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Full Length Article

Theoretical study on influence of CaO and MgO on the reduction of FeO by CO

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ABSTRACT

Coating of CaO or MgO on the particle surface can prevent the sticking among iron ore particles effectively during fluidization process. However, CaO and MgO promote the formation of iron whiskers at high temperature, leading to the catastrophic defluidization. The density functional theory (DFT) calculations were implemented to investigate the influence of CaO and MgO on reduction of FeO/Fe_2O_2 by CO. Our results show that the CO molecule tends to bind to FeO/Fe_2O_2 on CaO(100) and MgO(100) surfaces through newly formed C-Fe and C—O bonds. The CaO(100) surface will accelerate the reduction reactions which occur on it, in particular, in the initial stage of reactions, however, will slow down the reactions in the posterior stage. For the MgO(100) surface, the reduction reactions which occur on it will be promoted. The positive roles displayed by CaO and MgO in promoting the reduction of FeO by CO accelerate the precipitation of fresh iron and therefore, leading to the formation of iron whiskers.

1. Introduction

Fluidized beds have been widely employed in many industrial processes [1,2], due to its high efficiency of the heat and mass transfer between gas and particles [3,4]. For some non-blast furnace iron-making processes, fluidized beds are chosen as promising technologies for their reduction or pre-reduction units [5,6]. However, sticking among individual iron ore particles, which usually leads to an uncontrollable shutdown of fluidized reduction, is one of the main obstacles for the extensive applications of fluidized bed process in iron-making field [7–10]. According to the previous studies [11–15], coating of CaO or MgO on the particle surface can avoid the sticking problem effectively during fluidized reduction. This coating method has attracted more and more attention due to availability and simplicity.

The mechanism of sticking inhibition is physical spacer effect on the surface [12]. The reactions between CaO/MgO and Fe_2O_3/FeO generate CaO-FeO and MgO-FeO phases, respectively, which coat onto particle surface and prevent the connection of precipitated iron and therefore, inhibiting the sticking effectively [13]. However, this inhibition effect is weakened at high temperature since the CaO-FeO/MgO-FeO is reduced to metallic iron and cannot avoid the connection of fresh iron [12,16]. Moreover, the CaO and MgO can promote the formation of iron whiskers at high temperature (e.g. 1000 °C) because of increasing the diffusion of iron [17–24], leading to the agglomeration seriously. Hence, the study on influence of CaO and MgO on reduction of FeO is crucial to investigate the promotion effect on formation of iron whiskers.

The (100) surface is the most stable surface of both CaO and MgO [25,26]. Here, the CaO(100) and MgO(100) surfaces were adopted and the reduction of FeO by CO on those surfaces has been investigated on the atomic scale using density function theory (DFT) calculations in order to reveal the influence of CaO and MgO on reduction reactions. As a comparison, we have also investigated the reduction of FeO by CO on FeO(100) surface.

2. Computational methods and models

All the DFT calculations were carried out using the Vienna Ab Initio Simulation Package (VASP) [27–30] with the projector augmented wave (PAW) pseudopotentials [31] for electron-core interactions and the Perdew-Burke-Ernzerhof (PBE) type of generalized gradient approximation (GGA) for exchange and correlation functional [32]. The cutoff energy, convergence tolerance energy and max force on each atom were 400 eV, 1.0×10^{-6} eV/atom and 0.100 eV/Å, respectively. The Brillouin zone integration was per-

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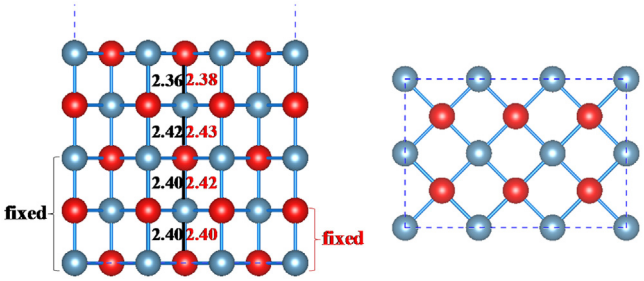

Fig. 1. The side view (left) and top view (right) of optimized CaO(100) surface. The bond lengths are shown in the unit of Å. Blue and red balls represent the Ca and O atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

formed within the Monkhorst-Pack scheme using the K-points set of $4 \times 8 \times 1$ for relaxation.

Here, we use CaO as an example to illustrate the surface models employed in our calculations. Solid CaO has a face-centered cubic structure with the lattice parameter of 0.2405 nm [33], in which the Ca and O atoms adopt the form of octahedral coordination. In our work, the CaO(100) surface of 3×2 supercell with five atomic layers were chosen [34] (Fig. 1), where the three bottom layers were fixed during the optimization process. To avoid the interaction between neighboring slabs, the vacuum space was set to 20 Å [26]. The binding energy E_b is defined as: $E_b = (E_{cs} + E_m) - E_{system}$, where E_{cs}, E_m, and E_{system} are the energies of the clean surface, the isolated molecule and the binding system, respectively.

