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Theoretical and Experimental Investigations of Mercury Adsorption on Hematite Surfaces

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Abstract

One of the biggest environmental concerns caused by coal-fired power plants is the emission of mercury (Hg), which is toxic metal. To control the emission of Hg from coal-derived flue gas, it is important to understand the behavior, speciation of Hg as well as the interaction between Hg and solid materials in the flue gas stream. In this study, atomic-scale theoretical investigations using density functional theory (DFT) were carried out in conjunction with lab-scale
experimental studies to investigate the adsorption behavior of Hg on hematite (α-Fe2O3).

According to the DFT simulation, the adsorption energy calculation proposes that Hg physisorbs to the α-Fe2O3(0001) surface with an adsorption energy of -0.278 eV, and the subsequent Bader charge analysis confirms that Hg is slightly oxidized. In addition, Cl introduced to the Hg-adsorbed surface strengthens the Hg stability on the α-Fe2O3(0001) surface as evidenced by a shortened Hg-surface equilibrium distance. The PDOS analysis also suggests that Cl enhances the chemical bonding between the surface and the adsorbate, thereby increasing the adsorption strength. In summary, α-Fe2O3 has the ability to adsorb and oxidize Hg, and this reactivity is enhanced in the presence of Cl.

For the lab-scale experiments, three types of α-Fe2O3 nanoparticles were prepared using the precursors Fe(NO3)3, Fe(ClO4)3, and FeCl3, respectively. The particle shapes varied from diamond to irregular stepped and sub-rounded, and particle size ranged from 20 to 500 nm depending on the precursor used. The nanoparticles had the highest surface area (84.5 m2/g) due to their highly stepped surface morphology. Packed-bed reactor Hg exposure experiments resulted in this nanoparticles adsorbing more than 300 µg Hg/g. The Hg LIII-edge extended x-ray absorption fine structure spectroscopy also indicated that HgCl2 physisorbed onto the α-Fe2O3 nanoparticles.

**Implications**

Atomic-scale theoretical simulations proposes that Hg physisorbs to the α-Fe2O3(0001) surface with an adsorption energy of -0.278 eV, and the subsequent Bader charge analysis confirms that Hg is slightly oxidized. In addition, Cl introduced to the Hg-adsorbed surface strengthens the Hg stability on the α-Fe2O3(0001) surface as evidenced by a shortened Hg-surface equilibrium
distance. The PDOS analysis also suggests that Cl enhances the chemical bonding between the surface and the adsorbate, thereby increasing the adsorption strength. Following lab-scale experiment of Hg sorption also shows that HgCl₂ physisorbs onto α-Fe₂O₃ nanoparticles which have highly stepped structure.

**Introduction**

Mercury (Hg) is a toxic pollutant, which is harmful to living organism’s immune, genetic, enzymatic, and nervous systems. (IPCS 1993) The concentration of Hg in the environment is increasing due to emissions from various anthropogenic sources, such as mining, pulp, and paper industries as well as from fossil fuel-fired power plants, artisanal small-scale gold mining, non-ferrous metal manufacturing, cement production, waste disposal, and caustic soda production (Pirrone et al. 2010). Among these sources, Hg emissions from coal-fired power plants contribute high levels of Hg to the environment. In particular, in the United States, more than 50% of anthropogenic Hg is released from coal-fired power plants. (EPA 2012) Therefore, when considering a large percentage of Hg emission, it is desirable to capture Hg from coal-derived flue gas streams. Mercury in flue gas could be removed by catalysts via adsorption and oxidation on the catalyst surface. Activated carbon (AC) has been widely used as a sorbent for Hg removal; however, due to its high cost (Krishnan, Gullett, and Jozewicz 1994, Ahmaruzzaman 2010, Wu et al. 2007) and environmental problems (Miller et al. 2006), finding cost-effective and environmentally-friendly alternatives to AC has been widely researched. Fly ash (Bhardwaj, Chen, and Vidic 2009) which is a by-product of coal-burning, and transition metal oxides which are components of fly ash, and noble metals such as gold (Au), palladium (Pd) and platinum
theoretical investigations using density functional theory (DFT) were carried out in conjunction with lab-scale experimental studies to investigate the adsorption behavior of Hg on α-Fe₂O₃. The work consists of two parts: atomic-scale DFT simulations and lab-scale experiments. The purpose of first part is to explain the relative role of each phenomenon during the Hg adsorption on α-Fe₂O₃(0001) surfaces based on the adsorption energy calculation and electronic properties. In addition, by packed-bed Hg exposure experiments to the synthetic α-Fe₂O₃ nanoparticles and the characterization of the reacted particles, the sorption and/or oxidation behavior of the different α-Fe₂O₃ nanoparticles will be explained.

