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 Co3O4 upon cyclic oxidation; CuO redox cycles prefer to be limited to a reduced form of Cu2O and an oxidized form of CuO; Mn microparticles were oxidized to a mixed phases of MnO and Mn3O4, 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 O2 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 nanostructures. The fundamental understanding of these metal oxide reactions is essential to designing the metal oxide-based oxygen carriers for chemical looping applications. © 2016 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Chemical looping is regarded as one of the most cost effective technique [1] for clean conversion of carbonaceous fuels along with CO2 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 Ni 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 TiO2 [15,16], ZrO2 [17,18], V2O5 [19–21] and CeO2 [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 N2. The reduction step used a 200 mL/min flow of gas containing 50% H2 balanced with N2. The oxidation and reduction steps lasted for 30 min each and were alternated with an intermediate 10 min flushing step using N2 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 JCPSD 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 O2 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 O2 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 O2/Metal system. The adsorption energies of O2 on transition metals are calculated using the expression as below:

\[
E_{\text{ad}} = E_{O_2} + E_M - E_{(O_2 + M)}
\]

(1)

where \(E_{O_2}\) is the energy of the optimized gas phase geometry of O2, \(E_M\) is the total energy of the respective transition metal surface, and \(E_{(O_2 + M)}\) is the total energy of the slab with adsorbed O2. Based on this definition, a more positive \(E_{\text{ad}}\) corresponds to a more stable configuration.

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

\[
E_f = E_{\text{tot}} - E_V - \frac{1}{2}E_{O_2}
\]

(2)

In Equation (2), \(E_{\text{tot}}\) 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 O2.

For O2 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
optimizer was chosen to ensure the convergence of the nudged elastic band algorithm.

To take into consideration realistic experimental conditions, the effect of temperature $T$ is included by explicitly taking into account the surrounding gas phase in terms of ab initio atomistic thermodinamics. We previously developed a modified Brønsted–Evans–Polanyi relationship to calculate the activation energy for the elementary steps of metathesis reaction [36]. Here, we extend this method to calculate the activation energy for $O_2$ dissociation at chemical looping condition as below:

$$E_a(T) = E_{a,DFT} + \alpha (\Delta H_{dis}(T) - \Delta E_{dis,DFT})$$

(3)

where $E_{a,DFT}$ corresponds to the forward activation energy barrier at 0 K, which is obtained from CI-NEB calculations. $\Delta H_{dis}(T)$ is the dissociation enthalpy at finite temperature, which is calculated from the individual enthalpies of the initial state and the final state for the constituent elementary reactions. $\Delta E_{dis,DFT}$ is the difference between the energies of final state and initial state at 0 K. The variable $\alpha$ denotes the relative position of the transition state compared to the initial (i.e., $\alpha = 0$) or final (i.e., $\alpha = 1$) state of the relevant elementary dissociation reaction. It can be obtained by considering which image in the CI-NEB calculations corresponds to the transition state. When the value of $\alpha$ is close to 0, it describes to an initial-like transition state; thus, the activation energy may be kept at the DFT value. When the value of $\alpha$ is close to 1, it

Fig. 1. SEM images of Co microparticles (a) cross section of an initial microparticle; (b) cross section of an oxidized microparticle; (c) cross section of an microparticle after one redox reaction cycle; (d) cross section of an microparticle after five redox reaction cycles; insets: EDS mapping with pink and white representing Co and O, respectively; (e) surface of the microparticle after one redox reaction cycle; (f) surface of the microparticle after five redox reaction cycles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
corresponds a final-like transition state [37].

3. Results and discussion

3.1. Evolution of nanoscale morphology

The morphology evolution of transition metal microparticles were probed over single and multiple oxidation–reduction cycles at 700 °C. The morphological and structural changes observed are discussed below.

3.1.1. Cobalt

The initial Co microparticles were observed by SEM in Fig. 1(a), the microparticle is dense with an average size of 2 μm. XRD spectrum (Fig. 2(a)) suggests both fcc (alpha phase) and hcp (beta phase) structures. However, the beta phase only exists in the original microparticles, consequently we mainly consider alpha phase in our DFT calculation during redox reaction to simplify our model.

