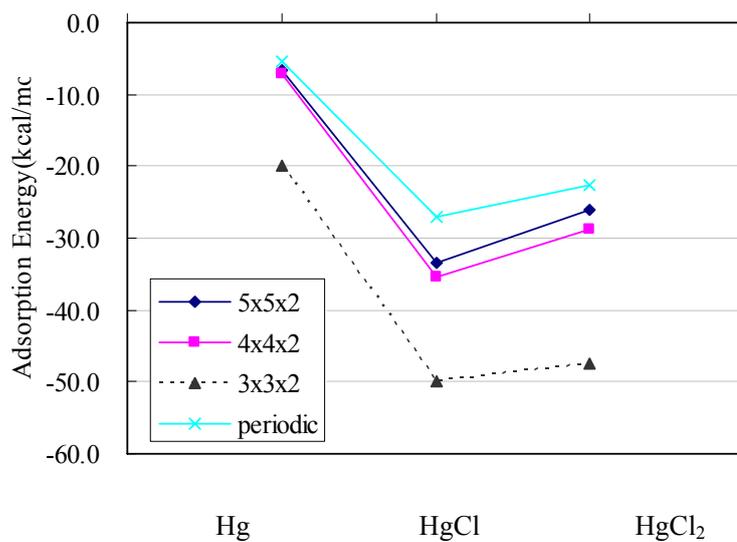


Figure 2. Predicted ΔE_{ads} (kcal/mol) of different cluster size and adsorbate species calculated by GGA/BLYP. The ΔE_{ads} got from periodic structure, 5x5x2 cluster and 4x4x2 cluster is close to each other. The adsorption energy obtained with the 3x3x2 cluster deviates too much from these results.

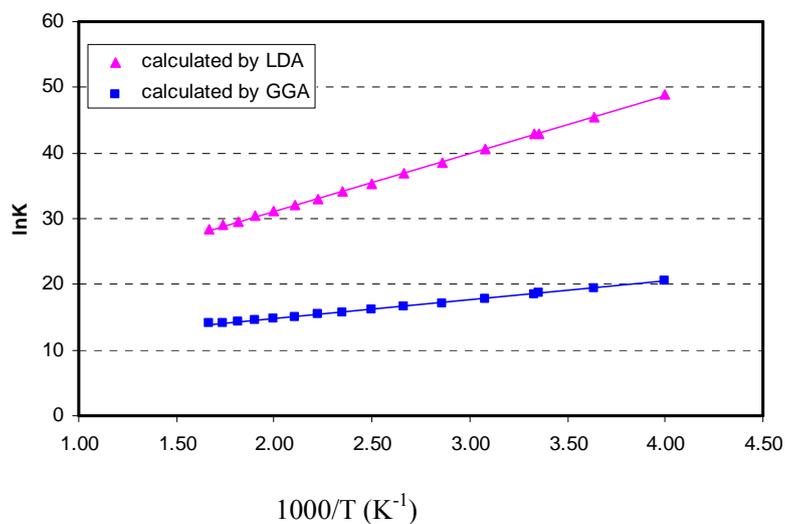


Figure 3. The predicted equilibrium constant for adsorption of Hg on CaO(001) as a function of temperature calculated by LDA and GGA functionals. The calculations show the same trend of the equilibrium constant getting larger with decreasing temperature.

Table 1 - A comparison of critical adsorbate-surface bond lengths for each Hg-containing species on the 4x4x2 and 5x5x2 simulated cluster by LDA/PWC and GGA/BLYP. All bond lengths are reported in Angstroms.

Cluster size	Species	Hg-O distance(Å)		Ca-Cl distance(Å)		Ca-Cl(2) distance(Å)	
		LDA	GGA	LDA	GGA	LDA	GGA
4x4x2	Hg	3.034	3.144	-	-	-	-
	HgCl	2.543	2.517	2.936	2.902	-	-
	HgCl ₂	2.406	2.666	3.001	3.215	3.048	3.294
5x5x2	Hg	3.039	3.194	-	-	-	-
	HgCl	2.539	2.549	2.933	2.943	-	-
	HgCl ₂	2.383	2.706	3.02	3.260	3.048	3.273

Table 2 – The adsorption energies obtained with LDA/PWC and GGA/BLYP functionals from different simulated structures. All energies are reported in kcal/mol.

Species	4x4x2		5x5x2		periodic	
	LDA	GGA	LDA	GGA	LDA	GGA
Hg	-19.8921	-7.0909	-20.3313	-6.5261	-20.4568	-5.4683
HgCl	-49.3850	-35.3288	-48.6320	-33.4460	-51.3303	-26.9829
HgCl ₂	-46.5676	-28.6772	-45.5311	-26.1044	-60.4292	-22.6530

APPENDIX B

A DENSITY FUNCTIONAL THEORY STUDY OF MERCURY-CONTAINING SPECIES ADSORPTION ON ALUMINUM OXIDE

Xinxin Li and Paul Blowers

Abstract

First principles computational quantum chemical methods are used to investigate the reaction environment, active sites, and thermodynamic properties important during mercury adsorption on aluminum oxide surfaces. The goal is to assist in the design of better sorbents for trace metal adsorption from coal combustion flue gases. Understanding adsorption of mercury-containing species on aluminum oxide surfaces is important for predicting the fate of mercury and its compounds in the environment, and in designing warm post-gasification gas clean-up systems for removing mercury from the flue gases in coal fired power plants.

This research investigated the binding of Hg, HgCl and HgCl₂ to the Al₂O₃(0001) surface using density functional theory (DFT) methods. In this work, the Al₂O₃ surface was modeled by a cluster terminated with hydrogen atoms. Structures optimized using the Harris approximation with the Perdew-Wang (PWC) local functional in LDA gave structural results close to experimental data. Adsorption energies for Hg, HgCl and HgCl₂ on the Al₂O₃ surface were calculated with GGA methods, indicating Hg adsorption is physical adsorption, and the other two species fall into the chemisorption range. Besides structures and energies, the temperature effect on adsorption was investigated.

Keywords: Mercury, Paper Waste Derived Sorbents, Density Functional Theory, Adsorption

Introduction

Mercury is one of the leading toxic metals due to its neurological impact on human beings(Pacyna & Pacyna, 2002). As a result of the toxicity issues surrounding mercury, the US EPA has reported that coal fired boilers generate the largest amount of mercury in U.S., and has set regulations on mercury emissions to reduce them to 0.1 ug/kg/day(Johansen, 2003; Pacyna & Pacyna, 2002). To meet this regulation, the need is to find economical, effective chemical/physical adsorption sorbents which adsorb Hg-containing species under real flue gas conditions.