**Computational Methodology**

Model Selection and Construction

The α-Fe₂O₃(0001) surfaces were constructed by cleaving bulk α-Fe₂O₃ perpendicular to the c-axis ([001] direction). Along the [001] direction, a double-sided slab model of α-Fe₂O₃ was constructed using the following unit cell parameters: \( a = 5.019 \, \text{Å}, \, b = 5.019 \, \text{Å}, \) and \( c = 13.760 \, \text{Å} \). This unit cell size is well matched with experimental values with an error less than 3% (Newnham and Haan 1962). A vacuum region of 30 Å was introduced to minimize fictitious interactions between periodic images. The slab was formed with 16 atomic layers, which is thick enough to maintain the bulk structure in the center region of the slab. Figure 1 shows the O-terminated (0001) surface after geometry optimization. The unit cell of the slab model consists of 34 atoms (12 Fe atoms and 22 O atoms). Calculations have been conducted on the (1x1) unit cell initially, followed by a larger (2x1) supercell.
Various configurations of each adsorbate on the $\alpha$-Fe$_2$O$_3$(0001) surface were examined in this study in order to determine the most plausible configuration based on the calculated lowest adsorption energy. For the cases of single Hg and single Cl adsorption, 12 different initial configurations were examined (Figure 2). To find the lowest energy configuration upon adsorption, total energy calculations were conducted for every possible site by relaxing the geometry of the entire slab. In each case, every atom was fully relaxed until the calculated total energy reaches the convergence criterion. After the total energies were calculated, the configuration showing the strongest adsorption was determined to be the final adsorption configuration. The adsorption energy of each configuration was calculated by the following equation:

$$E_{\text{ads}} = E_{\text{slab+adsorbate}} - E_{\text{slab}} - E_{\text{gas phase}}$$

where $E_{\text{slab+adsorbate}}$, $E_{\text{slab}}$ and $E_{\text{gas phase}}$ represent the total energies of the adsorbate on a slab, the clean slab, and the gas phase atom (Hg or Cl) in vacuum space, respectively.

Electronic Structure Calculation

In addition to the adsorption energy calculation, the electronic and charge properties of the adsorbates and $\alpha$-Fe$_2$O$_3$(0001) systems were investigated by analysing the Bader charge (Henkelman, Arnaldsson, and Jónsson 2006) and PDOS. Within the Bader analysis, the electron charge distribution from the DFT calculation was partitioned and assigned to individual atoms. The differences in the partitioned charge before and after adsorption indicate charge transfer between the surface and adsorbate, thereby determining the oxidation or reduction
characteristics of adsorption. The PDOS analysis examines chemical bonding interactions by showing the changes in the occupation of the electronic energy levels associated with adsorption.

Computational Parameters

All DFT calculations were carried out using the Vienna *ab initio* Simulation Package (VASP) code (Kresse and Furthmuller 1996a, b, Kresse and Hafner 1993, Kresse and Hafner 1994). The projector-augmented wave (PAW) method (Kresse and Joubert 1999, Blochl 1994) was employed to represent the electron-ion interactions, and the electron exchange-correlation functional was represented by the generalized gradient approximation (GGA) with the model of Perdew, Burke, and Ernzerhof (PBE) (Perdew, Burke, and Ernzerhof 1996, Perdew, Burke, and Ernzerhof 1997) for non-local corrections. A kinetic energy cutoff of 450 eV was used for the plane-wave basis set. Integration of the Brillouin zone was conducted using a 5×5×1 Monkhorst-Pack grid (Monkhorst and Pack 1976) including the Γ-point, and Gaussian smearing was applied with a width of 0.2 eV. All atoms were fully relaxed and optimized until the atomic forces were less than 0.03 eV/Å (Aboud, Wilcox, and Brown 2011). The convergence criterion for the energy was set to 10⁻⁶ eV. A (1x1) unit cell and (2x1) supercell were employed for all calculations with an energy convergence of 0.2 meV/atom. Additionally, spin polarization calculations were conducted to consider the magnetic moments of the individual Fe atoms, although bulk α-Fe₂O₃ has antiferromagnetic characteristics.
Experimental Methodology

Hematite Synthesis

Forced hydrolysis synthesis procedures with three different Fe precursors were used to produce \( \alpha \)-Fe\(_2\)O\(_3\) powders of varying surface areas, shapes, and particle sizes. A Fe-bearing salt with 0.2 M of Fe solution was aged in an oven for several days at 98 °C for hydrolysis. After aging, the solutions were centrifuged in order to achieve compact sediments. Finally, the sediments were triple washed with doubly de-ionized (DDI) water and dried, resulting in a powder. All synthesis methods are taken from the description of Schwertmann and Cornell (Schwertmann and Cornell 2008) and are described in Table 1 and supplementary information (Figure S1). Each sample is denoted as NP1, NP2, and NP3 depending upon the method used.

Packed-bed Reactor Hg Exposure Test

*Elemental Hg Exposure* In order to obtain baseline results for Hg\(^0\) uptake on the synthetic sorbents, an air environment was initially used with a packed-bed reactor system as shown in Figure 3. Approximately 52.5 mg ± 2.5 mg of the synthesized \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticles were placed in a 7 mm-diameter quartz packed-bed reactor with quartz wool maintained at 140 °C using a Carbolite tube furnace. Elemental Hg vapor was introduced into the system using a Hg calibration system (PSA 10.536 Mercury Calibration System, PS Analytical) at a concentration of 60 ppb. The initial Hg concentration is about 30× higher than that of a typical coal-fired flue gas in order to facilitate adsorption and increase the surface concentration required for effective application of the spectroscopic characterization techniques. The concentration of Hg\(^0\) and total...
Hg (Hg\textsuperscript{T}) in the outlet flow was measured using a PSA 10.525 Sir Galahad Hg analyzer (PS Analytical). By comparing the concentration of Hg\textsuperscript{0} and Hg\textsuperscript{T}, the amount of Hg\textsuperscript{2+} was calculated by difference. Using this information, breakthrough curves for each sorbent were generated. A variety of test conditions were used in order to investigate the effect of HCl and steam on Hg uptake and/or oxidation. Detailed test conditions are described in Table 2.