Particles that have undergone oxidation, on the other hand, experience substantial changes. Here, oxidation results in the formation of a porous microparticle center, as visualized in Fig. 1(b) with Co and O uniformly distributed throughout the microparticle. This is consistent with previous findings [14,38,39] in Fe and FeTi microparticles. These voids in the center reflect that Co atoms initially in the core underwent outward diffusion. Co atoms are ionized during the diffusion process and O ion diffusion occurs mainly through Schottky defects, as opposed to the direct interchange of atoms. A complete phase transformation to Co3O4 is shown in Fig. 2(b), suggesting the coexistence of trivalent cobalt and divalent cobalt. Redox cycles were also carried out with the Co microparticles at 700 °C. An SEM image of a particle that had undergone one full redox cycle displays nanopores of 500 nm inside the particle (Fig. 1(c)) and on the surface (Fig. 1(e)). The oxygen vacancies are created during reduction which contributes to nanopore formation. Most of the Co3O4 is converted to Co after one redox cycle with a small amount of CoO phase as shown in Fig. 2(c). The quantity of CoO increases dramatically after five redox cycles (Fig. 2(d)). This indicates that the recyclability of microparticles deteriorates due to sintering effects. The decreased surface area and less porous morphology (Fig. 1(d) and (f)) both hinder the mobility of oxygen ions which results in incomplete redox reactions.

3.1.2. Copper

Cu microparticles were also studied in chemical looping redox reactions for its application in oxygen uncoupling. The low Tamman temperature of Cu (~543 °C) results in a severe sample adherence to the internal wall of TGA sample holder and therefore is not suitable in this study. Consequently, we focus on the fundamentals of CuO in chemical looping oxygen uncoupling (CLOU) application in which the cyclic reactions take place between CuO and Cu2O.

\[
\text{CuO} + \text{reducing gas} \rightarrow \text{Cu}_2\text{O} \tag{4}
\]

\[
\text{Cu}_2\text{O} + \text{oxidizing gas} \rightarrow \text{CuO} \tag{5}
\]

The excellent recyclability of CuO microparticles is analyzed by XRD in Fig. 3. After cyclic redox reactions the crystal structure of CuO remains unchanged (Fig. 3(c) and (d)). However, based on the XRD analysis, the grain sizes of the microparticles after redox reaction vary substantially. The original average grain size of CuO microparticles is 172 nm, whereas the reduced microparticles has an average grain size of 722 nm and the average size of grains dropped to 400 nm and 365 nm after one and five redox cycles, respectively. This is in agreement with the fact that outward diffusion of oxygen can cause grain expansion. Despite of the sintering effect, the fast kinetics of CuO reduction plays an important role in grain size decrease after redox reactions. Specifically the change in grain size implies a grain boundary movement induced by ionic diffusion during oxygen vacancy exchange. The reduction and oxidation can be treated as creation and consumption of oxygen vacancies, respectively.

3.1.3. Manganese

Initial Mn microparticles are dense as shown in Fig. 4(a) and have a phase pure structure in Fig. 5(a). However, more than one oxidized phase appears during thermal oxidation. MnO and Mn3O4 co-exist in the oxidation phases and are both detected by XRD (Fig. 5(b)). The different expansion coefficients of Mn3O4 (8.8 × 10⁻⁶/K) [40,41] and MnO (3.45 × 10⁻⁶/K) [42] lead to delamination of the two phases shown in Fig. 4(b). The concentration gradient of oxygen from surface to the core of the microparticle causes an oxygen rich phase shell and a Mn rich core. Consequently, we can speculate that the layer on the surface is

![Fig. 2. XRD spectra of Co particle. (a) Initial (b) after oxidation (c) after one redox cycle (d) after five redox cycles at 700 °C.](image)

![Fig. 3. XRD spectra of CuO microparticles. (a) Initial (b) after reduction (c) after one redox cycle (d) after five redox cycles at 700 °C.](image)
Mn$_3$O$_4$ rich and the inner part of the microparticle is MnO rich. This is confirmed by EDS result in Fig. 4(d), the shell has less X-ray signals generated from Mn than the core. On the other hand, the delamination can be self-healed during the redox reaction. In Fig. 4(c) and (d) clearly show the gap between the shell and core diminishes and disappears, respectively. The self-healing mechanism can be explained: The delamination during oxidation leads to an air filled gap between the shell and core which has a high concentration of oxygen and zero concentration of Mn. Consequently, outward diffusion of oxygen from the core is difficult because of the high to low concentration gradient of oxygen from the gap to the core. This leads to a reducing phase of MnO instead of Mn in reduction reaction. Meanwhile, sintering effect will promote diffusion of Mn atom at 700 °C, which may fill in the gap after five cycles (Fig. 4(d)). Nevertheless, the delamination during oxidation may weaken mechanical strength of the Mn microparticles and hinders their applications in chemical looping. Moreover, the redox reactions are between MnO and Mn$_3$O$_4$, which has less oxygen capacity than looping between Mn and Mn$_3$O$_4$.

