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Density functional theory study on improved reactivity of alkali-doped Fe_2O_3 oxygen carriers for chemical looping hydrogen production

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ABSTRACT

The key obstacle preventing the widespread use of chemical looping hydrogen production is the scarcity of high-performance oxygen carrier (OC) materials. Here, for the first time we investigated improved reactivity of all the alkali-doped Fe_2O_3 OCs by means of density functional theory (DFT) calculations. Firstly, the location of alkali dopants (Li, Na, K, Rb and Cs) in the Fe_2O_3 crystal structure was studied. Our calculation results showed that all the alkali dopants prefer to be located at the surface of Fe_2O_3 rather than in the bulk. Then oxygen vacancy formation energies (E_{vac}) of Fe_2O_3 and alkali-doped Fe_2O_3 OCs, which could be used to evaluate the activity of OC surface oxygen, were calculated via DFT. It was found that the E_{vac} of surface oxygen adjacent to the dopants for all the alkali-doped Fe_2O_3 are much lower than that for undoped Fe_2O_3. The smaller the ionic radius is and the stronger the electronegativity is, the lower the E_{vac} of surface oxygen away from the dopants is. The surface oxygen adjacent to the dopants will show the better activity compared to the one away from the dopants. Finally, we analyzed the effect of alkali dopants on the reactivity of Fe_2O_3 OC. We concluded that the addition of Li, Na and K dopants are certainly able to enhance the activity of surface oxygen, thereby improving the reactivity of Fe_2O_3 OC. Compared with Li, Na and K, Rb and Cs will have a worse synergetic effect on the reactivity of Fe_2O_3 OC. Li, Na and K were identified as the optimal dopants. A quick screening of promising dopants for Fe_2O_3 OC could be realized by our DFT calculations.

1. Introduction

Hydrogen, an environmental friendly energy carrier, has been considered as a possible replacement for fossil fuels for the future [1]. Currently, steam methane reforming (SMR), which has been extensively used in industry, is the dominant technology for large-scale H_2 production [2]. Although a mature process, this technology is high cost due to the large amount of energy consumption. It also brings about high CO_2 emissions, aggravating global warming. Chemical looping hydrogen production (CLH) [3] developed from chemical looping combustion (CLC) and hydrogen production by the steam-iron process is attracting great attention. The CLH process is usually performed in three interconnect fluidized bed reactors, a fuel reactor (FR), a steam reactor (SR) and an air reactor (AR). The oxygen carrier (OC) is circulated between these reactors to transfer the oxygen, avoiding the direct contact between air and fuel. In the FR, the OC is reduced by fuels. Then the reduced OC is partially oxidized by H_2O, generating H_2 in the SR. Finally, the OC is regenerated by taking up oxygen from the air in the AR, closing the looping cycle. In this way, the high purity CO_2 and H_2 could be simultaneously obtained by condensation without costly energy consumption for separation and purification.

Selection and development of an efficient OC is one of the most important issues for CLH process [4]. A lot of OC materials such as Ni, Cu, Fe, Co and Mn oxides [5–11] have been widely investigated. Among them, Fe_2O_3 OC in particular has been of interest for CLH process due to its superior thermodynamic property for steam conversions, cheap cost and low toxicity [12,13]. Unfortunately, the main challenge for Fe_2O_3 OC is the poor reactivity during high temperature operation [14–17], hindering its application in the CLH process. A number of researches have been carried out for the purposes of improving the performance of OC. Li et al. [18,19] found that the support could significantly enhance the O^{2-} diffusivity by lowering the energy barrier of O^{2-} migration within the dense solid phase, thereby improving the OC reactivity. Tian et al. [20] reported a La-promoted strategy to promote the performance of Fe_2O_3/Al_2O_3 OC and for the first time found that the OC with the addition of 18 wt% La exhibited outstanding reactivity and redox stability. They [21] also studied the Fe-substituted Ba-hexaaluminates (BFA-x (x = 1–3), x indicates Fe content) OC. The results showed that

