



Full Length Article

Effect of surface Fe-S hybrid structure on the activity of the perfect and reduced α -Fe₂O₃(001) for chemical looping combustionXianbin Xiao, Wu Qin^{*}, Jianye Wang, Junhao Li, Changqing Dong

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ABSTRACT

Sulfurization of the gradually reduced Fe₂O₃ surfaces is inevitable while Fe₂O₃ is used as an oxygen carrier (OC) for coal chemical looping combustion (CLC), which will result in formation of Fe-S hybrid structure on the surfaces. The Fe-S hybrid structure will directly alter the reactivity of the surfaces. Therefore, detailed properties of Fe-S hybrid structure over the perfect and reduced Fe₂O₃(001) surfaces, and its effect on the interfacial interactions, including CO oxidation and decomposition on the surfaces, were investigated by using density functional theory (DFT) calculations. The S atom prefers to chemically bind to Fe site with electron transfer from the surfaces to the S atom, and a deeper reduction of Fe₂O₃(001) leads to an increasing interaction between S and Fe. The formation of Fe-S hybrid structure alters the electronic properties of the gradually reduced Fe₂O₃(001) surfaces, promoting CO oxidation on the surfaces ranging from Fe₂O₃ to FeO, but depressing carbon deposition on the surfaces ranging from FeO to Fe. The sulfurized FeO acts as a watershed to realize relatively high CO oxidation rate and low carbon deposition. Results provided a fundamental understanding for controlling and optimizing the CLC processes.

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1. Introduction

The rising level of atmospheric carbon dioxide results in global warming, which has alarmed the international scientific community and led to international agreements to reduce carbon dioxide emission. Carbon Capture and Storage (CCS) technology has been recognized as the best mitigation measure to reduce CO₂ emission. Unfortunately, most of the current CO₂ capture technologies, such as pre-combustion, post-combustion, or oxy-fuel technologies, are facing the challenge of high energy consumption for CO₂ capture. However, chemical-looping combustion (CLC) can excellently reduce the cost associated with its distinct inherent separation of CO₂ [1–3]. In addition, the CLC technology can also reduce the emission of NO_x [4] and increase the energy utilizing efficiency [5,6]. CLC provides a possibility to solve the energy and environment issues simultaneously.

Typically, the CLC system consists of two reactors, namely fuel reactor (FR) and air reactor (AR), as displayed in Fig. 1. In FR, fuel is oxidized by the lattice oxygen of OC instead of air, producing CO₂ and H₂O. After the condensation of water vapor, pure CO₂ stream can be obtained, which avoids extra energy consumption

for CO₂ separation. Then the reduced OC is transported back to the AR, where it is regenerated (oxidized by air into high oxidation state) for a new cycle. Thus, in CLC system, OC plays a critical role in linking AR and FR with continuously transferring oxygen and heat to maintain the successful operation. To date, various transition metal oxides, such as NiO, CuO, Mn₂O₃, Fe₂O₃, Co₃O₄, et al., have been widely studied as oxygen carrier [7–10]. And among them, iron based OC has become the investigative focus on its distinct advantages of lower cost, high mechanical strength, thermal stability, and good environmental friendliness [11–13].

Recently, much attention has been paid to direct coal CLC or coal-derived gas CLC. However, the existence of sulfur compounds is always inevitable during CLC processes. Hydrogen sulfide (H₂S), with the content of about 200–8000 ppm, is the most common sulfur-containing compound [14]. The presence of H₂S can lead to sulfurization of the OC surface [15–18], altering the physical properties and reactive behaviors of the surface. For example, it restrains CO adsorption and lattice oxygen diffusion [19] decreasing the redox reactivity of OC [20]. Actually, during a realistic CLC process, iron-based OC can be reduced into various oxidation states, such as magnetite (Fe₃O₄), wüstite (FeO) [13,21,22]. And the corresponding interfacial interactions and the reactivity of OC would alter on the surface with the different reduction degree [3,23]. We have reported the reduction effect of iron oxide on the

