



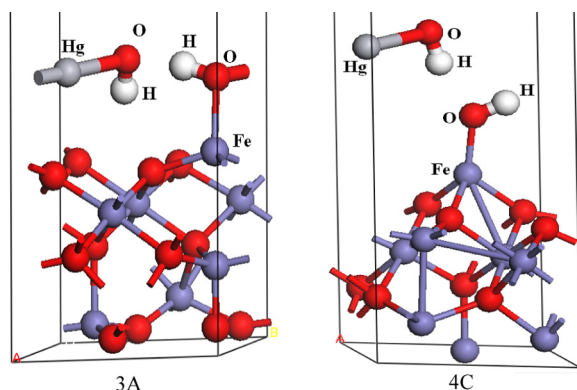
## Full Length Article

DFT studies of Hg<sup>0</sup> oxidation by gaseous advanced oxidation method: H<sub>2</sub>O<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> (1 1 1) and hydroxyl pre-adsorbed Fe<sub>3</sub>O<sub>4</sub> (1 1 1) surfaceChangsong Zhou<sup>a</sup>, Ben Wang<sup>b</sup>, Zijian Song<sup>b</sup>, Chuan Ma<sup>b</sup>, Jie Yu<sup>b</sup>, Zhiyue Zhang<sup>a</sup>, Hongmin Yang<sup>a,\*</sup>, Lushi Sun<sup>b,\*</sup><sup>a</sup> Engineering Laboratory for Energy System Process Conversion & Emission Control Technology of Jiangsu Province, School of Energy & Mechanical Engineering, Nanjing Normal University, 210042 Nanjing, China<sup>b</sup> State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, 430074 Wuhan, China

## HIGHLIGHTS

- The mechanism of H<sub>2</sub>O<sub>2</sub> decomposition and OH generation on Fe<sub>3</sub>O<sub>4</sub> (1 1 1) was studied.
- Hg<sup>0</sup> oxidation processes on hydroxyl pre-adsorbed surface were compared.
- The major reaction pathway of Hg oxidation product on Fe<sub>3</sub>O<sub>4</sub> (1 1 1) was discussed.

## GRAPHICAL ABSTRACT

The optimized configurations of Hg on Fe<sub>tet1</sub>-terminal and Fe<sub>oct2</sub>-terminal OH/Fe<sub>3</sub>O<sub>4</sub> (1 1 1) surface.

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## ABSTRACT

Elemental mercury oxidation mechanism by gaseous advanced oxidation method was studied using density functional theory on Fe<sub>3</sub>O<sub>4</sub> (1 1 1) surface containing H<sub>2</sub>O<sub>2</sub> molecule. Fe<sub>tet1</sub>- and Fe<sub>oct2</sub>-terminated Fe<sub>3</sub>O<sub>4</sub> (1 1 1) surfaces have been simultaneously considered both in H<sub>2</sub>O<sub>2</sub> decomposition and hydroxyl pre-adsorbed Fe<sub>3</sub>O<sub>4</sub> (1 1 1) interfaces. It is found that the Fe<sub>oct2</sub>-terminated surface was more favored for H<sub>2</sub>O<sub>2</sub> decomposition, and H<sub>2</sub>O<sub>2</sub> was easier to decompose and generate two hydroxyls than Fe<sub>tet1</sub>-terminated surface. Through the discussion of Fe<sub>tet1</sub>- and Fe<sub>oct2</sub>-terminal mechanisms, the Mulliken charge population, and the partial density of states, we found that OH had different reaction activity generated on different Fe-terminal. Hg strongly interacted with the free state OH mainly due to the highly reactive and strong electrophilic ability of OH radical. The oxidation of Hg formed stable oxidized mercury species on Fe-terminated surface and most of the lost electron transferred from Hg to unbonded hydroxyl during Hg oxidation. The result showed that the combination of Hg and hydroxyl was exothermic reaction, which was favorable to spontaneous processes of Hg oxidation. The OH–Hg–OH and Hg–OH intermediates had a lower desorption energy when they detached from the surface and was the major reaction pathway.