Mercury has three different oxidation states commonly found in coal fired utility boiler flue gas systems — elemental mercury-Hg(0), mercurous-Hg(I) and mercuric-Hg(II) species which predominantly form HgCl and HgCl₂(Niksa et al., 2001) promoted by Cl₂, HCl, and atomic chlorine(Sliger et al., 2000). Much experimental and theoretical work has been conducted on Hg reduction and various sorbents being used in the coal fired power plants(Ghorishi et al., 2002; Hocquel et al., 2001; Jurng et al., 2002; Karatza et al., 1996b; Lancia et al., 1996; Olson et al., 2003; Wilcox & Blowers, 2004; Wilcox, Marsden, & Blowers, 2004; Wilcox, Robles, Marsden, & Blowers, 2003). However, some remediation technologies are very expensive and some are ineffective(Ghorishi et al., 2002; Jurng et al., 2002). Finding novel and inexpensive sorbents by exploring their absorption properties is the challenge currently faced by researchers. A new sorbent named Paper Waste Derived Sorbent (PWDS) was developed recently and proved to be very effective for Hg control in a bench scale system(Wendt, 2005). Since Al₂O₃ is one of the primary

constituents of PWDS, accounting for about 15% of the sorbent material in this novel application, the adsorption of Hg, HgCl and HgCl₂ on the Al₂O₃ surface was investigated.

The study of adsorption of mercury on some sorbents has been investigated using experimental methods (Krishnan et al., 1994; Otani et al., 1984; Otani et al., 1989). However, there is no experimental study of adsorption of mercury-containing species on Al₂O₃. As the development of computational tools has intensified and the methods have become more robust, we turn to using computational quantum chemistry methods to explain the adsorption of mercury species on Al₂O₃. We have talked about the three different computational quantum chemistry methods in calculating the surface adsorption in a previous work (Li & Blowers, 2006b) and found it can be reasonable to represent the adsorbent surface with a smaller cluster of atoms, often terminating unfilled valencies with hydrogen atoms to mimic a continuous surface (Hoeft et al., 2001; Serrano-Andres & Merchan, 2005). These cluster approaches normally allow one to use higher levels of theory and larger basis sets so one is able to obtain more accurate energetic results (Neurock, 2003). In this work, the cluster method was used to describe the aluminum oxide surface.

We studied Hg, HgCl and HgCl₂ adsorption on the Al₂O₃ (0001) surface (Casarin, Maccato, & Vittadini, 2000; Rivanenkov et al., 2003) by performing DFT calculations on a cluster model. DFT methods have already been proved to be fairly robust (Gross, 2002) and can be used to calculate structural properties that are typically within 0.05 Å and 1-2° of experimental values, with overall adsorption and

reaction energies that are typically within 5-7 kcal/mol, and spectroscopic analyses to within a few percent of experimental data (Vansanten & Kramer, 1995; Vansanten & Neurock, 1995). The bond lengths, adsorption energies, and frequencies are the focus of this work while we are also interested in understanding the role of temperature on adsorption. To the best of our knowledge, the adsorption between Hg, HgCl, HgCl₂ species and Al₂O₃ has never been studied before with theoretical calculations. However, there are some publications employing Al₂O₃ cluster models to study other phenomena (Hass, Schneider, Curioni, & Andreoni, 1998; Liu, Kendelewicz, Brown, Nelson, & Chambers, 1998; Neyman, Nasluzov, & Zhidomirov, 1996; Rodriguez, Chaturvedi, Kuhn, & Hrbek, 1998; Wittbrodt, Hase, & Schlegel, 1998). Previous work involved a similar Al₂O₃ cluster that was allowed to relax during the geometry optimization, looking at small molecules, such as H₂O or CO being adsorbed on the surface. Other work has modeled a crystalline Al₂O₃ structure (Casarin et al., 2000), but for the Al₂O₃ in PWDS, there are no regular crystalline structures present. Instead, the material forms amorphous structures that are much more challenging to model (Gutierrez & Johansson, 2002; Sushko et al., 2005). It is generally accepted that cluster models and DFT calculations, as employed in the present work, will offer useful descriptions of the thermodynamic properties for adsorption on metal-oxides (Hoeft et al., 2001; Rivanenkov et al., 2003).

Methods

To calculate the ground state properties of Al₂O₃ and the adsorption of Hg-containing species on Al₂O₃, we used Density Functional Theory (DFT)

(Hohenberg & Kohn, 1964; Jones & Gunnarsson, 1989; Kohn & Sham, 1965; Zhang et al., 2005) with the DMol³(Delley, 1990) package in the Accelrys Materials Studio[®](2001). Geometry optimization was done with the local density approximation(LDA)(Hedin & Lundqvist, 1971). The basis set used in the simulations was double-numeric with polarization (DNP)(Delley, 1996), and the nuclei and core electrons were described with DFT semi-local pseudopotentials(Delley, 2002). In addition, the Harris approximation(Harris, 1984) was used in combination with LDA to increase the efficiency of the geometry optimizations to reduce computational cost, while the PWC functional(Perdew & Wang, 1992) was combined with the LDA method. After obtaining the optimized geometry, the adsorption energy was calculated at the GGA level combined with the BLYP functional with the zero point vibrational energy included. In this way, we could obtain tolerable geometries with less computer time while still obtaining relatively accurate energy results(Li & Blowers, 2006b; Zhang et al., 2005).

In this work, the (0001) surface of Al₂O₃ was modeled by an Al₃O(OH)₉²⁻ T3 cluster, as shown in Figure 1 for Hg atom adsorption. Hydrogen atoms were added as terminal atoms to fill the valencies of the edge atoms.

The adsorption energy is calculated as:

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

where ΔE_{ads} is the adsorption energy, and all energies are in kcal/mol.

$E_{Hg-species+surface}$ represents the energy of the adsorbate-surface species, $E_{Hg-species}$ is

the energy of the gas phase mercury-containing species, and $E_{surface}$ is the energy of the isolated cluster.

Results and Discussion

Figure 1(a) shows the model cluster structure for the Al_2O_3 cluster(0001) surface(Gutierrez & Johansson, 2002) based on previous work with other smaller adsorbates(Hass et al., 1998; Liu et al., 1998; Neyman et al., 1996; Rodriguez et al., 1998; Wittbrodt et al., 1998) calculated with the LDA functional. A full geometry optimization was done on this T3 cluster with LDA calculations and it was found that the Al-O distance was predicted to be 1.754 Angstroms. This shows excellent agreement with a previous theoretical result of an Al-O bond length of 1.760 Angstroms(Gutierrez & Johansson, 2002) and the experimental value of amorphous Al_2O_3 which is about 1.80-1.90 Angstroms(Campbell et al., 1999).

