Supporting Information

Manuscript title: Mechanisms of Elemental Mercury Transformation on α-Fe$_2$O$_3$(001) Surface

from Experimental and Theoretical Study: Influences of HCl, O$_2$ and SO$_2$

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Number of pages: 12

Number of Tables: 1

Number of Figures: 4

Experimental Apparatus and Procedures. The experimental system diagram is pictured in Figure S1, which consists of four parts: the gas distribution system provides the gas atmosphere requirements; the mercury generator with a mercury permeation tube (VICI, Metronics Inc.) embedded in an isothermal water bath generates Hg^0 vapor with specified concentration by regulating the bath temperature; the reaction equipment offers the place where the reaction occurred through the certain temperature and the online mercury measuring instrument(VM3000, Germany), which could real-timely and continuously measure the outlet Hg^0 concentration(measurement accuracy $\pm$ 0.1 µg/m^3).

To avoid the condensation of mercury vapor, the pipelines were tangled with heating tapes for heat preservation, which was set at 110℃. The surplus acid gases was adsorbed with 10% NaOH aqueous solution before flowing into the mercury analyzer and the sampling gas was dried by the allochroic silica gel desiccant.

X-ray Photoelectron Spectroscopy (XPS) Study. To verify the key elements on the surface of contrasted sorbents before and after adsorbing Hg^0 during the experiments, high resolution XPS spectra was conducted to characterize the available functional groups. The binding energy (BE) of the C1s level at 284.80 eV was used as an internal reference to calibrate every spectrum. Additionally, the XPS analysis on key elements were analyzed according to the NIST X-ray Photoelectron Spectroscopy Database.

Models and Computational Methods. The calculations in this paper are performed using the CASTEP (Cambridge Sequential Total Energy Package) software package[1, 2], which is developed by the condensed matter theory research group of Cambridge University based on

the DFT theory. Based on this software, DFT method is employed to perform a systematic study on the absorbing system[3]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange correlation function, which is proved to be a suitable function for the iron-oxygen system, is applied. The electronic wave functions are expanded in a plane wave basis set, and ultra-soft pseudo potentials are employed to describe the ionic cores.

Our calculations are based on the α-Fe_2O_3(001) surface, and the structure of α-Fe_2O_3 is an R-3c space group with lattice constants of a=b=5.04 Å, c=13.75 Å, α=β=90°, and γ=120°. Our researches have revealed that α-Fe_2O_3(001) was the low-index surface with the catalytic oxidation activity, and its iron terminal was more stable than the oxygen terminal[4]. A nine Fe-terminated atomic layer slab model of the α-Fe_2O_3 (001) surface is applied in this study. The vacuum region is set as 12 Å to eliminate the influence derived from the upper surface, and this surface is optimized by relaxing the outmost six layers and fixing the bottom three layers.

Based on the convergence results, a k-mesh of 4×4×1 and a cutoff energy of 350 eV is chosen in this paper, and the k point sampling with 0.5 nm^{-1} spacing is used. The adsorption energy in this paper can be defined as the energy variation between the reactants and products of the adsorption process. The value of adsorption energy can be used to show the possibility and degree of adsorption reaction, and the calculation formula is as the following reaction (1).

$$E_{ads} = E_{AB} - (E_A + E_B) \qquad (1)$$

In this formula, E_A and E_B respectively represents the energies of the adsorbate and substrate,

and E_{AB} is the total energy of the substrate together with adsorbate. The more negative the value is, the stronger the absorption is.

Mechanism of Hg^0 Removal with HCl and O$_2$ at Low Temperature. The optimized calculations results indicate that on the surface of α-Fe$_2$O$_3$(001) HCl dissolves and bonds with the surface Fe atom, forming the active Cl sites, and subsequently the Hg atom could bond with different Fe sites and form Fe-Hg bond. In conclusion, HCl could react with Fe sites in α-Fe$_2$O$_3$ and form the active Cl/α-Fe$_2$O$_3$, making the adsorption of Hg^0 more intensive. Additionally, the adsorption behaviors of O$_2$ on the capture of Hg^0 with α-Fe$_2$O$_3$ had also been demonstrated [5]. The dissociation of O$_2$ occurred with the binding of one O atom on Fe top site, thereby possessing Fe-O bond, and then Hg atom was successively placed on the adsorptive intermediates, belonging to weak chemisorption. Furthermore, the O atom coverage could significantly affect the adsorption of Hg^0 and higher coverage of O atom may promote Hg^0 removal.