\[
\text{MnO} + \text{oxidizing gas} \rightarrow \text{Mn}_3\text{O}_4 \tag{6}
\]

\[
\text{Mn}_3\text{O}_4 + \text{reducing gas} \rightarrow \text{MnO} \tag{7}
\]
shown in Fig. 8(a), with an adsorption energy of 1.44 eV. The dis- 

tance between O1 atom and M1 is 2.305 Å, and the distance be-


tween O2 and Cu surface is relatively weak. In summary, the 

adsorption energy on Cu surface is lower compared with that on the other 

transition metals, which suggests that the attraction interaction 

between O2 and Cu surface is relatively weak. In summary, the 

adsorption energies of the four 3d metal systems follow a periodic 

rule that the Ni microparticles 

adsorption of O2. 

have found the O–O bond elongation upon O2 adsorption on 

Cu(100) surface, which correlates well with the adsorption energies, i.e., the 
migration of oxygen molecule to form bridging structure. 

For the O2/Cu(100) system, similarly, we label four distinct-

guishable surface Co atoms as M1, M2, M3 and M4 as shown in 

Fig. 8(b). For the clean surface, we make full atomic relaxation of the 
two outermost Cu layers on each side while keeping the middle 
three layers fixed at their bulk values. These calculations are 
required to minimize numerical errors and determine accurately 
adsorption energies. With respect to the bulk spacing of 2.10 Å, the 
obtained interlayer relaxations are 0.8% between layer 1 and 2, and 
0.5% between layer 2 and layer 3, which is in good agreement with experimental values (0.7% and 0.3% [43,44]). This relaxation has not 
change the symmetric structure of Cu(110) top surface, thus M1- 
O1-O2-M3 and M2-O1-O2-M4 have the same adsorption geomet-

ries and adsorption energy (0.85 eV). M1-O1-O2-M2 adsorption 
configuration is 0.18 eV less stable than the adsorption involving 
M3 or M4 site. 

For the O2/Mn(100) system, three stable adsorption configu-

rations are found. The strongest adsorption is O1 binding into the M1 
and O1 binding to M3 site to form M1-O1-O2-M3 configuration 
with an adsorption energy of 1.54 eV, as shown in Fig. 8(c). The second and third stable configurations are O1 binding on two closer 
Mn surface atoms sites to form M2-O1-O2-M4 and M1-O1-O2-M2 
structure. The adsorption energies for these two configurations are 
1.32 and 1.19 eV, respectively. 

For O2 adsorption on transition metal Ni (100) surface, we found 
the adsorption configuration is similar with O2 adsorption structure 
and orientation on transition metal Cu (100) surface. M1-O1-O2-

M3 and M2-O1-O2-M4 both are the most favorable adsorption 
structures for O2 molecule, and the adsorption energy is 1.26 eV. 
We showed the M1-O1-O2-M3 in Fig. 8(d). The second stable adsorption structure is M1-O1-O2-M2, which has an adsorption 
energy of 1.03 eV. Although the surface geometry of Ni(100) is 
similar with Cu(100), we found the adsorption energy for the most 
stable configuration on Ni(100) is about 0.4 eV higher than that on 
Cu(100) surface. Actually, from Table 1, we can see the O2 adsorp-
tion energy on Cu surface is lower compared with that on the other 
transition metals, which suggests that the attraction interaction 
between O2 and Cu surface is relatively weak. In summary, the 
adsorption energies of the four 3d metal systems follow a periodic 
trend, i.e., lower chemisorption energy as one proceeds from left to 
right in the 3d series: Mn (1.54 eV) > Co (1.44 eV) > Ni (1.26 eV) > Cu 
(0.85 eV), which indicates that the early transition metals tend to 
have stronger interaction with O2 than the late transition metals. 
We have found the O–O bond elongation upon O2 adsorption on 
Co, Cu, Mn and Ni surface, which suggests electron transfer from 
the metal surface to the O2 molecule. To quantify the electron 
transfer between the surface and O2, a Bader analysis was carried 
out for four most stable O2/metal systems as shown in Fig. 8. The 
results shows the adsorbed O2 was reduced to about −0.93, −0.67, −1.12, and −0.79 eV on Co, Cu, Mn and Ni surface, 
respectively. Early transition metal surfaces tend to transfer more charge to the O2 molecule than the late transition metal surface, which correlates well with the adsorption energies, i.e., the 
more the electron transfer for the surface to O2, the stronger the 
adsorption of O2. 