Figure 1(b) shows Hg adsorption on the T3 Al_2O_3 model cluster obtained with the LDA functional. The prediction shows that the Hg atom approaches the O-atom instead of the Al-atom or H-atom, with an Hg-O distance of 4.166Å. Comparing it with Hg-O bond length of 2.064Å in the gas phase calculated with the LDA, we see the Hg atom adsorption on the Al_2O_3 cluster is not strong enough to form a chemical bond between the Hg and O atoms. Instead, the interaction tends towards longer range physical adsorption between the Hg(0) and the Al_2O_3 (0001) surface. It should be noted that the initial starting place of the Hg atom was varied and the optimization consistently led to Hg approach towards oxygen. The T3 cluster was held constant in these geometry optimizations of the Hg adsorption position in order to make the

computations tractable since there are many heavy atoms. The choice of fixing the cluster should lead to adsorption energies that are underpredicted in magnitude because relaxation of the surface to accommodate the adsorption site would lead to a lower final adsorbate-surface energy and drive the heat of adsorption to more negative values. Therefore, the heat of adsorption values we report in this work are less strong than what may be expected in experimental measurements.

Figures 1(c) and 1(d) show HgCl and HgCl₂ adsorption on the same T3 model cluster calculated with the LDA functional. We see that the Hg atom is again attracted to the oxygen atom in the center of the cluster. The Cl-atoms move towards the hydrogen atoms terminating the cluster, which may be leading to spurious results if the experimental surfaces are not truly terminated by hydrogen atoms. In the case of HgCl₂, we see the Hg-species becomes bent as the chlorine atoms both seek favorable interaction with the non-oxygen atoms of the surface. This is the same phenomena demonstrated in the CaO case(Li & Blowers, 2006b), so it is expected that the parent species will deform as it approaches the surface to enhance adsorption.

The size of the adsorbate relative to the cluster is about equal for HgCl₂. It is possible, then, that the T3 cluster is not large enough to adequately model the true Al₂O₃ interactions with the adsorbate without edge effects(Lv et al., 1998). This is why future work will investigate enlarging the cluster size to include more tetrahedral atoms to enlarge the cluster, which may lead to better representation of heats of adsorption.

Energy and temperature effects

Figure 2 shows the results for the adsorption energies calculated with GGA, for the Hg-species on the T3 Al_2O_3 cluster. Adsorption becomes stronger and more favorable as the mercury atom is oxidized by chlorine atoms, which is consistent with the experimental result derived by Schager(Schager, 1990). The adsorption energy for Hg atom adsorbed on $\text{Al}_2\text{O}_3(0001)$ surface is 8.0 kcal/mol which indicates physical adsorption(Adamson, 1997). We see that the heat of adsorption more than doubles as the first chlorine is added, and then gets slightly stronger as the second chlorine atom is added, leading to heats of adsorption of 50.8 and 59.5 kcal/mol, respectively, which indicates the adsorption of HgCl and HgCl₂ on the $\text{Al}_2\text{O}_3(0001)$ surface is chemisorption(Adamson, 1997). Table 1 shows some of the geometry parameters regarding the adsorbate-cluster optimized bond lengths. Obviously, the adsorption of HgCl and HgCl₂ on $\text{Al}_2\text{O}_3(0001)$ surface is much stronger. Thus, chlorine oxidation of mercury in the post-gasification gas clean-up systems, or modifying the sorbents with calcium hypochlorite, will enlarge the percentage of oxidization of Hg(0) to HgCl and HgCl₂, to promote the adsorption.

In Table 1, we see that the mercury distance becomes smaller as the mercury atom is oxidized. On the Al_2O_3 surface, the closest approach we have is for HgCl₂ with a distance of 3.88 Angstroms with calculations at the LDA level. On the other hand, we see that the chlorine atoms on the Hg-species are much closer to the cluster, interacting with the terminal hydrogens with a distance of 1.9 Angstroms. This

suggests that the adsorption benefits not just from Hg-adsorbate interactions, but also interactions with other species attached to mercury.

The bond length discussions, combined with the heats of adsorption shown in Figure 2 indicate that the chlorine-hydrogen interactions are enhancing the heat of adsorption. In the earlier case of CaO(Li & Blowers, 2006b), interactions between Ca-atoms and chlorine enhanced adsorption as well.

Figure 3 shows the predicted equilibrium constant for Hg adsorption on the T3 Al₂O₃ cluster as a function of temperature. This was generated by using the computed enthalpy and entropy from the simulations to calculate the Gibbs free energy followed by calculating the equilibrium constant with:

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

$$K = \exp(-\Delta G / RT) \quad (3)$$

where the ΔG is the change of Gibbs free energy for the adsorption process in kcal/mol. ΔH is the change of enthalpy in kcal/mol, ΔS is the change of entropy of the adsorption in kcal/mol·K, T is temperature in Kelvins, and R is 0.001986 kcal/mol·K. K is the equilibrium constant of the adsorption process. We see that we have the expected behavior of the equilibrium constant decreasing as the temperature increases, as one expects for exothermic systems. Meanwhile, this is the same trend with the experimental results that lower temperatures enhance adsorption capacity(Gullett & Jozewicz, 1993). We believe the adsorption of HgCl and HgCl₂ follows the same trend although those calculations are outside the scope of what has been calculated here.

Conclusions

The adsorption of mercury atom, mercurous chloride and mercuric chloride on a T3 Al_2O_3 model cluster was developed theoretically using density functional methods. The adsorption energies for different Hg species on Al_2O_3 cluster were calculated with the GGA functional after obtaining geometries with the LDA functional, as well as the equilibrium constants, which proved that elemental Hg adsorption on the Al_2O_3 substrate is a physical adsorption process and the adsorption ability decreases as the temperature increases to 600K, compatible with the equilibrium constants decreasing as temperature is raised for exothermic reactions. On the other hand, HgCl and HgCl_2 adsorption on the Al_2O_3 cluster is a chemisorption process based on the adsorption energies calculated with GGA. Thus, increasing the oxidization of Hg(0) to HgCl and HgCl_2 will promote adsorption by facilitating chlorine oxidation of mercury in the post-gasification gas clean-up systems or modifying the sorbents with calcium hypochlorite.