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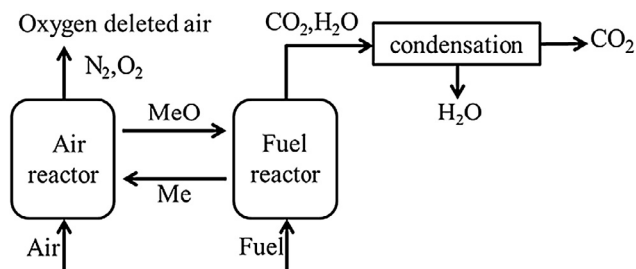


Fig. 1. Schematic of chemical-looping combustion.

related CLC reactions [24] and the interaction of HgO on the gradually reduced iron oxide surface during deep CLC process [25]. However, the details of interaction between the sulfur component and the gradually reduced Fe_2O_3 surfaces are not clear, and the effect of sulfur component on CLC reactions over these reduced surfaces during deep CLC processes remains still unknown. Hence, a systematic theoretical study of the effect of S component is essential to gain a fundamental understanding of the iron-based CLC process of the fuel containing sulfur and the optimization for CLC system.

Therefore, considering that $\alpha\text{-Fe}_2\text{O}_3(001)$ surface is one of the dominant crystal facets of the nature $\alpha\text{-Fe}_2\text{O}_3$ [26], we focused on not only the sulfurization of the perfect $\alpha\text{-Fe}_2\text{O}_3(001)$ surface but a series of reduced $\alpha\text{-Fe}_2\text{O}_3(001)$ surfaces. CO adsorption, the oxidation reaction (e.g. $\text{CO} + \text{Fe}_x\text{O}_y \rightarrow \text{CO}_2 + \text{Fe}_x\text{O}_{y-1}$), the decomposition reaction (e.g., $\text{CO}^* \rightarrow \text{C}^* + \text{O}^*$, where $*$ represents the active site), and the key step of carbon deposition [27,28] on the sulfurized perfect and reduced $\text{Fe}_2\text{O}_3(001)$ surfaces were introduced as the probe reactions to reveal the activity of the surfaces. Our results provide a fundamental understanding of the sulfurization and its effect on CLC reaction over the OC surfaces, which can promote the optimization of CLC processes with the fuel containing sulfur.

2. Computational details

The $\alpha\text{-Fe}_2\text{O}_3(001)$ surface is one of the dominant crystal facets of the nature $\alpha\text{-Fe}_2\text{O}_3$ [26], and Fe-terminated $\text{Fe}_2\text{O}_3(001)$ of $\text{Fe-O}_3\text{-Fe}\dots$ is the most stable [29]. Therefore, in the present work, Fe-terminated $\alpha\text{-Fe}_2\text{O}_3(001) 2 \times 2$ super cell with 32 Fe atoms and 480 atoms was modeled to initiate the calculations. The magnetic configuration (+ - - +) was set for Fe atoms in the primitive cell of iron oxide. + and - designated up-spin and down-spin directions with respect to the z-axis, which can reach its lowest total energy level [30,31]. A vacuum gap of 12 Å was used to avoid the

interaction between the periodic slabs. The reduced $\alpha\text{-Fe}_2\text{O}_3(001)$ surfaces were simulated by gradually removing oxygen atoms from the surface of the $\alpha\text{-Fe}_2\text{O}_3(001)$ model to do geometric optimization with all atoms relaxed. The stable perfect $\alpha\text{-Fe}_2\text{O}_3(001)$ surface and the obtained reduced surface slab models such as $\text{Fe}_2\text{O}_{2.25}$, Fe_2O_2 , $\text{Fe}_2\text{O}_{1.5}$, $\text{Fe}_2\text{O}_{0.75}$, and Fe are shown in Fig. 2, where χ represents the reduction degree of the iron-based oxygen carrier. χ can be calculated by the following equation

$$\chi = \frac{m_{\text{ox}} - m_{\text{actual}}}{m_{\text{ox}} - m_{\text{red}}} \quad (1)$$

where m_{actual} is the actual mass of sample, m_{ox} is the mass of the sample when it was fully oxidized, m_{red} is the mass of the sample in the fully reduced form. $\chi = 0\%$ refers to the completely oxidized state of iron oxide, while $\chi = 100\%$ refers to the completely reduced state of iron oxide.

