Full length article

Morphology evolution and nanostructure of chemical looping transition metal oxide materials upon redox processes

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ABSTRACT

Transition metal are heavily used in chemical looping technologies because of their high oxygen carrying capacity and high thermal reactivity. These oxygen activities result in the oxide formation and oxygen vacancy formation that affect the nanoscale crystal phase and morphology within these materials and their subsequent bulk chemical behavior. In this study, two selected earlier transition metals manganese and cobalt as well as two selected later transition metals copper and nickel that are important to chemical looping reactions are investigated when they undergo cyclic redox reactions. We found Co microparticles exhibited increased CoO impurity presence when oxidized to Co_3O_4 upon cyclic oxidation; CuO redox cycles prefer to be limited to a reduced form of Cu_2O and an oxidized form of CuO; Mn microparticles were oxidized to a mixed phases of MnO and Mn_3O_4, which causes delamination during oxidation. For Ni microparticles, a dense surface were observed during the redox reaction. The atomistic thermodynamics methods and density functional theory (DFT) calculations are carried out to elucidate the effect of oxygen dissociation and migration on the morphological evolution of nanostructures during the redox processes. Our results indicate that the earlier transition metals (Mn and Co) tend to have stronger interaction with O_2 than the later transition metals (Ni and Cu). Also, our modified Brønsted−Evans−Polanyi (BEP) relationship for reaction energies and total reaction barriers reveals that reactions of earlier transition metals are more exergonic and have lower oxygen dissociation barriers than those of later transition metals. In addition, it was found that for these transition metal oxides the oxygen vacancy formation energies increase with the depth. The oxide in the higher oxidation state of transition metal has lower vacancy formation energy, which can facilitate forming the defective nano-structures. The fundamental understanding of these metal oxide reactions is essential to designing the metal oxide-based oxygen carriers for chemical looping applications.

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1. Introduction

Chemical looping is regarded as one of the most cost effective technique [1] for clean conversion of carbonaceous fuels along with CO_2 capture [2]. In the past few decades, application of metal oxides in clean energy industry attracts numerous attentions. In particular, chemical looping requires highly efficient materials with low cost and high performance and durability. Transition metal oxides are among the most promising candidates, exhibiting a wide range of interesting physical and chemical properties. Clean energy can be harvested by chemical looping system from carbonaceous fuels [3]. The metal oxide composites play a key role as oxygen carriers and can be operated under various modes. In the chemical looping combustion (CLC) mode, the oxygen carriers react with fuels and are completely re-oxidized in a combustor, thus the whole combustion processes produce only heat. The chemical looping oxygen uncoupling (CLOU) process mode is based on CLC with metal oxides releasing gaseous oxygen to convert carbonaceous fuels. In both of these chemical looping modes of operation, the diffusion of metal ions, oxygen ions, and oxygen vacancies dictates the redox reactivity and recyclability of the metal oxide oxygen carriers [4].

The state of the art study on metal oxides in chemical looping application largely focus on the selection of materials using trial and error method and the relationship between morphology or

structure and reactions have yet been studied systematically. In previous study, we have discussed the reaction mechanism of iron based metal oxide composites at atomic level [4,5]. When supported by titanium oxide, the iron oxide oxygen carriers perform outstandingly in CLC application. Other transition metal oxide systems [5—9] have been discussed in CLC and CLOU because of their capability for being fully reduced and oxidized for multiple cycles. Based on experimental observation, oxides of manganese and copper have been studied in CLOU applications because they show a combination of reasonably high partial pressure of oxygen at relevant temperatures in addition to an exothermic reaction, which could result in a temperature increase in a reactor [10,11]. Similarly, oxides of cobalt and nickel have been extensively reported as oxygen carriers in CLC due to their high transport capacity [12,13]. However, fundamental redox mechanisms in the above-mentioned oxides are still not fully understood due to the lack of atomic level information on the structure and morphology related properties for these oxides. Specifically, the morphology and structure related reaction mechanism has not been discussed in any of the previous work.

The redox reactivity is intrinsically dependent on morphology, electron and crystal structures in metal oxides oxygen carrier. For example, Fe based oxide composites have been successfully demonstrated to recycle over thousands of times in chemical looping systems with the aid of Ti-based support [14]. This is because of the lower vacancy formation energy of Ti terminated surface compared to Fe terminated surface, which results in the formation of defective surface and large surface area with addition of Ti. Thus, it is critical to understand the oxygen migration and the morphology variation behavior of these materials upon the high temperature oxidation and reduction reactions of metal.