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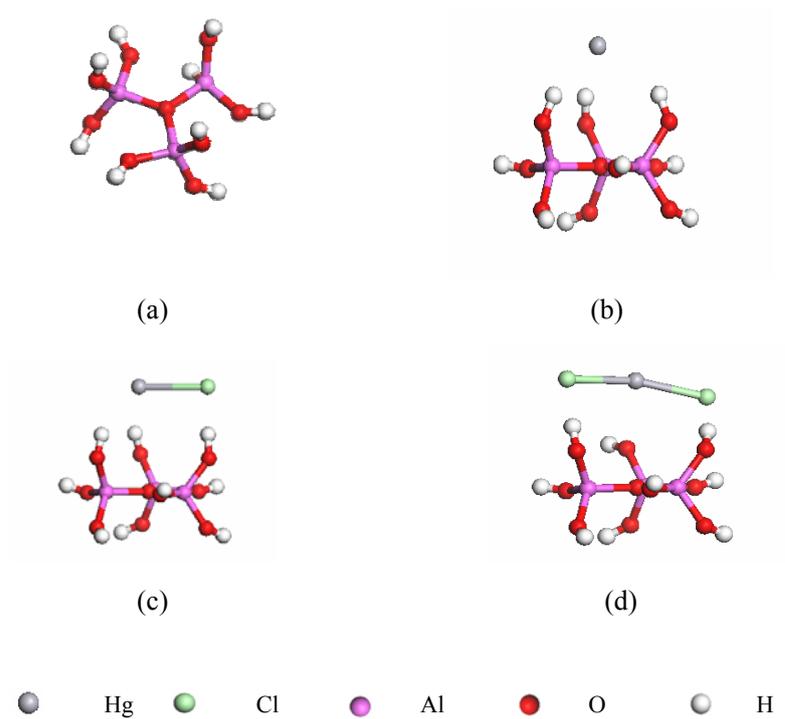


Figure 1. (a) Amorphous Al₂O₃ cluster structure terminated with hydrogen atoms. (b) Hg adsorption on a T3 Al₂O₃ model cluster calculated by LDA. (c) HgCl adsorption on a T3 Al₂O₃ model cluster. (d) HgCl₂ adsorption on a T3 Al₂O₃ model cluster. All geometry simulations were done with the LDA.

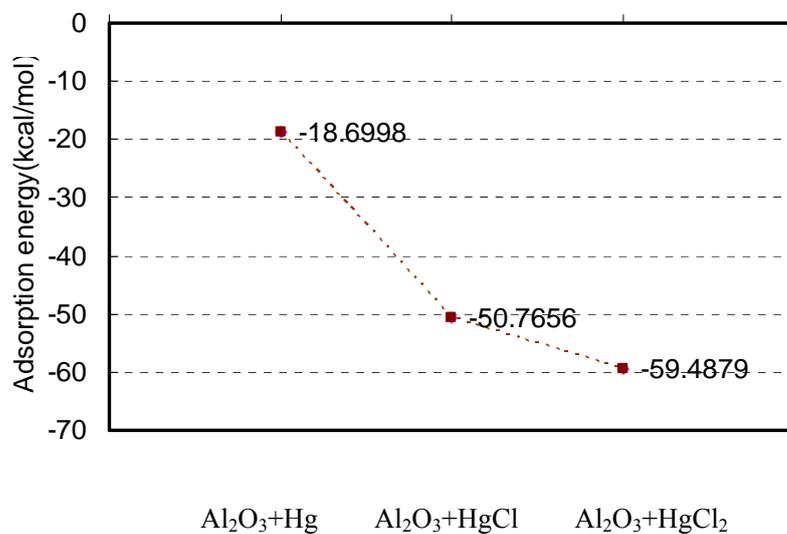


Figure 2. ΔE_{ads} plotted versus oxidation state for Hg-species on a T3 Al_2O_3 model cluster

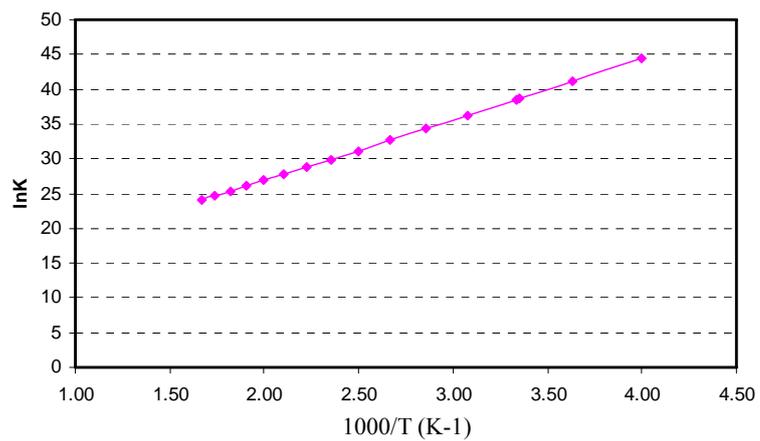


Figure 3. The predicted equilibrium constant for adsorption of Hg on on a T3 Al_2O_3 model cluster as a function of temperature

Table 1 - A comparison of critical adsorbate-surface bond lengths for each Hg-containing species on the T3 Al₂O₃ model cluster calculated with the LDA

Species	Hg-O distance(Å)	H-Cl closest distance(Å)	H-Cl(2) closest distance(Å)
Hg	4.166	-	-
HgCl	4.087	1.875	-
HgCl ₂	3.881	1.912	1.919

APPENDIX C

A DFT STUDY OF ADSORPTION OF
MERCURY-CONTAINING SPECIES ON SILICON
DIOXIDE

Xinxin Li and Paul Blowers

Abstract

The binding of Hg, HgCl and HgCl₂ to the SiO₂(0001) surface was investigated with density functional theory (DFT) methods. The results allow us to understand the adsorption of mercury species on SiO₂. The SiO₂ surface was modeled by an SiO₃(SiH₃)₃⁺ T3 cluster, a 5-membered ring cluster and a modified 5-membered ring cluster terminated with hydrogen atoms. Structures optimized using the Harris approximation and Perdew-Wang (PWC) local functional with the LDA proved tractable. Adsorption energies for Hg, HgCl and HgCl₂ on the SiO₂ clusters were then calculated with the GGA functional with the previously optimized structures. Besides structures and energies, the temperature effects on adsorption were investigated.

Introduction

Mercury is one of the most important trace elements emitted to the atmosphere due to its toxic effects on environmental and human health, as well as its role in the chemistry of the atmosphere (Pacyna & Pacyna, 2002). To reduce mercury emissions is of importance to mitigate its effects. Since the largest amount of mercury is released from coal fired boilers (Johansen, 2003), many researchers have studied the properties and reduction mechanisms of mercury species in flue gases system of coal fired power plants or have investigated the properties of various sorbents on which the mercury species adsorbs (Ghorishi et al., 2002; Hocquel et al., 2001; Jurng et al., 2002; Karatza et al., 1996b; Lancia et al., 1996; Olson et al., 2003; Sliger et al., 2000). In the flue gases, there are elemental mercury-Hg(0), mercurous-Hg(I), and mercuric-Hg(II) species, with the oxidized forms mostly promoted by chlorine and atomic chlorine, forming HgCl and HgCl₂ (Niksa et al., 2001).