\textit{HgCl\textsubscript{2} Exposure Test} In addition to the Hg\textsuperscript{0} exposure test, a HgCl\textsubscript{2} exposure test using the same packed-bed reactor system was carried out. The main difference between two tests is the use of a HgCl\textsubscript{2} generator. The generator has an internal catalyst that oxidizes Hg\textsuperscript{0} to form HgCl\textsubscript{2}, which is then fed into the packed-bed reactor. Approximately 200.00 mg ± 5.0 mg of the synthesized α-Fe\textsubscript{2}O\textsubscript{3} nanoparticles were placed in a packed-bed reactor. 230 ppb of Hg\textsuperscript{0} vapor was introduced into the system and then at the outlet of the generator HgCl\textsubscript{2} was introduced to the packed-bed reactor until breakthrough occurred. The measurement of Hg\textsuperscript{0} and Hg\textsuperscript{T} was conducted in the same way as that of the Hg\textsuperscript{0} exposure test. The Hg concentration from the recovered particles was measured using a pyrolysis technique. The schematic of the experimental setup is provided in the supplementary information (Figure S2).

Characterization methods

The crystalline phase identification of the synthesized samples was analyzed using powder X-ray diffraction (XRD) and the X-ray Photoelectron Spectroscopy (XPS) analyses were performed using a Physical Electronics (PHI) 5000 VersaProbe Scanning XPS system. The morphology, size and structure of the synthesized particles were investigated using 5kV Sirion FEI XL30 scanning electron microscopy (SEM) and 200 keV FEI Tecnai transmission electron microscope.
(TEM), i.e. TF20. All these characterizations were performed at the Stanford Nano Shared Facilities (SNSF) at Stanford University. In addition, Nitrogen (N₂) adsorption experiments at 77 K were conducted to determine the specific surface area of the test samples using a Quantachrome Autosorb iQ2 instrument. The Brunauer-Emmett-Teller (BET) model was applied to fit the N₂ adsorption isotherms and evaluate the specific surface area of the samples.

Mercury uptake onto the synthesized \(-\text{Fe}_2\text{O}_3\) nanoparticles using Hg pyrolysis system built at Stanford University (Figure S3 in the supplementary information). Mercury L_\text{III}-edge EXAFS data were collected at the Stanford Synchrotron Radiation Lightsource on beam line 11-2. The detailed characterization methods are described in supplementary information.

**Computational Results and Discussion**

**Adsorption Energy Calculation**

The optimized coordinates of Hg and Cl and their adsorption energies of each 12 initial case are shown in Figures 4(a) and (b). Table S1 in the supplementary information lists the final configuration of the adsorbed Hg atom. In most cases, Hg converged on the three-fold site of three O atoms and the lowest calculated adsorption energy of Hg was -0.278 eV, which indicates physisorption (-0.1 – -1.0 eV(Müller et al. 2012)) of Hg binding to the surface. The equilibrium distance of Hg-O is approximately 2.24 Å and Hg is coordinated with three oxygen atoms in the first surface layers forming tri-dentate structures. Comparing the adsorption energies of the (1x1) unit cell and the (2x1) supercell, the energy calculation using the (2x1) supercell, -0.480 eV, shows more stable and stronger adsorption than the result for the (1x1) unit cell, which is -0.278 eV.
This result might be due to less dispersive forces present in the larger cell than the smaller unit cell, but the optimized coordinates of the adsorbates are the same for both cells. As for Cl adsorption, stronger adsorption energies compared to Hg were observed as shown in Table S2 of the supplementary information. The most stable Cl adsorption site (Figure 4(b)) is, therefore, top of the O atom with a short equilibrium distance (1.70 Å), whereas Hg is stable on the hollow and threefold sites of three O atoms. The adsorption energy is -1.372 eV in the (1x1) unit cell, which corresponds to chemisorption (> -1.0 eV(Müller et al. 2012)). Similar to the Hg adsorption case, a larger unit cell results in a lower adsorption energy, and equilibrium distances in each case are given in Table 3. Also, similar to the Hg adsorption case, the final coordinates of Cl are the same both in smaller and larger unit cells. Based on these two calculated results, Cl appears to be more reactive to the surface than Hg for the α-Fe₂O₃(0001) surface. This tendency is consistent with the result of the α-Fe₂O₃(1102) surface.(Jung et al. 2015)

In addition to adsorption of each single adsorbate, we investigated the optimized configuration of HgCl with two different scenarios. First, we introduced Cl to the Hg pre-adsorbed surface, and later we introduced Hg to the Cl pre-adsorbed surface. Initial Hg and Cl pre-adsorbed surfaces were identical to those of the Figures 4(a) and (b) configuration. A total of six different initial configurations were tested including three initial sites per Hg and Cl adsorption cases. Three initial sites of the adsorbate were chosen as one vertical and two horizontal from the optimized pre-adsorbate. For most of the cases examined, Cl tends to be coordinated vertically on top of the Hg atom (Figure 4(c)). The adsorption energy of HgCl on the surface is -2.944 eV in the (2x2) supercell, which is much stronger than both the Hg and Cl singly-adsorbed cases. This is also
confirmed by a shorter equilibrium distance of Hg to the O atom as shown in Figure 4(c) and Table 3.