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## 1. Introduction

The control method of the trace element mercury ( $\text{Hg}^0$ ) from flue gas has been extensively researched due to its high toxicity, volatility, and bioaccumulation. Coal-fired power plants and municipal solid waste (MSW) incinerators have been considered to be major sources of anthropogenic mercury emission [1–3]. More and more studies have been carried out to explore an efficient and low-cost treatment to solve  $\text{Hg}^0$  pollution, including sorbent adsorption (activated carbon [4], porous MOFs [5]), catalytic oxidation ( $\text{Fe}_2\text{O}_3$  [6],  $\text{CeO}_2$  [7],  $\text{TiO}_2$  [8]), and oxidation absorption ( $\text{KMnO}_4$  [9],  $\text{NaClO}_2$  [10], Fenton reagent [11]). In these techniques,  $\text{Hg}^0$  oxidation method was widely used due to  $\text{Hg}^{2+}$  soluble in water and can be efficiently removed by wet flue gas desulfurization (WFGD) [12].

The reactivity of  $\text{H}_2\text{O}_2$  or  $\text{H}_2\text{O}$  molecules to metal and metal oxide surfaces is important in the context of advanced oxidation technology. The highly reactive hydroxyl radicals produced during the reaction have been detected and contribute to oxidize and remove various pollutants through a simple and effective process, that requires low energy consumption and generates no secondary pollution [13]. Several studies have recently explored the mechanisms underlying hydroxyl radical production and pollutant oxidation on a catalyst surface. Lousada et al. [14] performed density functional theory (DFT) study of the  $\text{H}_2\text{O}_2$  reaction on  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , and  $\text{Y}_2\text{O}_3$  surfaces. The previous results indicated that  $\text{H}_2\text{O}_2$  decomposition yields different products, including the hydroxyl radical and  $\text{H}_2\text{O}$  on different surfaces. Ren et al. [15] systematically studied methanol decomposition on the  $\text{Cu}(110)$  surface with and without the presence of  $\text{H}_2\text{O}$  molecules. The results showed that  $\text{H}_2\text{O}$  molecule on the  $\text{Cu}(110)$  surface and the pre-adsorbed hydroxyls from  $\text{H}_2\text{O}$  dissociation both remarkably alter the reaction pathway and adsorption configurations of methanol decomposition. In addition, the methanol on the  $\text{H}_2\text{O}/\text{Cu}(110)$  surface is conducive to both thermodynamic and kinetic decomposition than that on the clean  $\text{Cu}(110)$  surface. Nurazar et al. [16] investigated the adsorption and stepwise decomposition of  $\text{H}_2\text{O}_2$  on two different structural zigzag silicon carbide nanotubes (SiCNTs) surfaces by DFT calculation.  $\text{H}_2\text{O}_2$  effectively dissociates into OOH and H species, which are active in capturing pollutant molecules. Zhou et al. [17] found that  $\text{H}_2\text{O}$  molecule could undergo dissociative chemisorption to form a surface hydroxyl group with a favorable thermochemical energy and a moderate activation barrier on the  $\text{Fe}_{\text{OCT-TET1}}$ -terminated  $\text{Fe}_3\text{O}_4(111)$  surface.

It is important to investigate the interactions between Hg species and solid catalyst surface in order to understand Hg behaviors during its oxidation. Although some studies have explored  $\text{Hg}^0$  oxidation using heterogeneous catalysts, the specific mechanism of  $\text{Hg}^0$  oxidation occurs on different heterogeneous catalyst surfaces is complex and not exactly known. Steckel [18] characterized the interaction of Hg with several transitional metal element surfaces through plane-wave DFT calculations and Hg bound relatively strongly to these surfaces studied. The adsorption of Hg bond did not readily break, making the catalyst reactivation difficult. First principle calculations were used to clarify the  $\text{Hg}^0$  adsorption reaction mechanism on an  $\alpha\text{-Fe}_2\text{O}_3$  surface containing  $\text{H}_2\text{S}$  in coal-fired flue gases [19]. It is reported that  $\text{H}_2\text{S}$  promoted the efficiency of  $\text{Hg}^0$  adsorption due to the dissociation reaction of HS and thus S species generation. In addition, current evidences indicate that easy decomposition of small molecule additives also significantly influences  $\text{Hg}^0$  oxidation in flue gases [20–22]. However, in spite of several research experience,  $\text{Hg}^0$  oxidation mechanism on gas-solid surfaces is often poorly understood, especially containing  $\text{H}_2\text{O}_2$  molecule and hydroxyl species.