The sorbents used for mercury control must be effective in adsorbing the three forms of mercury species while remaining cost-effective. Among many sorbents being considered for use in industry, the Paper Waste Derived Sorbent (PWDS) proved to be very effective in a bench-scale Hg control system (Wendt, 2005). In this newly developed sorbent, SiO₂ accounts for about 15% of the components. Since this is one of the primary constituents in the novel sorbent that could be used in coal fired power plants, the adsorption of Hg, HgCl and HgCl₂ on the SiO₂ surface was investigated in this paper. Understanding adsorption of mercury-containing species on SiO₂ surfaces is important for predicting the fate of mercury and its compounds in the environment,

and in designing warm post-gasification clean-up systems for removing mercury from the flue gases in coal fired power plants.

There have been many experimental studies of adsorption of mercury on different sorbents (Gullett & Jozewicz, 1993; Karatza et al., 1996a, 1996b; Krishnan et al., 1994; Lancia et al., 1993; Otani et al., 1984; Otani et al., 1989; Tseng et al., 1990). From these results, it was found that: (i) the adsorption phenomena are strongly sensitive to temperature; (ii) the lower the temperature, the higher the adsorption capacity; and (iii) oxidized mercury is more easily adsorbed than elemental mercury. However, there have been no experimental studies of adsorption of mercury species on SiO₂.

As the development of computational tools has improved, we turn to computational quantum chemistry methods to explain the adsorption of mercury species on SiO₂. DFT methods have already proved to be fairly robust (Gross, 2002; Vansanten & Kramer, 1995; Vansanten & Neurock, 1995), and were used in this work. Besides, three modeling methods in calculating the surface adsorption have been discussed in previous work (Li & Blowers, 2006b) and we found it reasonable to represent the adsorbent surface with a smaller cluster (Hoeft et al., 2001; Serrano-Andres & Merchan, 2005) of atoms, often terminating unfilled valencies with hydrogen atoms to mimic a continuous surface. In this work, the cluster method was used to describe the SiO₂ surface. Also, one of the main advantages of the cluster approach is that it is inherently local in nature and can be easily applied not only to bulk crystals, but also to amorphous materials (Mukhopadhyay et al., 2004, 2005),

surfaces(Sushko et al., 2002; Sushko et al., 2000) and complex interfaces(Johnson et al., 1998). The SiO₂ in PWDS exists in an amorphous form, which is another reason we employed the cluster model in this research.

There are some publications employing SiO₂ cluster models(Mukhopadhyay et al., 2004, 2005; Mysovsky, Sushko, Mukhopadhyay, Edwards, & Shluger, 2004; Stirling & Pasquarello, 2005; Sushko et al., 2005; Tanaka, Nakajima, & Yamashita, 2002; van Ginhoven, Jonsson, & Corrales, 2005) studying other phenomena. Some work involved similar amorphous SiO₂ clusters that were allowed to relax during the geometry optimization, looking at small molecules, such as NH₃ or CO and other species being adsorbed(Mukhopadhyay et al., 2004, 2005; Stirling & Pasquarello, 2005; Sushko et al., 2005; Tanaka et al., 2002), and some used 3- or 5-membered rings to simulate the SiO₂ surface, which is another form of SiO₂ existing as amorphous SiO₂(Tanaka et al., 2002).

In this work, we studied Hg, HgCl and HgCl₂ adsorption on the SiO₂ surface by performing DFT calculations on a T3 cluster, a 5-membered ring cluster and a modified 5-membered ring cluster model. The bond lengths and adsorption energies are focused on in this work while we are also interested in understanding the role of temperature on the adsorption ability. It is generally accepted that cluster models and DFT calculation, as employed in the present work, will offer useful descriptions of the thermodynamic properties for adsorption on metal-oxides(Hoeft et al., 2001; Rivanenkov et al., 2003).

Methods

Calculations were done using density functional theory(DFT) with the DMol³(Delley, 1990) package in the Accelrys Materials Studio[®](2001). All simulations used double-numeric with polarization (DNP) basis sets(Delley, 1996), and the nuclei and core electrons were described with DFT semi-local pseudopotentials(Delley, 2002). The effects of spin polarization were investigated by spin unrestricted methods. The local density approximation (LDA)(Perdew & Wang, 1992) to the exchange-correlation functional was used to obtain geometries of the cluster models, and the generalized gradient approximation (GGA)(Becke, 1988a, 1988b; Lee et al., 1988) was used to acquire the adsorption energies after the geometries were optimized at the lower level of theory. In addition, the Harris approximation(Harris, 1984) was used in combination with LDA so geometry optimizations could be done more efficiently to reduce computational cost, while the PWC functional(Perdew & Wang, 1992) was combined with the LDA method and the BLYP correlation functional(Becke, 1988a; Lee et al., 1988) was combined with the GGA method.

In this work, the surface of SiO₂ was modeled by an SiO₃(SiH₃)₃⁺, T3 cluster, as shown in Figure 1, a 5-membered ring cluster, as shown in Figure 2 and a modified 5-membered ring cluster, shown in Figure 3. The DFT adsorption energy is calculated as:

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

where ΔE_{ads} is the adsorption energy, $E_{Hg-species+surface}$ represents the energy of the adsorbate-surface species, $E_{Hg-species}$ is the energy of the gas phase

mercury-containing species, and $E_{surface}$ is the energy of the isolated cluster. All are in kcal/mol.

Results and Discussion

SiO₃(SiH₃)₃⁺ T3 cluster

The SiO₃(SiH₃)₃⁺ cluster calculated with the LDA functional was shown in Figure 1(a). This is a T3 cluster, with hydrogen atoms terminating most of the unfilled valencies of three of the four silicon atoms, and the oxygen atoms being satisfied by bonding to Si. The three principles for cluster modeling — the neutrality principle, stoichiometry, and the coordination principle (Lv et al., 1998; Xu et al., 2004) were considered as this SiO₃(SiH₃)₃⁺ T3 cluster was chosen.

The T3 SiO₂ cluster was fully optimized and we predicted a Si-O bond length of 1.649 Angstroms. Our calculated results agree very well with the CRC Handbook of Chemistry and Physics (Lide, 2002), which reports a bond length of 1.650 Angstroms.