Electronic Structure Calculation

**Bader Charge Analysis** Results of the Bader charge analysis and the resulting differences in atomic charge following the adsorption of Hg and Cl to the \( \alpha \)-Fe\(_2\)O\(_3\)(0001) surface are shown in Figure 5 and Table 4. Figure 6 shows labels of the surface atom for the results. In the case of Hg adsorption, Hg is positively charged and the surface Fe and O atoms are negatively charged, which is expected based on the difference in the electronegativity of each element. Hg donates +0.63\( e \) to the surface atoms and becomes oxidized while all surface atoms are slightly reduced upon Hg adsorption. This small electron transfer and the weak binding energy suggest a physisorption mechanism.

For the Cl-adsorbed \( \alpha \)-Fe\(_2\)O\(_3\)(0001) surface, Cl also becomes oxidized through the donation of electron density from the surface atoms. This might be related to the stronger electronegativity of surface O atoms (e.g., 3.44 on the Pauling scale) than Cl atoms (e.g., 3.16 on the Pauling scale). This might also be related to the surface termination of the model. The top layer of the \( \alpha \)-Fe\(_2\)O\(_3\)(0001) surface is terminated with O atoms, and so Cl atoms can interact only with these O atoms rather than Fe. Even though the configuration of Cl was close to one specific O atom, all the surface atoms donate a similar amount of charge. The amount of transferred charge of Cl (+0.33\( e \)) was less than that in the Hg case (+0.63\( e \)), which does not match with the adsorption energy comparison of Cl vs. Hg. However, this smaller amount of transferred charge might be explained by the electronegativity difference between surface atoms and Cl. When Cl was added
to the Hg-adsorbed $\alpha$-Fe$_2$O$_3$(0001) surface, Hg donated more electron density to the surface ($+0.72e$) compared to the case of singly-bound Hg ($+0.63e$). In this case, Cl was reduced by gaining $-0.52e$ of electrons. This result can be explained by the optimized configuration of Cl on top of the Hg atom. Chlorine interacted with Hg more than with the surface O atoms, which are located far from the Cl atom. Also, the total amount of transferred charge of the adsorbate and surface atoms is significantly larger than for the singly-adsorbed case. This result indicates that more active charge transfer occurred during the HgCl adsorption than during the adsorption on single Hg or single Cl atoms, which is consistent with the general trend of Hg and Cl adsorption on the $\alpha$-Fe$_2$O$_3$($1\bar{1}02$) surface. (Jung et al. 2015)

Projected Density of States Analysis A PDOS analysis was conducted to determine the occupation and energy distribution of each orbital. In Figure 7, the PDOS plots of gas-phase Hg, the $\alpha$-Fe$_2$O$_3$(0001) surface, the Hg-adsorbed surface, the Cl-adsorbed surface, and the HgCl-adsorbed surface are displayed. For each atom, the occupation of the Hg $s$-, O $p$-, Fe $d$-, and Cl $p$-states are displayed, since most correlations were observed within the density of states of these atoms. Iron and O of the $\alpha$-Fe$_2$O$_3$ surface are strongly held together by covalent bonding (Blake et al. 1966), and this interaction is seen in Figure 7(b) by the overlapping Fe $d$-state and O $p$-state. Compared to the gas-phase Hg $s$-state, which has one peak around -0.5 eV (Figure 7(a)), the $s$-state of adsorbed Hg (Figure 7(c)) is distributed both above and below the Fermi level upon adsorption. The shift to below the Fermi level indicates that Hg is slightly more stable in the adsorbed state than in the gas phase (Figure 7(c)). There is a slight overlap in electron states in the case of the Hg $s$-, Fe $d$-, and O $p$-states; however, the distribution of the Fe $d$- and O $p$-states are largely distorted compared to the clean $\alpha$-Fe$_2$O$_3$(0001) surface. This phenomenon is in
reasonable agreement with the significant electron transfer from the Hg to the surface in the Bader charge analysis. When Cl atoms are present on the surface, there is significant interaction between Cl $p$- and O $p$- states, while there is little overlap between the Fe $d$- and Cl $p$-states (Figure 7(d)). This characteristic may be caused by the optimized Cl configuration on the $\alpha$-Fe$_2$O$_3$(0001) surface, where Cl is adsorbed on the top of the O atom. In the case of HgCl adsorption, the slight overlap of Hg $s$-, Fe $d$-, O $p$-, and Cl $p$-states is observed (Figure 7(e)). The overlaps are located around -2.0 eV in the occupied state and +1.8 eV in the unoccupied state. Interestingly, the peaks of the Cl $p$-state are mostly in line with the Hg $s$-state that is already hybridized with the surface atoms, which may indicate the hybridization and chemical bonding between the Cl and Hg. This may also be caused by the coordination of Cl, which is on top of the Hg. This observation may be in reasonable agreement with the results of charge transfer explained in the previous section.