To our best knowledge, studies on  $\text{H}_2\text{O}_2$  heterogeneous catalytic reactions mainly focused on solid/liquid interfaces. Gaseous advanced oxidation on a gas/solid interface is newly-developed compared with that on a traditional solid/liquid interface [23–25]. As one of the most wide used spinel oxides,  $\text{Fe}_3\text{O}_4$  has unique properties containing both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions at octahedral sites [26]. Studies have also shown that  $\text{Fe}_3\text{O}_4$  structure has three different surfaces, the (110), (001), and (111) orientations, of which (111) orientation has been evidenced the predominant natural growth facet and exhibits highly catalytic activity [27,28]. Wang et al. [29] confirmed the promoted generation of OH and  $\cdot\text{O}_2^-/\text{HO}_2\cdot$ -radicals in the  $\text{Fe}_3\text{O}_4\text{-H}_2\text{O}_2$  system by electron spin resonance (ESR) measurements and the reactive oxygen species (ROS) scavengers experiments. Our previous work also indicated the formation of OH radicals on bonded to the 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) species due to  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox pairs exposed on the  $\text{Fe}_3\text{O}_4(111)$  surface [30].

Despite the increased interest in performing theoretical methods in obtaining an understanding of  $\text{Hg}^0$  oxidation mechanisms on different catalyst surfaces. Recently, few researchers have recently investigated the detailed  $\text{H}_2\text{O}_2$  decomposition paths and possible intermediate species generated on the solid heterogeneous catalyst surface. In addition, no calculations have been studied on the binding mechanism between Hg and  $\text{Fe}_3\text{O}_4(111)$  in the presence of  $\text{H}_2\text{O}_2$  molecule. In the present work, hydroxyl formation mechanism from  $\text{H}_2\text{O}_2$  decomposition on  $\text{Fe}_3\text{O}_4(111)$  surface was investigated by performing DFT calculations.  $\text{Hg}^0$  oxidation reaction was systematically examined considering both  $\text{Fe}_{\text{TET1}}$  and  $\text{Fe}_{\text{OCT2}}$  terminals. Moreover, hydroxyl pre-interacted OH/ $\text{Fe}_3\text{O}_4(111)$  was also selected as the model catalytic surface to explore  $\text{Hg}^0$  oxidation processes. Results are essential for helping us to understand the catalytic mechanism of gaseous advanced oxidation processes.

## 2. Computational methods and catalyst surface model

### 2.1. Computational methods

All of the DFT calculations were performed using the Cambridge Sequential Total Energy Package (CASTEP), which can attach spin polarization for ferromagnetic materials [31]. The optimized calculation of the lattice constants was applied within the generalized gradient approximation (GGA) [32], and the Perdew-Burke-Ernzerhof (PBE) functional was used to calculate the exchange correlation energy [33]. The electronic wave functions were analyzed by plane-wave expansion method. In order to reduce the computational cost, the ionic cores were represented by ultrasoft pseudopotential [34]. The cutoff energy for the expansion of 550 eV was used, and Brillouin zone was sampled with a  $3 \times 3 \times 1$  Monkhorst-Pack k-points mesh throughout this study, which was sufficient to ensure the error at the level of cutoff was within 0.02 eV [35]. Considering the magnetic properties of  $\text{Fe}_3\text{O}_4$ , which has been confirmed through vibrating sample magnetometer (VSM) in our previous report [30], spin polarization has been performed using spin-polarized DFT throughout the study. It should be mentioned that both of the equilibrium geometry and the energy of  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$ , OH, and Hg species including Hg, Hg–OH, and OH–Hg–OH were examined in a cubic crystal cell of  $10 \text{ \AA} \times 10 \text{ \AA} \times 10 \text{ \AA}$  before calculating the cases when they adsorbed and detached from the surface. Gamma point was set for Brillouin zone and the free energy normalization of these unimolecules was performed relative to the summation of adsorbent and substrate energies.

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