Figure 1(a) shows the interaction of mercury atom with the T3 SiO₂ cluster. We see here that the Hg moves to a position directly over the unfilled Si-atom valence, as expected. The geometry optimization was run from several different starting positions for the Hg-atom and it moved to this position instead of bonding to the oxygen atom as it did in the earlier cases (Li & Blowers, 2006a, 2006b). The adsorption energy for Hg on the SiO₂ surface is 31.9 kcal/mol, which is a chemical sorption process (Adamson, 1997) due to its moderately strong interaction.

Figures 1(b) and 1(c) show HgCl and HgCl₂ adsorption on the SiO₂ model cluster. It should be noted that the geometries of the clusters were fixed to model HgCl and

HgCl₂ adsorption to reduce computational cost. Unlike the Al₂O₃ case we studied before (Li & Blowers, 2006a), we find different adsorption behavior for each of the Hg-containing species. The Hg(0) atom adsorbs atop the Si atom, while HgCl has Cl approach the Si atom and Hg moves into an interstitial space between the two tetrahedral moieties terminated by hydrogen atoms. Obviously, Cl will dominate the adsorption with Si rather than Hg, because of its high electronegativity (Griesinger, Sorensen, & Ernst, 1985). HgCl₂, on the other hand, has mercury move over the oxygen atom while one chlorine bends back to overlap with the unfilled valence of the Si atom in the center, while the other chlorine attempts to overlap with one of the hydrogens terminating the cluster. With all of these different behaviors, it is highly suspected that this cluster is not large enough for modeling the Hg-containing species as they approach the cluster.

Due to the large variation in adsorption mechanism for the different forms of mercury, it is not relevant to report all calculated bond lengths. The Hg atom moves to be 2.765 Angstroms away from the center Si-atom, while the HgCl species has a distance of 2.284 for the Cl-center Si atom. This is similar to the 2.315 Angstroms found for HgCl₂ for one Cl-Si-center atom distance. In general, the Cl atoms are bound closer to the Si unfilled valence position than Hg.

Figure 4 shows that the adsorption energy obtained from GGA, which increases as the oxidation state of mercury is increased, in agreement with the results we obtained in our previous work (Li & Blowers, 2006a, 2006b). The heat of adsorption more than doubles with HgCl to a value of 66.5 kcal/mol. Further oxidation of

mercury leads to a larger heat of adsorption of 78.3 kcal/mol for HgCl₂. These results suggest that the oxidation state of the mercury species as they approach the PWDS will be very important for capturing the mercury species in the flue gases.

Finally, Figure 5 shows the equilibrium constant preliminarily examined with the GGA for Hg adsorption on the SiO₂ model T3 cluster. The temperature range is 250-600K. This figure was generated by using the computed enthalpy and entropy from the simulation to calculate the Gibbs free energy followed by calculating the equilibrium constant.

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

$$K = \exp(-\Delta G / RT) \quad (3)$$

where the ΔG is the change of Gibbs free energy for the adsorption process in kcal/mol. ΔH is the change of enthalpy in kcal/mol, and ΔS is the change of entropy of the adsorption in kcal/mol·K. T is temperature in K. R is 0.001986 kcal/mol·K. K is the unitless equilibrium constant of the adsorption process. From the figure, we can see that we have a decrease in the equilibrium constant as the temperature increases, as one expects for exothermic systems(Lancia et al., 1996). We believe the adsorption of HgCl and HgCl₂ will show the same trend with the Hg atom adsorption on the SiO₂ surface but those results are outside the scope of this preliminary work.

5-membered ring cluster

The geometry of the 5-membered ring cluster calculated with the LDA functional was shown in Figure 2 with Hg and HgCl and HgCl₂ molecules adsorbed on the

cluster. The bond length of Si and O on the ring is 1.631 Å, which is very close to the experimental value of 1.650 Å, and the distances of Hg-O are shown in the figure. Formation energies for each species were calculated with the GGA functional, and the positive adsorption energies obtained (+5.9 kcal/mol for Hg adsorption, +87.9 kcal/mol for HgCl adsorption and +95.1 kcal/mol for HgCl₂ adsorption) indicate that these adsorption processes will not occur spontaneously. The adsorption of Hg species is not favorable on this cluster since the cluster is saturated (Pacchioni, 1995).

Modified 5-membered ring cluster

The modified 5-membered ring cluster was based on 5-membered ring cluster, but with elimination of one terminal hydrogen on a Si atom. Therefore, the cluster had a charge of +1 and it is an open-shell system due to iron's unsaturated electronic configuration (Koch & Holthausen, 2000). The geometry of the modified 5-membered ring cluster calculated with the LDA functional was shown in Figure 3 with Hg and HgCl and HgCl₂ molecules adsorbed on the cluster. The distances of important atoms are shown in the figure. Formation energies for each species were calculated with the GGA functional, and the adsorption energies obtained were 9.9 kcal/mol for Hg adsorption, 17.7 kcal/mol for HgCl adsorption and 15.8 kcal/mol for HgCl₂ adsorption, which indicated that the cluster with a pair of unsaturated electrons could work well which corresponds to the result Pacchioni reported (Pacchioni, 1995).

The equilibrium constant preliminarily examined with the GGA for Hg adsorption on the modified 5-membered ring cluster is shown in Figure 5 also. The temperature range is 250-600K. From the figure, we can see that we have behavior

of the equilibrium constant decreasing as the temperature increases, as one expects for exothermic systems(Lancia et al., 1996).

From the results, the adsorption energies obtained from T3 cluster are estimated to be too high for this adsorption process, which leads to the conclusion that the T3 cluster is not big enough to be able to describe the adsorption processes of Hg species on amorphous SiO₂. The modified 5-membered ring cluster is more feasible for simulating the Hg species adsorption according to the magnitude of the calculated adsorption energies. Also, the Hg(0) adsorption is physical adsorption, which agrees with our previous investigation on CaO and Al₂O₃(Li & Blowers, 2006a, 2006b). On the other hand, the HgCl and HgCl₂ adsorption is close to chemical adsorption. Thus, increasing the oxidization of Hg(0) to HgCl and HgCl₂ will promote adsorption by facilitating stronger interactions with the surface. This agrees with recent experiments(Zeng, Jin, & Guo, 2004). Chlorine oxidation of mercury in the post-gasification gas clean-up systems or modifying the sorbents with Cl may lead to enhanced adsorption and better removal.

Conclusions

For this surface, as for others, increasing the oxidation state of mercury leads to enhanced adsorption with stronger binding to the surface. The stronger binding is due to secondary effects because chlorine interacts with other surface atoms to strengthen the binding. Further orbital calculations may demonstrate what phenomena are leading to the enhanced adsorption in order to understand how the complex behavior seen in real systems can be explained.

