Full Length Article

A mechanistic study of CO oxidation over spinel $MnFe_2O_4$ surface during chemical-looping combustion

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ABSTRACT

Spinel $MnFe_2O_4$ is a potential oxygen carrier owing to its low cost, non-toxicity and good thermal stability during the chemical-looping combustion (CLC) redox cycles. The reactivity of $MnFe_2O_4$ and the mechanism of CO oxidation over $MnFe_2O_4$ surface were investigated by using the density functional theory (DFT) method. It is found that CO chemisorbs preferably at the octahedral Fe^{3+} site with C-down orientation. Particularly, a Mn atomic layer lying on the top of Mn-terminated surface occupies some active O sites and weakens the surface activity. The adsorbed CO then reacts with a bridging surface O to generate a surface CO_2 complex, revealing the key intermediate for CO_2 production. CO_2 desorption ultimately takes place by surmounting an energy barrier. Based upon the DFT-derived energetics, CO oxidation over the spinel $MnFe_2O_4$ surface is identified as a three-step process involving CO adsorption, CO diffusion and CO_2 desorption. The pathway analysis illustrates that the surface O with three Fe^{3+} ligands shows superior reactivity than that with two Fe^{3+} and one Mn^{2+} ligands. Further, it is noted that the consumption of lattice O primarily occurs around Fe sites, which indicates that Fe^{3+} can be easily reduced to Fe^{2+} accompanying with $MnFe_2O_4$ transformation to (Fe, Mn)O. These results are well consistent with the experimental kinetics.

1. Introduction

Chemical-looping combustion (CLC) is a novel combustion technology that has been suggested as a better alternative for low cost CO_2 capture [1,2]. It converts carbonaceous fuels efficiently while producing a relatively pure sequestration-ready CO_2 stream without significant energy penalty. In a CLC system, as shown in Fig. 1, metal oxide is employed as oxygen carrier to transport oxygen from air reactor to fuel reactor, which can avoid the direct contact between combustion air and fuel. This arrangement also gives rise to a higher energy conversion efficiency [3].

Oxygen carrier is the foundation of CLC and is identified as one of the determining factors for successful operation of CLC. Up to now, oxides of Fe, Mn, Cu, Co and Ni are feasible candidates to be used as oxygen carriers. Fe-based oxides show a lot of positive properties such as low cost, high mechanical strength and environmental friendliness. However, the redox characteristics of this oxide are relatively weaker than that of other metal oxides, especially for the CLC with methane or coal. In addition, Fe-based oxides with thermodynamic limitation results in a low oxygen transport capacity, because only the transformation from Fe_2O_3 to Fe_3O_4 is applicable for CLC system to fully convert

fuels to CO_2 and H_2O [4]. Mn-based oxides are also inexpensive and nontoxic. Moreover, it can be used in the chemical-looping with oxygen uncoupling (CLOU) process for the solid fuel combustion because of its oxygen release characteristic at high temperatures [5]. Nevertheless, Mn-based oxygen carrier owns the disadvantages of low reactivity and high tendency to react with support oxides [6–8]. Therefore, single metal oxide of either Fe-based or Mn-based oxide with these disadvantages cannot sufficiently meet the criteria of oxygen carrier during practical CLC application [9–14].

Recently, mixed Mn/Fe oxides combining the advantages of both Fe- and Mn-based materials have been developed as the oxygen carriers [15–18] and have received great attention for their better performance due to the synergistic effects [19–21]. The reduction pathway of bimetallic Fe/Mn with CH_4 and H_2 was studied by Lambert et al. [15], they found that the reduction of spinel (Fe, $Mn)_3O_4$ to (Fe, Mn)O is rather fast. Further reduction to MnO and Fe^0 could be observed when H_2 was used as a reducer. Azimi et al. [16] synthesized a series of mixed Mn/Fe oxygen carriers with different Mn/Fe ratios, and found that the particles with Mn content in the range from 25% to 33% exhibited the best methane conversion at 950 °C. This is because the formation of spinel phase of (Mn, $Fe)_3O_4$ enhances the chemical reactivity and
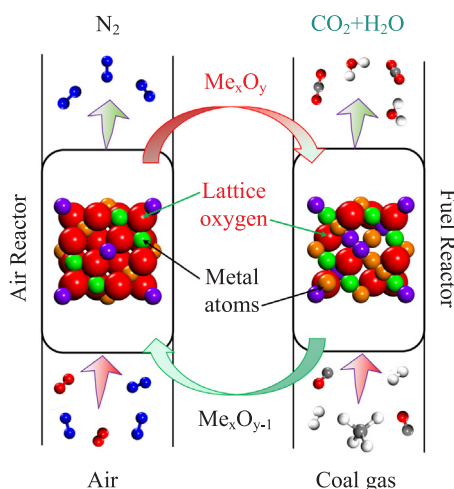
Fig. 1. Simplified schematic of coal gas fuelled chemical-looping combustion. The gray, white, red, and blue spheres represent C, H, O, and N atoms, respectively. The purple, green and orange spheres represent different transition metal atoms.

stability of the oxygen carrier during multiple CLC cycles. Similar results were obtained by Larring et al. [17]. In many studies [20–22], the synergetic effects of mixed oxygen carriers were primarily ascribed to the formation of various new crystalline phases, such as spinels or perovskites. Further, Wang et al. [23] prepared spinel $MnFe_2O_4$ using sol-gel combustion synthesis method and suggested that $MnFe_2O_4$ showed superior reactivity with coal as compared to the single reference oxides of Mn_3O_4 or Fe_2O_3. Hence, $MnFe_2O_4$ could be a potential oxygen carrier candidate better than the corresponding single metal oxide applied in CLC process. Moreover, spinel $MnFe_2O_4$ is regarded as a promising catalyst with good activity [24], which is beneficial to coal gasification and gas reforming in fuel reactor. More importantly, spinel $MnFe_2O_4$ with good magnetic property can greatly facilitate the separation of oxygen carrier from ash [25].