**Experimental Results and Discussion**

**Hematite Characterization**

*Color and Phase Identification* The three types of synthesized $\alpha$-Fe$_2$O$_3$ nanoparticles show reddish color, which is the signature color of $\alpha$-Fe$_2$O$_3$ (see Figure S4 in the supplementary information). The XRD pattern shown in the supplementary information (Figure S5) verified that the synthesized samples are $\alpha$-Fe$_2$O$_3$ (ICDD no. 01-089-0599). Also, there are no diffraction peaks indicative of any other impurities, indicating high purity and good crystallinity of the
synthesized α-Fe₂O₃. Average particle sizes of as-prepared samples were determined using the Scherrer line broadening equation,

\[ D_{hk\ell} = \frac{K\lambda}{\beta_{hk\ell} \cos \theta_{hk\ell}} \]

such that \( D_{hk\ell} \) is the average particle size perpendicular to the normal line of the \((hk\ell)\) plane, \( K \) is a dimensionless shape factor equal to 0.9, \( \lambda \) is the X-ray wavelength, \( \beta_{hk\ell} \) is the full length at the half-maximum of the \((hk\ell)\) diffraction peak, and \( \theta_{hk\ell} \) is the Bragg angle of the \((hk\ell)\) diffraction peak. Based on the (104) diffraction peak’s data from the three samples, the average particle sizes are 19.45, 15.29, and 32.91 nm for NP1, NP2, and NP3, respectively.

In addition, XPS was employed to further reveal information on the samples. The samples contain Fe, O, and C peaks (see Figure S6 in the supplementary information) and the origin of C is attributed to the double-sided tape, which was used to glue the powders to the holder. All of the spectra are calibrated to the binding energy of the C1s photoelectrons at 284.6 eV. Similar to the XRD results, there is no difference in the patterns of the three types of nanoparticle samples. In order to investigate the oxidation state of these Fe-O compounds, high-resolution spectra of Fe and O are shown in Figure 8. Samples have two clear peaks for Fe2p1 and Fe2p3, which could be attributed to α-Fe₂O₃. NP2 shows another peak around 718 eV, which has a shape and intensity similar to that observed by Zhu et al. (Zhu et al. 2012) Detailed peak information is summarized in the supplementary information (see Table S3 in the supplementary information). All three types of nanoparticle samples show the same peak difference (\( \Delta E \)) of 13.6 eV, indicating that the Fe oxidation states are Fe³⁺ as shown in previous work (Teng et al. 2003).

Size and Morphology Figure 9 shows the morphology and crystalline structure of the three types of α-Fe₂O₃ nanoparticles prepared in this study. According to Cornell and Schwertmann,
and Schwertmann 2003) synthesized particles are often rounded and rhombohedrally shaped in general when additives are not added during the synthesis process, which is consistent with the present study. For instance, as shown in Figure 9(a), the NP1 has rhombohedral shape and an average diameter of approximately 20 nm, which matches well with 19.45 nm as determined by the Scherrer equation and XRD data. The rhombohedral shape has been found in previous studies that used a similar precursor and methodology (Mou et al. 2012, Rodriguez et al. 2007, Cornell and Schwertmann 2003). Similar to the work of Rodriguez et al (Rodriguez et al. 2007), NP1 exhibits particles with an angle of 112° between two (104) facets. Both sides of the exposed planes showed the (104) plane with a lattice spacing of 0.27 nm (Figure 10(a)). In contrast, NP2 has very irregular, wing-shaped structures with stepped sites. The size of the NP2-type nanoparticles is also larger, having average diameters between 300 to 500 nm (Figure 9(b)). As shown in Figure 9(b), each of the NP2-type nanoparticles consists of many stacked layers with some of these layers being about 10 nm thick, which is similar to the calculated particle size of 15.28 nm using the Scherrer equation. These irregular shapes look similar to the “double-ellipsoid” suggested by Bailey (Bailey, Brinker, and Mecartney 1993) however, due to limitations of the high-resolution image and differences in the synthesis method in Bailey’s study, it is difficult to compare the morphologies of the two particles directly. The lattice-resolved HR-TEM image of these intergrowths is shown in Figure 10(b). The interplanar spacings were measured to be approximately 0.37 nm and 0.27 nm, which are in good agreement with the d-spacings of the (012) and (104) crystal planes from the ICCD database and other literature studies (Chen et al. 2010, Guo, Xu, and Barnard 2013). The presence of (102) facets along the crystal surface of NP2-type nanoparticles is a major difference relative to NP1-type
nanoparticles, which have only the (104) crystal planes exposed. In addition to the exposed facet, the NP2-type nanoparticles have terraces, edges, and kinks, which are more active sites than those on the planar surfaces. Finally, the NP3-type nanoparticles in Figure 9(c) shows 30-50 nm of sub-rounded morphology. These particles are also well matched to the particle size calculated by the Sherrer equation, i.e. 32.91 nm. This sub-rounded morphology is similar to that identified in other studies (Theissmann et al. 2007) using the same precursor, FeCl$_3$·6H$_2$O, and a similar methodology. According to the HR-TEM image (Figure 10(c)), the most common plane of the NP3-type nanoparticles is also the (012) plane with a lattice spacing of 0.37 nm.