The adsorption of mercury atom, mercurous chloride and mercuric chloride on the SiO₂ cluster was developed theoretically using density functional methods. The adsorption energies for different Hg species on SiO₂ cluster were calculated with the GGA functional after obtaining optimized geometries with the LDA functional, as well as the equilibrium constants, which proved that adsorption ability decreases as the temperature increases to 600K, compatible with the equilibrium constants decreasing for exothermic reaction. The more oxidized forms showed the strongest interactions with the surface. Thus, to enlarge the percentage of oxidization of Hg(0) to HgCl and HgCl₂ will promote the adsorption by facilitating chlorine oxidation of mercury in the post-gasification gas clean-up systems or modifying the sorbents with calcium hypochlorite.

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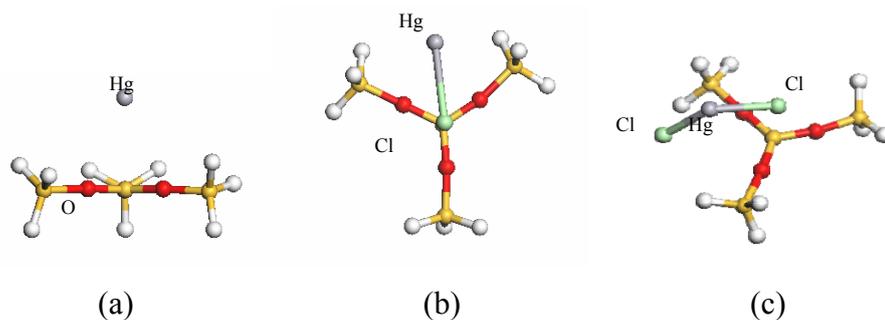


Figure 1(a) Hg adsorption on a T3 SiO₂ model cluster. (b) HgCl adsorption on a T3 SiO₂ model cluster. (c) HgCl₂ adsorption on a T3 SiO₂ model cluster. All geometry simulations were done with the LDA.

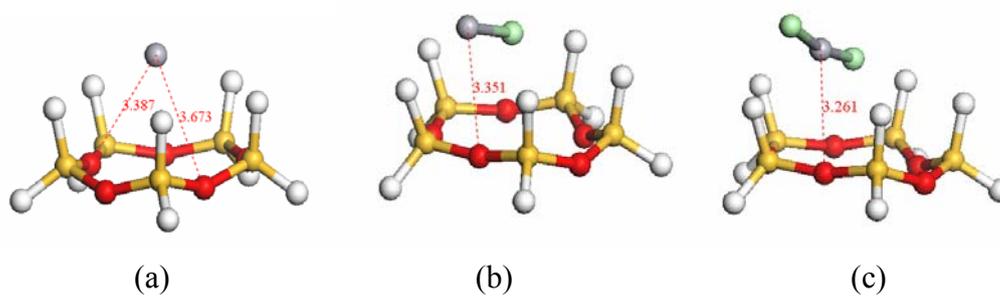


Figure 2(a) Hg adsorption on a 5-membered ring SiO_2 model cluster. (b) HgCl adsorption on a 5-membered ring model cluster. (c) HgCl_2 adsorption on a 5-membered ring model cluster. All geometry simulations were done with the LDA.

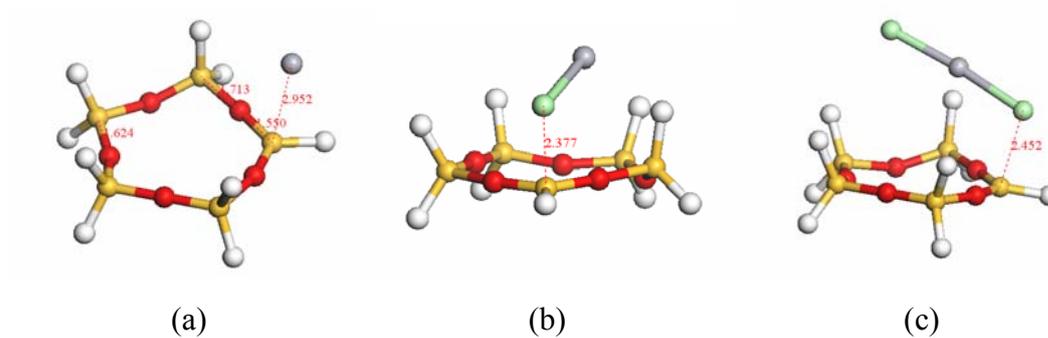


Figure 3(a) Hg adsorption on a modified 5-membered ring SiO₂ model cluster. (b) HgCl adsorption on a modified 5-membered ring model cluster. (c) HgCl₂ adsorption on a modified 5-membered ring model cluster. All geometry simulations were done with the LDA.

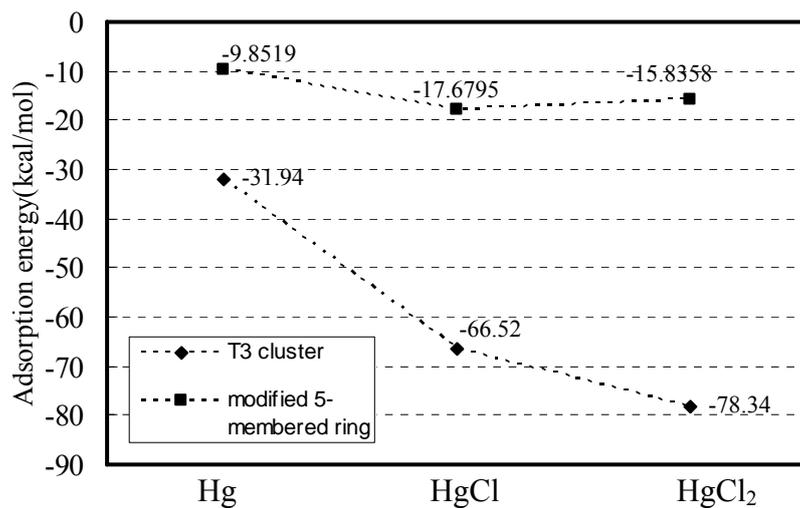


Figure 4. ΔE_{ads} plotted versus oxidation state for Hg-species on a T3 SiO₂ model cluster and a 5-membered ring cluster. All energies were obtained at the BLYP/GGA level.