As depicted in Figure S3a, the Hg4f peak with binding energy of 101.1, 100.4 and 101.3eV are observed, which can be assigned to the Hg^{2+}. It's in accordance with the available X-ray photoelectron spectrum peaks of HgCl$_2$ and HgO, corresponding to the binding energy of 101.4 and 100.8eV. The Hg4f results reveals that Hg^{2+} appears in simultaneous Hg^0 adsorption with HCl and O$_2$, implying that Hg^0 could be oxidized with the addition of HCl and O$_2$. A further research on HgO species is still needed.

As can be seen in Figure S3b, the Cl 2p peak of HCl/α-Fe$_2$O$_3$ sample mainly centers around 198.6 eV, which is in accordance with the available X-ray photoelectron spectrum

peak of $FeCl_2$ and $FeCl_3$, corresponding to the binding energy of 198.8 and 199.0eV. The results reveal that chlorine species is captured, demonstrating that HCl can dissolve on α-Fe_2O_3, which is consistent with the experimental conclusions. The binding energy of Cl2p peak at 198.6eV represents the probable generation of Cl^- in $HgCl_2$, which is consistent with the spectrum peak of $HgCl_2$, corresponding to the binding energy of 198.7eV.

Reference

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3. Liu, T.; Xue, L.; Guo, X.; Huang, Y.; Zheng, C. DFT and Experimental Study on the Mechanism of Elemental Mercury Capture in the Presence of HCl on α‑Fe2O3(001). *Environ.t Sci. Technol.* **2016,** *50*, 4863-4868.

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5. Liu, T.; Xue, L. C.; Guo, X.; Zheng, C. G. DFT study of mercury adsorption on α-Fe2O3 surface: Role of oxygen. *Fuel* **2014,** *115*, 179-185.

Table captions:

Table S1. The schematic diagram of experimental system.

Table S1 SO_2, SO, S and Hg^0 adsorption configuration parameters

/	Configuration	E_{ads} (kJ/mol)	R_{Fe-S} (Å)	R_{S-O}(Å)		R_{Fe-O}(Å)		R_{Hg-S} (Å)
				R_{S-O1}	R_{S-O2}	R_{Fe-O1}	R_{Fe-O2}	
SO_2 on α-Fe_2O_3	A	-87.8	-	1.55	1.45	1.95	-	-
	B	-118.7	-	1.54	1.54	2.06	2.02	-
	C	-47.3	2.51	1.47	1.47	-	-	-
SO on α-Fe_2O_3	D	-122.5	-	1.62		1.95		-
	E	-122.5	2.29	1.51		-		-
S on α-Fe_2O_3	F	-374.1	2.04	-		-		-

Figure captions:

Figure S1. The schematic diagram of experimental system**.**

Figure S2. The stable configutations on α-Fe$_2$O$_3$(001) surface in the presence of HCl and O$_2$.

Figure S3. XPS spectra of Hg 4f and Cl 2p for the contrastive samples.

Figure S4. The stable adsorption configuration of Hg^0 on O、S/α-Fe$_2$O$_3$(001) surface.