**Surface Area** The surface areas of the as-prepared α-Fe$_2$O$_3$ were measured using N$_2$ BET analysis. The BET surface areas of NP1-, NP2-, and NP3-type nanoparticles are 58.5, 84.5, and 22.0 m$^2$/g, respectively. Even though the particle size of the NP2-type nanoparticle is 10 times larger than those of the other two types, it has the highest surface area. This higher surface area of the NP2-type nanoparticles is consistent with the irregular stepped morphology. In contrast, the sub-rounded NP3-type nanoparticle has the lowest surface area compared to the more crystalline nanoparticle types. In the supplementary information (Table S4), the surface area values from other studies are summarized and compared with those of our study. There are two high surface area materials reported (130 m$^2$/g (Cao et al. 2012) and 152.42 m$^2$/g (Wei et al. 2012)) in the literature, in addition to the surface area of the NP2-type nanoparticle we prepared, suggesting that this material may serve as a promising sorbent for Hg uptake. Based on our characterization results, no differences were found in compositional purity among the three types of α-Fe$_2$O$_3$ nanoparticles synthesized using different methodologies; however, each method produced a unique particle type and size, morphology, exposed facet, and surface area. By
combining all of these results, NP2-type nanoparticles stand out as the most promising for Hg uptake.

Packed-Bed Reactor Hg Exposure Tests

*Elemental Mercury Adsorption and Oxidation* When the three types of $\alpha$-Fe$_2$O$_3$ nanoparticles were exposed to the Hg$^0$, breakthrough occurred just after the reaction compared to the blank test that was an identical experiment but was carried out in a tube without sorbent. The breakthrough curves are shown in the supplementary information (see Figure S7). The breakthrough results indicate that only a small amount of Hg$^0$ adsorbs and/or oxidizes and adsorbs to the $\alpha$-Fe$_2$O$_3$ nanoparticles. These results are similar to those from a previous study conducted by Kong et al. (Kong et al. 2011), which suggests no obvious Hg$^0$ oxidation occurred in a pure N$_2$ environment. They also suggest that the presence of O$_2$ and a lower water vapor concentration may promote Hg oxidation; however, in the current study, the sorption efficiency was not enhanced even in the presence of HCl and steam. Additionally, there was no difference in the samples in terms of their Hg$^0$ uptake ability.

*Oxidized Mercury Adsorption* In order to further investigate Hg uptake behavior of the three types of $\alpha$-Fe$_2$O$_3$ nanoparticles, its oxidized form, HgCl$_2$, was fed into the sample using an HgCl$_2$ generator. Among the three types of $\alpha$-Fe$_2$O$_3$ nanoparticles synthesized via different methodologies, only the NP2-type nanoparticles showed high uptake of HgCl$_2$. NP2 captured about 60% of the exposed HgCl$_2$ and breakthrough occurred after 120 minutes *(Figure S8)*. From the pyrolysis data, it was found that the Hg concentration in NP2 was approximately 300 $\mu$g Hg/g, whereas NP1 and NP3 only contained approximately 100 $\mu$g Hg/g *(Table S5)* in the
supplementary information). These differences in Hg uptake indicate that the surface area of the nanoparticle may play an important role in the amount of Hg uptake as predicted (Ghorishi et al. 2005). Compared to literature studies conducted using the same sorbent (Kong et al. 2011, Wu, Azharuddin, and Sasaoka 2006), α-Fe₂O₃, the nanoparticles in this study showed sorption of oxidized Hg as a HgCl₂ species, rather than sorption or oxidation of Hg⁰. This difference might be caused by the different simulated gas, morphology of sorbent, etc.

**Equilibrium Distance** A more detailed sorption mechanism can be suggested from the extended x-ray absorption fine structure (EXAFS) data (Table 5). EXAFS analysis of NP2 indicates two scattering pathways, a Hg-Cl scattering pathway with a distance of 1.72 ± 0.03Å, and a Hg-O scattering pathway with a distance of 2.21 ± 0.01Å. The Hg-Cl distance is very similar to Hg-Cl pathway fit for Hg associated with Fe in fly ash reported in Jew et al. of 1.75 ± 0.01Å (Jew et al. 2015). Conversely, the Hg-O pathway is significantly longer than the 1.82 ± 0.01Å from Jew et al. (Jew et al. 2015). The longer Hg-O pathway coupled with the lack of a detectable Hg-Fe pathway suggests outer-sphere sorption of hydrated Hg species and Hg-Cl species. The equilibrium distances predicted by DFT were 2.2 Å and 2.3 Å and were different from the EXAFS result. However, these distances were also one of the bond lengths of HgCl₂ crystal as well as well matched with gas phase Hg-Cl distance. The Hg-O distance from EXAFS results was well matched with DFT results in Table 5. Therefore, even though there are some discrepancies between theory and experimental value, both of results could be supported each other of Hg physisorption on the α-Fe₂O₃ surface.
Summary