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BFA-3 ($BaFe_3Al_9O_{19}$) OC could demonstrate superior reactivity and recyclability, which was attributed to the highest amount of the reacted lattice oxygen in the mirror plane (0.77 mmol/g). Zhao et al. [22] investigated the influence of Co doping on the characteristics and the stabilities of the perovskite-type oxides $LaFe_{1-x}Co_xO_3$ (x = 0.1, 0.3, 0.5, 0.7, 1.0) OCs and found that the optimal degree of Co substitution is x = 0.3. Recently, an effective strategy by introducing alkali metal ions into Fe_2O_3 OC has been proposed to enhance its reactivity. Gu et al. [23] firstly developed a K_2CO_3-modified Fe_2O_3 OC and found that it could significantly improve the carbon gasification rate and the conversion of carbonaceous gases into CO_2 in the CLC process. Subsequently, they studied the reactivity of 6% K_2CO_3-modified Fe_2O_3 OC with CO and H_2 in the thermogravimetric analyzer (TGA) reactor and analyzed that K as an electric donor could weaken the Fe-O bond, enhancing its reactivity [24]. Liu et al. [25] investigated the performance of KNO_3-modified Fe_2O_3 OC for CLH process and found that adding KNO_3 accelerates the reduction processes and hydrogen generation. The K_2CO_3-modified Fe_2O_3 OC was also used in the CLH process and it demonstrated a beneficial effect on suppressing carbon formation [26]. In addition, Ge et al. [27] reported that the reduction kinetics of Fe_2O_3 OC could be promoted by the incorporation of Na into Fe_2O_3 OC. Similar to K, it is also attributed to the weakening of Fe—O bond with the assistance of Na. Recently, Huang et al. [28] investigated the redox performance of Na-doped Fe_2O_3 OC using syngas as reducing agent in the TGA and lab-scaled semi-fluidized bed reactor. It was observed that the Na dopant in Fe_2O_3 OC can significantly enhance the reduction behavior compared with the raw OC. Moreover, Liu et al. [29] systematically evaluated the enhanced performance of alkali metals (Na, K and Cs) doped Fe_2O_3 OCs in a fixed bed reactor. The results showed that all alkali doping could stabilize the reactivity of Fe_2O_3 OC and K-doped OC exhibited the best performance.

Phenomenologically, the alkali dopants have been noted to improve the performance of Fe_2O_3 OC. However, the atomistic mechanisms behind such improvement remain elusive. Is there any rules that may govern how the alkali dopants affect the reactivity of Fe_2O_3 OC? The knowledge of these mechanisms is highly desirable for the design and development of high-performance Fe_2O_3 OC. And so far, the screening of effective dopants is mainly based on trial-and-error experiments. There is an urgent need to switch to a new strategy for computational selection. This approach could significantly accelerate the identification of promising dopants. First-principle calculations based on density functional theory (DFT) have been extensively employed to describe the properties of Fe_2O_3 OC at the atomic level, providing reasonable compromise between accuracy and computational time [30–33]. Therefore, we proposed a systematic DFT calculation for all the alkali-doped Fe_2O_3 OCs to develop a theoretical system that not only helps to understand the influence mechanism of alkali dopants on the reactivity of Fe_2O_3 OC but also can screen out the potential candidates effectively and quickly.

In this paper, the improved reactivity of all the alkali-doped Fe_2O_3 OCs was investigated by using DFT calculations. It is widely accepted [10,11,18,34,35] that the reaction between OCs and fuel involves the following processes. The fuel is oxidized by the oxygen atoms from the OC surface layer. The oxidation products desorb, leaving behind the oxygen vacancy on OC surface. Then the oxygen anion migrate from sub-layers to the surface layer to participate in the reaction continuously. Therefore, the activity of surface oxygen is of significance for the OC performance. Previous studies [36–38] have confirmed that the oxygen vacancy formation energy (E_{vac}), as a measure of the oxygen binding strength, could well describe the ability of surface oxygen to act as an oxidizing agent. Firstly, we studied the location of alkali dopants in the Fe_2O_3 crystal structure and established the models of Fe_2O_3 and alkali-doped Fe_2O_3 surfaces. Then the oxygen vacancy formation energies of Fe_2O_3 and alkali-doped Fe_2O_3 OCs were calculated via DFT. Finally, we comprehensively evaluated the effect of alkali dopants on the reactivity of Fe_2O_3 OC.