Oxygen vacancies will form with the oxygen migration. For years oxygen vacancies have been examined and investigated by a variety of spectroscopic techniques. Nevertheless, it is still difficulty to experimentally determine the vacancy-induced lattice relaxations, and the vacancy formation energy. A great number of theoretical studies on oxygen migration and vacancy formation from transition metal oxides have been reported, such as TiO_2 [15,16], ZrO_2 [17,18], V_2O_5 [19—21] and CeO_2 [22—25]. However, oxygen migration and vacancy formation in oxides of cobalt, copper, manganese and nickel, used as important chemical looping oxygen carrier materials, still remain unclear.

In this work, we systematically study Co, Cu, Mn and Ni to explore the morphological evolution of the active systems under the redox reactions using the crystal phase study combined with atomic modeling. The comprehensive understanding of the oxygen adsorption, dissociation and diffusion in these metal oxide composites is obtained, which is useful in directing the development of metal oxide-based oxygen carriers for chemical looping applications.

2. Methods

2.1. Experimental

Cu (99%), Ni(99.5+%), Mn(99.5%), Co(99.8%) powders were purchased from Goodfellow. An SEM analysis shows particle sizes between 40 and 60 μm. The powders were washed with acetone three times and dried at room temperature prior to further examination. Approximately 0.1 g powder samples were mounted in an alumina crucible and run through either one oxidation step or between one and five oxidation-reduction cycles at 700 °C using a Setaram SETSYS Evolution Thermogravimetric Analyzer (TGA). Oxidation was performed using a 200 mL/min flow of gas consisting of 50% air balanced with N_2. The reduction step used a 200 mL/min flow of gas containing 50% H_2 balanced with N_2. The oxidation and reduction steps lasted for 30 min each and were alternated with an intermediate 10 min flushing step using N_2 at 100 mL/min. All samples were analyzed using a Rigaku SmartLab X-Ray Diffractometer (XRD) with eliminated fluorescence. Scans were run from 20 to 80° at a rate of 1° per minute with an accelerating voltage and filament current of 40 kV and 44 mA, respectively. All the XRD spectra were analyzed using PDXL software and identified with the JCPDS database.

2.2. Computational

The first-principle calculations were performed within the framework of density functional theory (DFT), using the Vienna Ab Initio Simulation Package (VASP) [26—28]. The generalized gradient approximation of Perdew, Burke and Ernzerhof [29] was used to represent the exchange-correlation energy. The projector-augmented wave (PAW) method [30,31], with a 400 eV energy cutoff, was used to describe the wave functions of the atomic cores. The tetrahedron method with Blöchl corrections [32] was used to set the partial occupancies for the orbitals. The chemisorption of oxygen molecule to surfaces (100) was modeled for Co, Cu, Mn and Ni. Identical surfaces were modeled for the convenience of comparison of intrinsic metal properties and their impact on O=O bond activation. In all cases, the slab models were initially constructed from the optimized lattices. A five-layer periodic slab was constructed along the (100) Miller plane, with a ~15 Å vacuum along the c-axis which ensures negligible interaction between periodic replicas. To achieve excellent numerical accuracy, the real-space cutoff for the calculation of both the oxygen atom and oxygen molecule is increased to 20 Bohr. The binding energy of O_2 is calculated to be 2.88 eV/O atom, while the bond length and vibrational frequency are 1.22 Å and 1530 cm^{-1}, respectively, in agreement with experimental results (the corresponding values are 2.56 eV/atom, 1.21 Å, and 1580 cm^{-1} [33]).

For O_2 adsorption, different starting configurations were considered, including different adsorption sites and various molecular orientations, to help identify the location of the global minimum for the O_2/Metal system. The adsorption energies of O_2 on transition metals are calculated using the expression as below:

$$E_{ad} = E_{O_2} + E_M - E_{(O_2+M)} \tag{1}$$

where E_{O_2} is the energy of the optimized gas phase geometry of O_2, E_M is the total energy of the respective transition metal surface, and $E_{(O_2+M)}$ is the total energy of the slab with adsorbed O_2. Based on this definition, a more positive E_{ad} corresponds to a more stable configuration.

For transition metal oxides, the oxygen vacancy formation energies are calculated based on the following expression:

$$E_f = E_{tot} - E_V - \frac{1}{2}E_{O_2} \tag{2}$$

In Equation (2), E_{tot} is the total energy of the stoichiometric surface, E_V is the total energy of the reduced surface with one oxygen vacancy, and E_{O_2} is the total energy of the optimized gas phase O_2.

For O_2 dissociation and diffusion barrier calculations, the climbing-image nudged elastic band (CI-NEB) method was used [34,35]. This method enabled the stationary points to be mapped out along the minimum energy paths and identify transition states for each of the diffusion processes. Because these paths were directed by force projection, the energy was not necessarily consistent with the force being optimized; thus, the force-based