3.2. O2 adsorption on transition metals 

To explore the morphological evolution mechanism driven by 
surface reaction, we first modeled O2 chemisorption on the tran-
sition metal surface, which is the initial step of oxidation of tran-
sition metals. 

For the O2/Co(100) system, we label the surface Co atom closest 
to the oxygen molecule as M1, the Co atom closest to M1 as M2, the Co atom closest to M2 as M3, and the Co atom closest to M3 as M4. 
The two oxygen atoms are labelled as O1 and O2. Based on this 
definition, we can describe oxygen adsorption configurations on Co surface. Various adsorption configurations are modeled, optimized 
and calculated as reported in Table 1. For the considered configu-
rations, the oxygen molecule shows a strong interaction with the Co 
(001) surface. In the most favorable case, one oxygen atom adsorbs 
at the M1 site while the other oxygen atom binds to the M3 site as 
shown in Fig. 8(a), with an adsorption energy of 1.44 eV. The dis-
tance between O1 atom and M1 is 2.305 Å, and the distance be-
tween O2 atom and M2 is 2.308 Å. An elongation in the O−O 
distance of adsorbed O2 may be expected during oxygen activation. 
In this case, the O−O distance is 0.21 Å larger than the O−O bond of 
oxygen molecule in gas phase. In the second stable configuration, 
M1-O1-O2-M2, oxygen molecule is bonded to M1 and M2 site with 
O−O bond of 2.411 Å and 2.408 Å, respectively. M2-O1-O2-M4 
configuration is found to be 0.19 eV less stable than M1-O1-O2-M3 
configuration. The third stable configuration M2-O1-O2-M4 is 
about 0.61 eV less stable than M1-O1-O2-M3. We also have per-
fomed calculations on the perpendicular adsorption of oxygen 
molecule on one surface Co atom site, but this led to spontaneous 

adsorption of O2. 

3.3. O2 dissociation and diffusion 

Adsorption of O2 is followed by breaking of the coordinated O−O 
bond with electron transfer. Thus, the resulting structure will be 
two oxygen adatoms (2O\textsubscript{ad}). Oxygen adatom has higher activity compared to O2 molecule. To build up a systematic study of oxygen 
atom interactions on the metal surface, we have calculated the 
adsorption energies of O on Co, Cu, Mn, Ni (110) surface for a range 
of coverages θ. We define θ as ratio of the number of adsorbed
atoms to the number of atoms in an ideal substrate layer. For on-surface adsorption at each of these coverages, the oxygen adatoms are placed in the surface hollow site, metal-metal bridge site and metal atop sites.

The average adsorption energy per oxygen atom \( E_{\text{ad}}(O) \) is calculated using the equation below:

\[
E_{\text{ad}}(O) = \frac{1}{N_O} \left( E_M + N_O E_O - E_{O-M} \right)
\]

where \( N_O \) is the number of oxygen atoms in the surface supercell. The total energies of the adsorbate-surface system, the clean transition metal surface, and the free oxygen atom are represented by \( E_{O-M}, E_M \), and \( E_O \), respectively. The average adsorption energy can alternatively be referred to the dissociation energy of the \( O_2 \) molecule by subtracting half the binding energy of \( O_2 \). The calculated average \( O \) adsorption energies are presented in Table 2.