The DFT calculations were carried with the function of Perdew-Burke-Ernzerhof (PBE) [32] at GGA (Generalized Gradient Approximation) level [33] was adopted to describe the electron exchange correlation energy, and an accurate prediction of the electronic and physical properties of $\alpha\text{-Fe}_2\text{O}_3$ could be obtained with GGA in the previous investigations [34]. The ionic core was described by the ultrasoft pseudopotential [35]. The electronic wave functions were expanded in a plane-wave basis set with the cutoff energy of 350 eV and a k point mesh of $4 \times 4 \times 1$ in Brillouin zone [36], which was followed by the scheme of Monkhorst and Packin [37] for the calculations of energy, surface structure, and electric properties. Considering the strong correlation between 3d-electrons of Fe atom, a Hubbard U ($U = 5$ eV) [38] was used to correct the calculated electronic structures by providing an on-site Coulomb repulsion to the DFT Hamiltonian [39,40]. The values of convergence criteria for energy, maximum force, maximum stress, and displacement in Self Consistent Field (SCF) were set as 2.0×10^{-5} eV/atom, 0.002 Ha/Å, 0.1 GPa, and 0.002 Å, respectively. The transition state (TS) was searched by the complete linear/quadratic synchronous transit (LST/QST) method [41] for each reaction.

In order to investigate the interaction of S [CO] and the surfaces, the interaction energies (E_{int}) are determined using the relation

$$E_{\text{int}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}} \quad (2)$$

where E_{AB} refers to the energy for the interaction system, E_{A} and E_{B} denote the pure substrate and adsorbate, respectively. A negative value of E_{int} means an exothermic process. The more negative adsorption energy is obtained, the stronger the interaction will be.

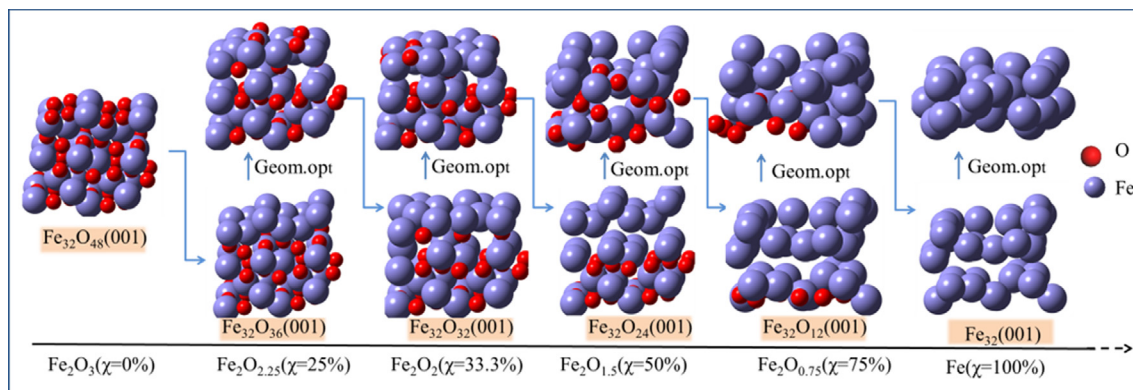


Fig. 2. Scheme of the perfect and reduced $\alpha\text{-Fe}_2\text{O}_3(001)$ surface models. (● O atom, ● Fe atom).

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