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Full Length Article

Insights into the heterogeneous Hg^0 oxidation mechanism by H_2O_2 over Fe_3O_4 (0 0 1) surface using periodic DFT method

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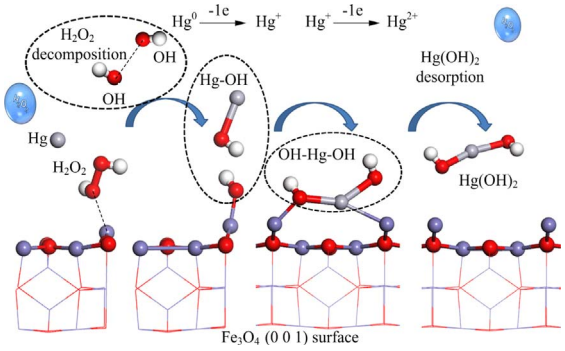
GRAPHICAL ABSTRACT



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ABSTRACT

The gaseous oxidation process for Hg^0 oxidation is regarded as an efficient and low-cost option for mercury control in solid fuel combustion devices. The heterogeneous Hg^0 oxidation by gaseous H_2O_2 over Fe_3O_4 (0 0 1) surface was calculated using periodic density functional theory (DFT) method to gain a fundamental understanding of Hg^0 oxidation mechanism on H_2O_2/Fe_3O_4 (0 0 1) surface. The results showed that on the Fe_3O_4 (0 0 1) surface, the Fe_{tet} site (A layer) is more active than the Fe_{oct} site (B layer). H_2O_2 can easily undergo dissociation process to form two OH radicals, which have highly active in Hg^0 oxidation over the A layer. The Mulliken charge population analysis showed that a large amount of electron transfer occurred from Hg^0 to the produced OH. The calculated reaction energy barriers suggested that the interaction between OH and Hg^0 is exothermic and Hg^0 oxidation processes by OH produced from H_2O_2 are thermodynamically and kinetically favorable. In addition, Hg^0 oxidation processes on the H_2O_2/Fe_3O_4 (0 0 1) surface may simultaneously undergo through three different pathways. The possible Hg-OH product will easily desorbs from the surface, whereas the $Hg(OH)_2$ is stable on the surface and belongs to chemisorption. The detailed mechanism for the oxidation reaction over Fe_3O_4 makes it an attractive method for Hg control from flue gases.

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1. Introduction

The solid fuel combustion are the primary source of anthropogenic mercury (Hg) emissions around the world [1–3]. There is growing awareness that Hg is a dispersed toxic and persistent pollutant emitted to the environment mainly from coal-fired power plants and municipal solid waste (MSW) incinerators [4–15]. Hong et al. [16] measured the mercury speciation in a coastal city of the Yangtze River Delta, China from July 2013 to January 2014 and found that coal combustion was an important contributor to increase atmospheric Hg concentrations. Zheng et al. [17] reported that the 2008 total mercury emissions in the Pearl River Delta (PRD, China) region were estimated to be 17,244 kg, of which 85% were released as Hg^0. Unfortunately, however, Hg^0 is practically water insoluble and hence very difficult to capture from flue gas using the existing air pollution control devices [18,19]. Accordingly, a catalytic oxidation of Hg^0 to Hg^{2+} is considered to be the most efficient and economical method, which has been recommended by the U.S. Environment Protection Agency (EPA).

To data, several metal oxide catalysts have been used for Hg^0 oxidation, such as (CeO_2 [20], Fe_3O_4 [21], V_2O_5 [22]). Among these catalysts, Fe_3O_4 have unique properties containing both Fe^{2+} and Fe^{3+} ions at octahedral sites and thus have received a lot of attention because of their nontoxicity, low-cost, and easy magnetic separation [23–25]. However, some researchers found that only the iron oxide species exists some defects due to the rapid consumption of the surface reactive oxygen species, and competitive effect by other flue gas components [26,27]. Therefore, the development of high efficiency, low contamination and economical technology for Hg^0 removal is still necessary and urgent.

Studies show that in the gas-phase advanced oxidation process, H_2O_2 (hydrogen peroxide vapour) performs high reactivity when it towards catalyst surface because of hydroxyl radicals (OH) generation [28–31]. OH radicals have highly reactive and have been used to remove various contaminants through a simple and effective process, which requires low energy consumption and generates no secondary pollution [32,33]. Nurazar et al. [34] found that the isolated H_2O_2 molecule can be effectively dissociate into OOH, OH, and H species over the SiCNTs using density functional theory (DFT) method. Lousada et al. [35] performed an experimental and DFT studies of the H_2O_2 reaction on ZrO_2, TiO_2, and Y_2O_3 surfaces and found that the differences in the affinity of the different surfaces for the primary product of H_2O_2 decomposition. Micoli et al. [36] investigated the vapour phase H_2O_2 decomposition on Mn-based monolithic catalyst and found that the primary radicals were produced by the hemolytic scission of the O—O bond of H_2O_2. Our previous study also indicated the formation of OH radicals due to Fe^{2+}/Fe^{3+} redox pairs exposed over the Fe_3O_4 catalyst [21].