We have tested the clean surface for comparison of the optimized CaO(100) surfaces with bottom two and three layers fixed, respectively. As shown in Fig. 1 (left), the bond length between topmost layer of O atom and second layer of Ca atom is 2.36 Å after relaxation when the bottom three layers are fixed, which decreases by about 1.7% compared to the bond length before relaxation. As a comparison, this bond length becomes to 2.38 Å after relaxation when the bottom two layers are fixed, which decreases by about 0.8%. Our test demonstrates that the CaO(100) surface exhibits a stable characteristic and our approach of fixation of bottom three layers is credible. We have also tested the influence of supercell size on binding energy of FeO onto CaO(100) surface. The binding energy of FeO onto 3×2 CaO(100) surface is 2.58 eV (Fig. 2a), while this binding energy is 2.60 eV for 3×3 supercell. The binding energy increases by about 0.8% when supercell size expands from 3×2 to 3×3. This test indicates that the 3×2 supercell is reasonable for obtaining the binding energy of FeO onto CaO(100) surface.

3. Results and discussion

3.1. The binding of FeO and Fe_2O_2 onto surfaces

The coating layer on the particle surface mainly contains CaO-FeO and MgO-FeO phases, which are reduced by CO at high temperature. Therefore, We firstly investigated the binding of FeO onto CaO(100), MgO(100) and FeO(100) surfaces, respectively, and subsequently, revealed the influence of CaO and MgO on reduction of FeO by CO.

Previous reports demonstrate that the FeO cluster can be used to investigate the reduction reaction of FeO by CO. Reddy et al. [35–37] have studied on FeO, Fe_2O_2, Fe_3O_4 and Fe_2O_3 representative clusters in order to investigate the mechanism for oxidation of CO by iron oxide clusters. Nelly M. Reilly et al. [38,39] have presented synergistic studies employing experiments in the gas phase and theoretical first principles calculations to investigate the structure, stability, and reactivity toward CO of iron oxide cluster anions. Wei Xue et al. [40] have investigated the reactions of small neutral iron oxide clusters ($FeO_{1\text{-}3}$ and $Fe_2O_{4,5}$) with carbon monoxide (CO) by experiments and first-principle calculations. Changqing Dong et al. [41] have employed Fe_2O_3 cluster from Fe_2O_3(1–102) surface for detecting deep reduction of oxygen carrier for CO oxidation using DFT calculations. Wu Qin et al. [42] have investigated the synergetic effect of MgO on the interaction between CO and different active site of Fe_2O_3 and interaction between O_2 and the reduced Fe_2O_3. The DFT calculations were performed and Fe_2O_3 was supported on MgO(100) surface to form a cluster shape on MgO(100), denoted as Fe_2O_3/MgO, where the Fe_2O_3 was activated by MgO(100). Here, we used the FeO and Fe_2O_2 clusters to represent the FeO, which is reduced by CO on CaO and MgO surfaces. Fig. 2 shows the binding of FeO and Fe_2O_2 onto CaO(100), MgO(100) and FeO(100) surfaces. For the FeO (Fig. 2A–C), all the Fe atoms bond to surface O atoms, while the O atoms form new bonds with surface Ca, Mg and Fe atoms, respectively. The binding energies of these three configurations are 2.58, 1.90 and 2.78 eV, respectively. For the Fe_2O_2 (Fig. 2D–F), the binding energies are 3.49, 2.69 and 3.61 eV when Fe_2O_2 binds onto CaO(100), MgO(100) and FeO(100) surfaces, respectively. The binding energies exhibit the character that the binding of FeO and Fe_2O_2 onto FeO(100) surface is more stable than that onto CaO(100) and MgO(100) surfaces.

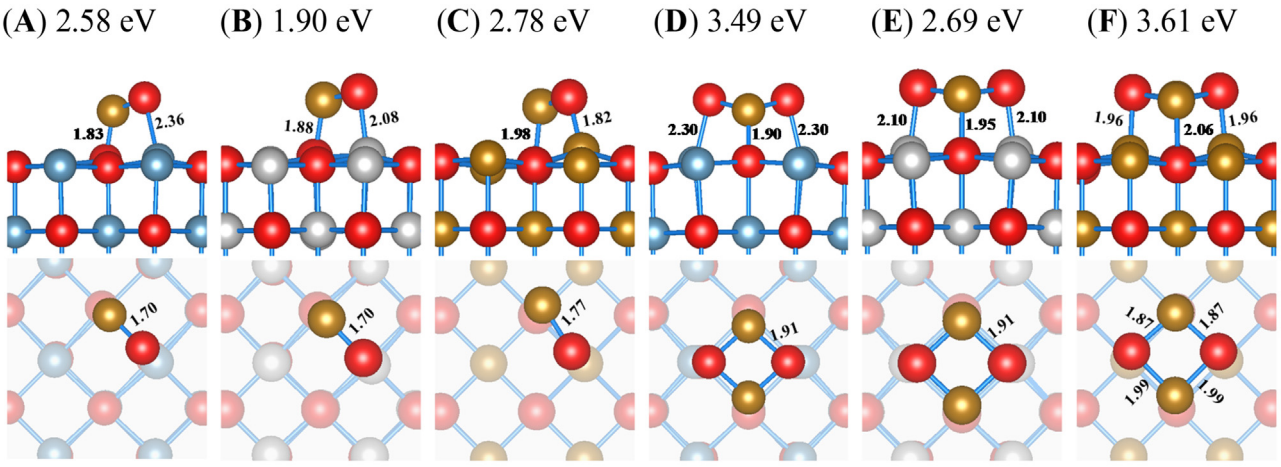

Fig. 2. The binding of FeO and Fe_2O_2 onto CaO(100) (A, D), MgO(100) (B, E) and FeO(100) (C, F) surfaces. Upper, side view; lower, top view. The bond lengths are shown in the unit of Å. Blue, silvery, brown and red balls represent the Ca, Mg, Fe and O atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)