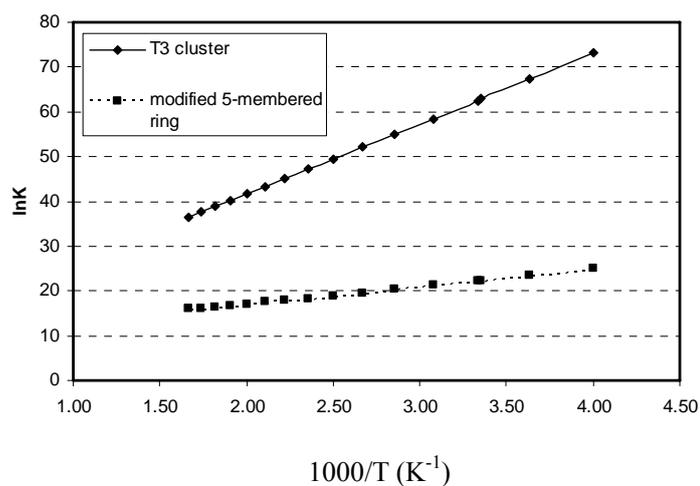


Figure 5. The predicted equilibrium constant for adsorption of Hg on a T3 SiO₂ cluster and a 5-membered ring cluster as a function of temperature

Table 1 - A comparison of critical adsorbate-surface bond lengths for each Hg-containing species on the T3 SiO₂ model cluster calculated with the LDA. All values are in Angstroms

species	Hg-center Si distance	Hg-H distance	Cl-center Si	Cl-closest H distance
Hg	2.765	-	-	-
HgCl	-	2.220	2.284	-
HgCl ₂	-	3.641	2.315	3.044

FUTURE WORK

As studied and shown in Appendices A, B and C, we investigated the cluster structures for CaO, Al₂O₃ and SiO₂ and compared the adsorption energies for different Hg species while also studying the temperature effect on adsorption.

The cluster structures have shown a good compromise between accuracy and computational cost. However, larger clusters could be applied to Al₂O₃ and SiO₂ to reduce edge effects, especially when the larger molecules, HgCl and HgCl₂, approach the adsorbent surfaces. For instance, the T3 clusters of Al₂O₃ and SiO₂ could be enlarged to T5 or even larger clusters (Rivanenkov et al., 2003), as shown in Figure 1. The increase of cluster size should be able to increase the accuracy of the calculational results, with a great increase in computational costs, possibly making them intractable on the existing hardware. On the other hand, these results will help to further determine the structure of PWDS.

From a chemical point of view, besides the three components of PWDS we discussed in this work, there are still other components affecting the PWDS's adsorption ability, such as CaCO₃, whose structure will be a point in the following work. It will be possible to meld the surfaces together into a simulated larger surface after getting the clusters of all the components. One may also modify the sorbents

with hypochlorite or chlorine to promote mercury species adsorption, as suggested in prior experimental work (Wendt, 2005).

While studying the temperature effect on the adsorption ability, the physical adsorption of Hg(0) became a focus. In order to further explore the PWDS's adsorption ability, several improvements could be made in the future research. The effects of temperature changes on the adsorption processes of HgCl and HgCl₂ on PWDS, which has been proved to be chemisorption in this work, could be examined as a function of temperature. Also, there could be chemical reactions happening on the adsorbent surfaces with other flue gases, such as HCl and Cl₂, etc., which could complicate and enhance the adsorption processes.

The PWDS is an inexpensive, newly developed sorbent for Hg species adsorption in the coal fire power plants which has a promising future to replace the activated C (Zeng et al., 2004) presently used in industry. The adsorption energies of Hg species on activated C could be calculated and applied as a comparison of our work since more experimental data is available to test our computational methods against.

Reference

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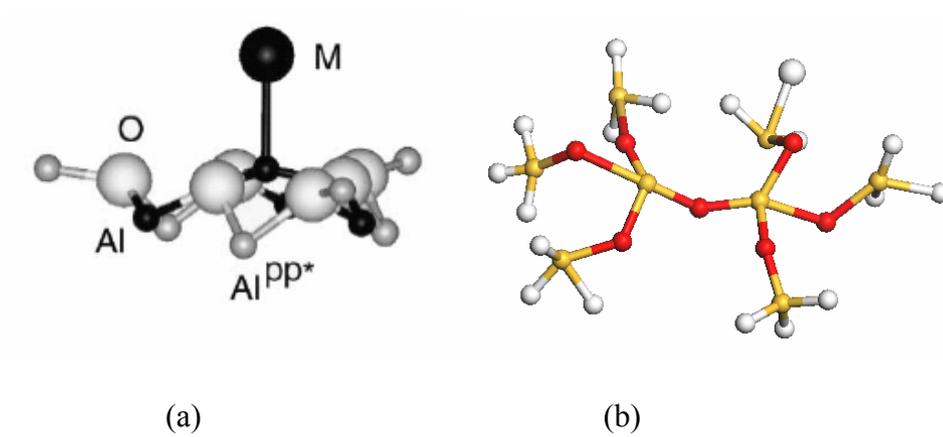


Figure 1(a). Cluster model $M/[Al_4O_6]/(Al^{pp*})_n$ $M=Hg$. (b) Estimated cluster model $Si_8O_7H_{18}$.

DATA ACCESS

The data are mainly in the following MS Modeling files which could be accessed. All the calculation jobs could be accessed through C:\Program Files\Accelrys\MS Modeling 3.1\Gateway\root_default\dsd\jobs.

File 3.1 and 3.21

Calculations on Ca(OH)_2 periodic structure.

File 7.12

The CaO periodic structure calculations could be found in the folders marker with “bulk” or “CaO (001)”. And some other CaO clusters calculations which could be identified by the folder names. Besides, there are calculations about Ca(OH)_2 clusters which are in the folders marked with “ Ca(OH)_2 ” and some calculations on Ca(OH)_2 clusters could be found in File 4.25 and 5.10.

File 8.29

There are calculations on CaO clusters. The folder names with “CaO small cluster fix” or “CaO 33” are the calculations on 3×3 clusters, names with “CaO 4 4” are the 4×4 clusters, names with “CaO 5” are the 5×5 clusters. The LDA and GGA functionals are marked in most folders; otherwise, it could be traced in calculations. The other folders in this file are the tentative results of other CaO clusters.

File 9.9

The Al_2O_3 data could be found in the folders named as “ Al_2O_3 -2 + Hg”, “ Al_2O_3 -2 + HgCl”, and “ Al_2O_3 -2 + HgCl₂”, or “ Al_2O_3 fix + Hg”, “ Al_2O_3 fix + HgCl”, and “ Al_2O_3 fix + HgCl₂”.

SiO_2 data are in the folders named as “ SiO_2 +1”, “ SiO_2 + Hg +1”, “ SiO_2 + HgCl +1” and “ SiO_2 + HgCl₂ +1” or “ SiO_2 + Hg fix”, “ SiO_2 + HgCl fix” and “ SiO_2 + HgCl₂ fix”.

There are a couple of folders called CaCO_3 with CaCO_3 structures in. They are preliminary calculation results.

The remaining folders in this file are the tentative calculation results for reference.