Both experimental and theoretical investigations indicated that some easy decomposition of small molecule additives greatly promote Hg^0 oxidation reaction over metal oxide catalyst in flue gases. Liu et al. [27] reported that H_2S promoted the efficiency of Hg^0 removal due to the dissociation reaction of HS and thus S species generation. HBr and HCl were also selected as the oxidant for mercury oxidation by magnetic ferrite spinel to evaluate the heterogeneous reaction mechanism [22,37]. They found that the dissociation energy barriers of these small molecules are relatively high and the step of Hg-Cl and Hg-Br combination is the rate determining step during Hg^0 oxidation. In our previous study, the mechanism of Hg^0 oxidation by the surface OH over Fe_3O_4 (1 1 1) was studied [38]. However, up to date, there is still little investigation on the mechanisms of H_2O_2 decomposition and OH generation on Fe_3O_4 (0 0 1) surface, one of the low-index faces of Fe_3O_4. Furthermore, the theoretical studies are very lacking for Hg^0 oxidation under the existence of gaseous H_2O_2 molecule on Fe_3O_4 (0 0 1) surface.

In this study, DFT method was used to provide insight into the detailed OH formation from H_2O_2 decomposition and Hg^0 oxidation mechanism over Fe_3O_4 (0 0 1) surface. The binding energies, the optimized geometries, and the Mulliken charge population analysis before and after co-interaction between Hg^0 and H_2O_2/Fe_3O_4 (0 0 1) surface were investigated. In addition, the energy profiles of Hg^0 oxidation reaction, and the structures of the related transition states during Hg^0 oxidation processes were calculated based on the transition state theory. The results of this study will provide insight into the detailed interaction mechanism of OH generation from vapour phase H_2O_2 and Hg^0 oxidation by OH over Fe_3O_4-based catalyst.

2. Computational methods and surface models

2.1. Methods

The calculations were performed using the Cambridge Sequential Total Energy program package (CASTEP) based on Perdew-Burke-Ernzerhof (PBE) functional in the generalized gradient approximation (GGA) scheme [39,40]. The electron-ion interactions were described by ultrasoft pseudopotentials. The attached spin polarization correction was addressed to followed the lowest energy principle [41]. Considering the magnetic properties of Fe_3O_4, which has been confirmed through vibrating sample magnetometer (VSM) in our previous report [21], the formal spin of Fe cations from top to bottom of the unit cell was set to (a) the Fe_{oct} of 4 and (b) the Fe_{tet} of −4. The electronic wave functions were analyzed by plane-wave expansion method [42]. A cutoff energy of 380 eV was used to sufficiently obtain the converged results and a Fermi smearing of 0.1 eV was used to speed up convergence throughout this study. The surface Brillouin zone integration was sampled using 3 × 3 × 1 Monkhorst-Pack k-points mesh. An SCF tolerance of 2.0×10^{-6} eV/atom, an energy tolerance of 2.0×10^{-5} eV/atom, a maximum force tolerance of 0.05 eV/Å, and a maximum displacement tolerance of 0.002 Å, were set as the convergence criteria for the structure optimization and energy calculation [43–45]. In order to compare the binding energies with different configurations, the binding energies (E_{bind}) were calculated as follows:

$$E_{bind} = E_{AB} - (E_A + E_B) \quad (1)$$

where E_{AB}, E_A, and E_B represent the total energies of the chosen surface with bonded species, the substrate surface, and the isolated H_2O_2 and Hg^0, respectively. The higher negative E_{bind} value is, the stronger interaction between Fe_3O_4 (0 0 1) surface and adsorbates is.

The transition states along the possible Hg oxidation reaction pathways based on linear synchronous transit/quadratic synchronous transit (LST/QST) method were searched to calculate the energy barriers during the reactions [46,47]. Among this, the maximum energy pathway between reactant and product was obtained by the LST method. While the transition state approximation was performed from QST maximization. In addition, the transition states calculated from above method were analyzed through imaginary vibrational with one negative frequency calculation and a normal mode corresponding to the reaction coordinate. Thus the energy barriers ($E_{barrier}$) were calculated according to the expression:

$$E_{barrier} = E_{transition} - E_{intermediate} \quad (2)$$

where $E_{transition}$ and $E_{intermediate}$ represent the total energies of the transition states and the intermediate states, respectively.

2.2. Models

The unit cell of Fe_3O_4 contains Fe^{2+} and Fe^{3+} cations with 1/2 of Fe^{3+} occupy the tetrahedral sites, and additional Fe^{3+} and all Fe^{2+} occupy the octahedral sites [48]. The optimized lattice constant of Fe_3O_4 unit cell was a = b = c = 8.3942 Å and α = β = γ = 90°, which agreed very well with the experimental values (a = b = c = 8.394 Å) [49,50]. Fe_{tet} (A layer) and Fe_{oct} (B layer) terminations (shown in Fig. 1) were the energetically favorable Fe_3O_4 (0 0 1) surfaces. The clean selected layers were modeled in the form of a slab, which had a