In this study, stable configurations, adsorption energies and electronic properties of Hg on $\alpha$-Fe$_2$O$_3$(0001) surfaces were investigated using DFT. Hg physisors to the $\alpha$-Fe$_2$O$_3$ surface with an adsorption energy of -0.103 eV. Stronger adsorption, as well as the larger amount of transferred charge, indicated that Cl adsorbs on the $\alpha$-Fe$_2$O$_3$ surface more actively compared to Hg. Also, in the presence of Cl, Hg adsorption on the $\alpha$-Fe$_2$O$_3$ surface was strengthened compared to single Hg adsorption, evidenced by a shorter equilibrium distance of Hg to the surface, a larger amount of transferred charges as well as overlapping DOS. For the $\alpha$-Fe$_2$O$_3$(0001) surface, Hg also physisorbed to the surface with an adsorption energy of -0.278 eV, but the stability of Hg enhanced in the presence of Cl was similar to the results for the $\alpha$-Fe$_2$O$_3$(1$\bar{1}$02) surface. Compared to the $\alpha$-Fe$_2$O$_3$(1102) surface, stronger adsorption energy and more charge transfer were observed for the $\alpha$-Fe$_2$O$_3$(0001) surface. Also, the vertically coordinated HgCl also differs from the parallel coordination of HgCl for the $\alpha$-Fe$_2$O$_3$(1$\bar{1}$02) case. Compared to the results of the $\alpha$-Fe$_2$O$_3$(1$\bar{1}$02) surface which was conducted by same research group (Jung et al. 2015), Hg adsorption is more active on the $\alpha$-Fe$_2$O$_3$(0001) surface than the $\alpha$-Fe$_2$O$_3$(1$\bar{1}$02) surface, and difference in the surface terminations of the structures is a key factor causing different surface reactivity.

The nano-sized -Fe$_2$O$_3$ particles were successfully synthesized and characterized to investigate their abilities to uptake Hg in order to understand the factors affecting Hg adsorption on a lab-scale. Three as-synthesized nanoparticles were confirmed to be pure -Fe$_2$O$_3$, but different compositions of the precursors and different durations of aging resulted in dissimilar sizes from 20 to 500 nm and morphologies varying from rhombohedra to irregular to subrounded. NP2 had
a large surface area of 84.5 m²/g due to numerous stepped surfaces, which might be an important factor for Hg adsorption. From the packed-bed reactor Hg exposure experiments, NP2 physically adsorbed more than 300 μg Hg/g, while NP1 and NP3 only adsorbed less than 100 μg Hg/g. It can also be concluded from this work that the surface area of the nanoparticle may play an important role in the amount of Hg uptake as predicted (Ghorishi et al. 2005). The equilibrium distances of Hg-Fe, Hg-Cl and Hg-O measured by EXAFS indicated that HgCl₂ physisorbed onto NP2 nanoparticles.

Although atomic-scale simulations in this study did not consider transition-state information, such information will be important in revealing the entire mechanism of adsorption in the given system in a future study. Also, there was a discrepancy between the calculated equilibrium distances of Hg-Fe and Hg-O and those determined experimentally, which showed shorter distances than those determined from the DFT results. This inconsistency may be due to the approximations used in DFT calculations in this study, which deal with clean (i.e., no other gases) surfaces with limited surface coverage. In order to compensate for this discrepancy, more detailed calculations using bigger cell sizes will be needed with appropriate computational cost increases for the future work. For the lab-scale experiments, a more detailed analysis of the relationship between Hg uptake and the nanoparticles’ characteristics may be helpful in order to understand the adsorption mechanism. Also, it would be useful to investigate the methodology involved in being able to tune the nanoparticles to increase their catalytic and/or adsorbing activity.
Acknowledgement

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Gordon E. Brown Jr: Department of Geological Sciences, School of Earth, Energy, and Environmental Sciences, Stanford University/ Department of Photon Science and Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory
Table 1. Details of Synthesis Procedure of $\alpha$-$\text{Fe}_2\text{O}_3$ Nanoparticles

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Solution</th>
<th>Aging</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP1</td>
<td>16.60 g of Fe(NO$_3$)$_3$·9H$_2$O</td>
<td>2 L of 0.002 M HNO$_3$</td>
<td>7 days</td>
</tr>
<tr>
<td>NP2</td>
<td>51.64 g of Fe(ClO$_4$)$_3$·9H$_2$O</td>
<td>500 mL of H$_2$O</td>
<td>7 days</td>
</tr>
<tr>
<td>NP3</td>
<td>10.81 g of FeCl$_3$·6H$_2$O</td>
<td>2 L of 0.002 M HCl</td>
<td>10 days</td>
</tr>
</tbody>
</table>
Table 2. Packed-Best Hg Exposure Test Conditions

<table>
<thead>
<tr>
<th>Condition (1)</th>
<th>Temperature (°C)</th>
<th>Air (L/min)</th>
<th>Hg\textsuperscript{0} Concentration (ppb)\textsuperscript{1}</th>
<th>HCl Flow Rate (mL/min)</th>
<th>H\textsubscript{2}O Flow Rate (g/hr)</th>
<th>HgCl\textsubscript{2} concentration (ppb)\textsuperscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>140</td>
<td>0.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Condition</td>
<td>140</td>
<td>0.7</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Condition</td>
<td>140</td>
<td>0.7</td>
<td>60</td>
<td>30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Condition</td>
<td>140</td>
<td>0.7</td>
<td>60</td>
<td>30</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Condition</td>
<td>140</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>230</td>
</tr>
</tbody>
</table>