The knowledge of micro-interaction mechanism between fuel molecules and oxygen carriers is useful for understanding the relationship between structure and their properties, which will facilitate the design and optimization of efficient oxygen carriers. Although some experimental studies have been performed to study the reaction performance of $MnFe_2O_4$ with various fuels [21,23], heretofore, there is no theoretical research on CO molecule adsorption and oxidation mechanism over $MnFe_2O_4$ surface in CLC process. Moreover, the quantitative structure-activity relationship of spinel $MnFe_2O_4$ are still lacking, and the detailed interaction mechanism between spinel $MnFe_2O_4$ and CO molecule also await elucidation.

Theoretical methods, for instance, density functional theory (DFT) can be utilized to understand variations in adsorption activity and to explicate the surface chemical reactions in detail from one material to another [26–28]. Importantly, DFT calculations are ideally suitable for providing valuable information about the active sites of the structure and the energy of the adsorbed species interacting with surface at an atomic level [29–32], which can make complements to the experimental studies. Herein, based on the periodic slab models and DFT calculations, the detailed adsorption behavior of CO molecule over $MnFe_2O_4$ surface is studied, and then the oxidation mechanism of CO molecule over this surface is proposed through pathway analysis. To the best of our knowledge, this is the first detailed theoretical study involving CO adsorption and oxidation mechanism on $MnFe_2O_4$ surface.

2. Computational details

All calculations were performed using the plane-wave based DFT as implemented in CASTEP package [33]. The spin-polarized calculation

was applied due to the magnetic properties of $MnFe_2O_4$. The generalized gradient approximation (GGA) with ultrasoft pseudopotentials [34] was adopted to describe ion-electron interactions using Perdew-Burke-Ernzerhof [35] (PBE) exchange-correlation, which has been proved to be an appropriate functional for studying the spinel systems [36,37]. The explicitly treated valence electrons were ($3d^54s^2$), ($3d^64s^2$), ($2s^22p^2$), and ($2s^22p^4$) for Mn, Fe, C, and O atoms, respectively. The kinetic energy cutoff for the plane-wave functions was set to 340 eV. The Monkhorst-Pack k-point sampling [38] was used in the Brillouin zone with a $4 \times 4 \times 4$ mesh for bulk optimization, and a $4 \times 4 \times 1$ mesh for surface relaxation and CO adsorption. Self-consistent field (SCF) calculations were converged until the energy differences between electronic iterations were smaller than 1.0×10^{-6} eV/atom. Furthermore, the structural parameters and internal coordinates were relaxed with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method [39]. The energy, force and maximum displacement tolerances were 1.0×10^{-5} eV/atom, 0.03 eV/Å and 0.001 Å, respectively.

The adsorption energy (E_{ads}) can be calculated according to the following expression:

$$E_{ads} = E(CO\text{-}MnFe_2O_4) - (E_{CO} + E_{MnFe_2O_4}) \qquad (1)$$

where $E_{(CO\text{-}MnFe2O4)}$, E_{CO}, and $E_{MnFe2O4}$ represent the total energy of CO molecule over $MnFe_2O_4(100)$ surface system, CO molecule in the gas-phase, and $MnFe_2O_4(100)$ surface, respectively. Under this definition, a more negative E_{ads} value corresponds to a stronger interaction.

In addition, to further understand CO oxidation mechanism, the transition state (TS) structures are identified by using the complete LST/QST method [40]. The activation energy (E_a) is defined as follows:

$$E_a = E_{TS} - E_{IM} \qquad (2)$$

where E_{TS} and E_{IM} are the energies of transition state and intermediate (IM) state in each elementary reaction, respectively.

3. Results and discussion

3.1. Bulk optimization and surface relaxation

$MnFe_2O_4$ is an important spinel oxide, and it naturally crystallizes in a mixed phase consisting of both normal and inverse spinel structures. However, this compound is believed to be of primarily normal spinel structure [41,42]. Accordingly, normal spinel $MnFe_2O_4$ is used as substrate structure in this study. The unit cell of normal spinel $MnFe_2O_4$ is displayed in Fig. 2.

To find the ground state of spinel $MnFe_2O_4$, the non-magnetic as well as two magnetic ↑↑ and ↑↓ configurations were taken into account. The ↑ and ↓ represent up- and down-spin directions of Fe or Mn atoms, respectively. The optimization results are listed in Table 1. The lowest
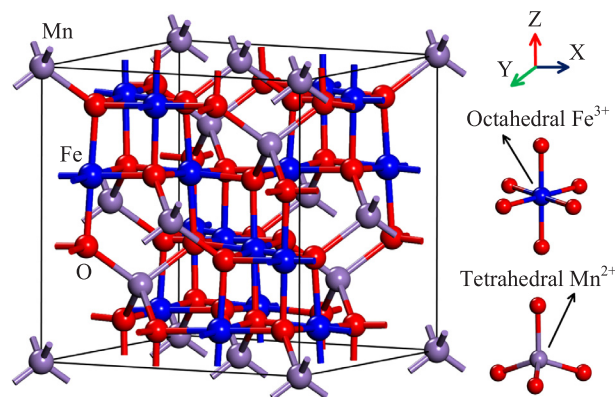

Fig. 2. Crystal structure of the normal spinel $MnFe_2O_4$, Fe^{3+} atoms are in octahedron while Mn^{2+} atoms in tetrahedron. The red, blue, and purple spheres represent O, Fe, and Mn atoms, respectively.