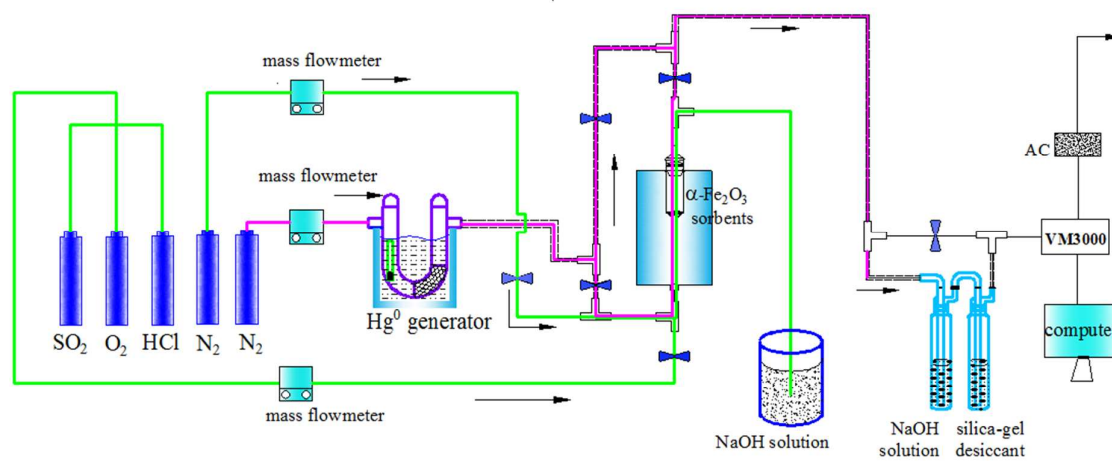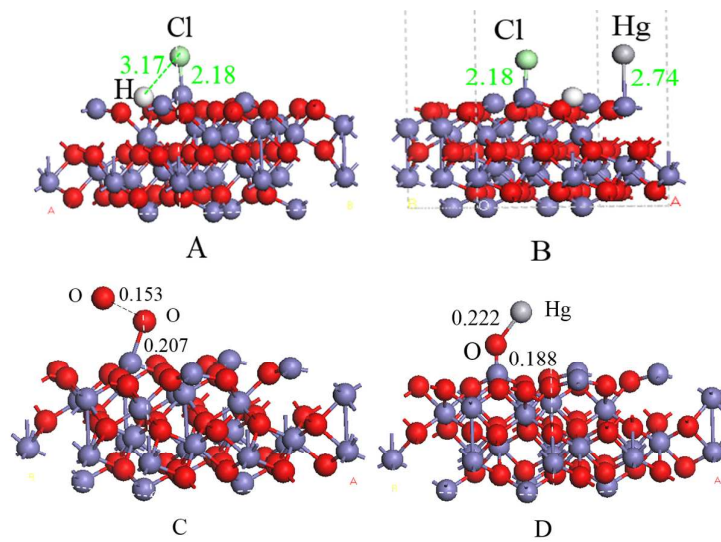**Figure S1.** The schematic diagram of experimental system

Figure S2. The stable configurations on α-Fe$_2$O$_3$(001) surface in the presence of HCl and O$_2$.

A

B

C

D

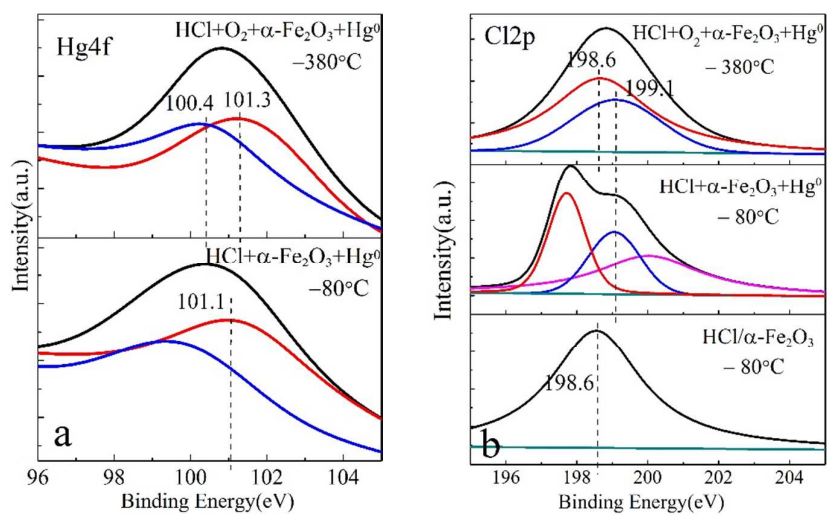**Figure S3.** XPS spectra of Hg 4f and Cl 2p for the contrastive samples.

Figure S4. The stable adsorption configuration of Hg^0 on O、S/α-Fe$_2$O$_3$(001) surface.

Configuration G

Configuration H