2. Computational details

We performed all the DFT calculations by using the Vienna Ab-initio Simulation Package (VASP) [39–41] in this paper. To describe electron exchange and correlation, the generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE) [42,43] was applied. We used the projector-augmented wave (PAW) [44] approach proposed by Kresse and Joubert [41] for the treatment of the electron-ion interactions. We performed the convergence tests of the cutoff energy and k-point in this work. A range of different cutoff energy values from 360 eV to 440 eV with an incremental step of 10 points was tested. It was found that the error between the step values was less than 0.01 eV when the cutoff energy reached 400 eV. Thus, the cutoff energy of 400 eV is justified. The Brillouin zone integration was calculated with a 2 × 2 × 1 Monkhorst-Pack k-point mesh for surface relaxation to ensure the convergence of total energy. The Gaussian smearing approach with $\sigma = 0.2$ eV was employed to ensure accurate energies with errors less than 1 meV per atom. The spin-polarization calculations [45] were carried out due to its magnetic property. We considered four magnetic configurations for four Fe atoms in the rhombohedral primitive cell of Fe_2O_3, including ↑↑↑↑, ↑↓↑↓, ↑↓↓↑ and ↑↑↓↓, where ↑ and ↓ represent the up-spin and down-spin directions with respect to the z-axis. The total energy of anti-ferromagnetic arrangement (↑↓↓↑) is the lowest, which is in agreement with previous theoretical works [46,47]. The magnetic moments of alkali dopants were set to follow the same sign as the substituted Fe atoms. We also tested the scenario with the dopants having the magnetic moments opposite to the substituted Fe atoms, and the total energy of first scenario is lower. The strong electron correlation in the localized 3d electrons is not described very well in a spin-polarized DFT treatment. To accurately consider the strong electron correlation, we introduced the strong on-site Coulomb repulsion parameter U and the screened exchange interaction parameter J ($U = 5$ eV and $J = 1$ eV) [48]. The electronic energies and force criteria for convergence were kept to be 10^{-5} eV and 0.03 eV/Å, respectively. The local minima was located with the conjugate-gradient algorithm for the geometry optimization. Table 1 summarizes the numerical details for our DFT calculations. The α-Fe_2O_3 bulk were optimized and the calculated lattice parameters are $a = b = 5.028$ Å and $c = 13.697$ Å, which agrees well with the experimental values [49] ($a = b = 5.038$ Å and $c = 13.772$ Å).

The X-ray photoelectron diffraction study [50] showed that α-Fe_2O_3(0 0 1) surface orientation is dominant and Fe-O_3-Fe termination [33,50] was found to be most stable among three possible surface terminations, including an O-layer (O_3-Fe-Fe), a double Fe-layer (Fe-Fe-O_3) and a single Fe-layer (Fe-O_3-Fe). Therefore, we employed α-Fe_2O_3(0 0 1) surface with Fe-O_3-Fe termination in this work. The (2 × 2) periodic supercell with 36 O atoms and 24 Fe atoms was chose to model this surface in all calculations. A 15 Å thick vacuum region was adopted to ensure negligible interaction between periodic slabs. The bottom three layers were fixed with the remaining six layers and adsorbates relaxed. The optimized configuration of Fe_2O_3(0 0 1) surface is shown in Fig. 1.

Table 1
The numerical details for DFT calculations.

Cutoff energy (eV)	k-point	σ[a] (eV)	U and J values (eV)	Electronic energies criterion (eV)	Force criterion (eV/Å)
400	2 × 2 × 1	0.2	U = 5, J = 1	10^{-5}	0.03

[a] The Gaussian smearing approach with $\sigma = 0.2$ eV.