\textsuperscript{1} The concentration of exposed Hg is calculated based on the flow rate of Hg.
Table 3. Adsorption energies and equilibrium distances of Hg, Cl, and HgCl with the (2x1) supercell

<table>
<thead>
<tr>
<th>Adsorption Energy (eV)</th>
<th>Equilibrium distance (Å) **</th>
<th>X-O</th>
<th>X-Fe</th>
<th>Hg-Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>-0.480 (-0.278)</td>
<td>2.24</td>
<td>3.70</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>-1.454 (-1.372)</td>
<td>1.70</td>
<td>3.10/3.34</td>
<td>-</td>
</tr>
<tr>
<td>HgCl</td>
<td>-2.340</td>
<td>2.10(Hg-O)</td>
<td>3.50(Hg-Fe)</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.74 (Cl-O)</td>
<td>4.73(Cl-Fe)</td>
<td></td>
</tr>
</tbody>
</table>

* Numbers in parenthesis is the adsorption energy with a (1x1) unit cell

** X denotes an adsorbate in a given system (Hg or Cl).
Table 4. Calculated Bader charge transfers upon adsorption (unit: $e$)

(O1-O3 and Fe1-Fe2 represent the label of surface atom in the unit cell, see Figure 6)

<table>
<thead>
<tr>
<th></th>
<th>Hg</th>
<th>Cl</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>Fe1</th>
<th>Fe2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg adsorbed $\alpha$-$\text{Fe}_2\text{O}_3$</td>
<td>0.63</td>
<td>-0.14</td>
<td>-0.11</td>
<td>-0.05</td>
<td>0.00</td>
<td>-0.01</td>
<td></td>
</tr>
<tr>
<td>Cl adsorbed $\alpha$-$\text{Fe}_2\text{O}_3$</td>
<td>0.36</td>
<td>-0.05</td>
<td>-0.03</td>
<td>-0.02</td>
<td>-0.03</td>
<td>-0.05</td>
<td></td>
</tr>
<tr>
<td>HgCl adsorbed $\alpha$-$\text{Fe}_2\text{O}_3$</td>
<td>0.72</td>
<td>-0.52</td>
<td>-0.11</td>
<td>-0.03</td>
<td>-0.02</td>
<td>0.03</td>
<td>0.03</td>
</tr>
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</table>
Table 5. The equilibrium distances of Hg and adjacent atoms

<table>
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<tr>
<th>Remarks</th>
<th>Hg-Cl (Å)</th>
<th>Hg-O (Å)</th>
<th>Hg-Fe (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>1.72</td>
<td>2.21</td>
<td></td>
</tr>
<tr>
<td>DFT (Jung et al. 2015)</td>
<td>2.30</td>
<td>2.43</td>
<td>3.47</td>
</tr>
<tr>
<td>DFT (Jung 2016)</td>
<td>2.20</td>
<td>2.10</td>
<td>3.50</td>
</tr>
<tr>
<td>Fly ash exposed to Hg⁰</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg-associated Fe oxides</td>
<td>1.75</td>
<td>1.82/2.65</td>
<td>3.09</td>
</tr>
<tr>
<td>investigated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas-phase distance</td>
<td>2.36-2.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HgCl</td>
<td>2.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2HgOHg₂Cl₂)</td>
<td>2.25-2.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HgCl₂ crystal</td>
<td>1.80/2.11</td>
<td></td>
<td>HgCl₂ crystal</td>
</tr>
<tr>
<td>Exp. (Brakken and Scholten 1934)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.27/2.69</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Side and top views of the $\text{Fe}_2\text{O}_3(0001)$ surface.
Figure 2. Possible Hg and Cl adsorption sites for $\text{-Fe}_2\text{O}_3(0001)$ surface (top view).
Figure 3. Schematic of the baseline packed-bed reactor exposure test.
Figure 4. Stable configurations, equilibrium distances and adsorption energies of (a) Hg, (b) Cl and (c) HgCl on the α-Fe₂O₃(0001) surface.
Figure 5. Results of the Bader charge analysis.
Figure 6. Label of the surface atom for the Bader charge analysis results.
Figure 7. PDOS of Hg, Cl, HgCl, and the α-Fe₂O₃(0001) surface (a) gas-phase Hg, (b) Fe and O atom of the clean α-Fe₂O₃(0001) surface, (c) Fe and O atoms adjacent to adsorbed Hg atom on the α-Fe₂O₃(0001) surface, (d) Fe and O atoms adjacent to adsorbed Cl atom on the α-Fe₂O₃(0001) surface, and (e) Fe and O atoms adjacent to adsorbed HgCl atoms on the α-Fe₂O₃(0001) surface.
Figure 8. The high-resolution XPS signals of the Fe2p peaks for nanoparticles; NP1 (top), NP2 (middle), and NP3 (bottom).
Figure 9. TEM and SEM images of α-Fe₂O₃ nanoparticle samples; (a) NP1, (b) NP2, and (c) NP3.
Figure 10. Lattice-resolved HR-TEM images of $\alpha$-Fe$_2$O$_3$ nanoparticle samples; (a) NP1, (b) NP2, and (c) NP3.