We can see the adsorption energy of \( O \) on transition metal almost keep constant at low coverage (0.06–0.25 ML), but thereafter decreases with increasing coverage (0.25–1 ML), indicating a repulsive interaction between surface \( O \) ions. After dissociation, we found the oxygen ion binding energies on transition metal surfaces are similar when coverage is high. In addition, we found that the binding energies of \( O \) at subsurface sites change slightly when the coverage is from 0.25 to 1.00 ML, suggesting that the repulsive effect between the subsurface oxygen and the energy needed to

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**Fig. 6.** SEM images of Ni microparticles (a) cross section of an initial microparticle; (b) cross section of an oxidized microparticle; (c) cross section of a microparticle after one redox reaction cycle; (d) cross section of a microparticle after five redox reaction cycles; insets: EDS mapping with blue and white representing Ni and O, respectively; (e) surface of the microparticle after one redox reaction cycle; (f) surface of the microparticle after five redox reaction cycles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
deform the transition metal lattice which usually decreases with increasing coverage interact each other.

Based on the stable adsorption structure before and after O$_2$ dissociation, we can explore the O$_2$ dissociation and initial oxygen ion diffusion process by NEB method. Vibrational frequencies were calculated to locate each transition state. For example, in the hollow dissociation path, the adsorbed O$_2$ molecule (M1-O1-O2-M3 configuration) migrates into hollow site, then dissociates into two oxygen ions. In this paper, we only show the most favorable dissociation and diffusion path for comparison (Fig. 9).

For the Co(100) surface, two transition states were located as shown in Fig. 9. The first transition state TS1 is obtained in the dissociation of O1–O2 bond of oxygen molecule, and the second transition state TS2 was found when dissociated O ion diffusion into the subsurface to form a three-fold Co-O structure. The reaction barrier for the first transition state is 0.5 eV, suggesting Co has a high activity for O$_2$ dissociation. For Cu, Mn and Ni (100) surfaces, the structures of the transition states found were similar to TS1/Co system, and the barriers were calculated to be 0.85, 0.28, and 0.73 eV, respectively. Therefore, Co, Mn and Ni are more active for O$_2$ dissociation thus more favorable to produce O ion for redox reaction in CLC system. From Fig. 9, we also can see the oxygen ion diffusion barrier in Cu is lower than O$_2$ dissociation barrier, which results in that the surface lattice oxygen atoms of Cu oxide are easy to diffuse and release. It is notable that the O$_2$ dissociation process on Mn and Co surfaces is very exothermic, releasing 2.6 eV/O$_2$ of heat and 1.5 eV/O$_2$ of heat, respectively. Given the relative magnitudes of the adsorption energy, dissociation energy barrier and overall reaction exothermicity, adsorbed O$_2$ molecules will dissociate, rather than desorb, upon heating of the surface to form two chemisorbed O species. The surface relaxation and reconstruction indicate a high level of flexibility during the dissociation process, especially after the transition state. It also indicates substantial involvement of surface Mn and Co atoms in facilitating the scission of the O–O bond. For comparison, we also plot the oxygen dissociation energy profiles using the second favorable adsorption configuration as initial states as shown in Fig. 9 (dash lines). We can see the O$_2$ dissociation barrier for M1-O1-O2-M2 path on Co is ~0.3 eV lower than M1-O1-O2-M3 path, and M1-O1-O2-M4 path on Mn is ~0.5 eV lower than M1-O1-O2-M3 path. However, for Ni and Cu, the O$_2$ dissociation barriers via M1-O1-O2-M2 path and M1-O1-O2-M3 path are close.

![Fig. 7. XRD spectra of Ni particle. (a) Initial (b) after oxidation (c) after one redox cycle (d) after five redox cycles at 700 °C.](image)

![Fig. 8. The most stable adsorption structures of O$_2$ on transition metals (Co, Cu, Mn, Ni). The distance of O–O bond and O–metal bond are indicated (Å). Upper: side view; bottom: top view.](image)
In general, the reaction barriers will keep the same trend with the reaction energies. Moreover, the total reaction barriers \( \Delta E_{\text{a,t}} \) and the reaction energies \( \Delta E_{\text{r}} \) follow a linear relationship for the O–O bond scission of \( \text{O}_2 \). The modified BEP relationship was developed as: \( y = 0.275x + 0.962 \) as shown in Fig. 10. This relationship is significant in estimating reaction barriers on other transition metal surfaces for the O–O bond scission of \( \text{O}_2 \).

We further analyze the O diffusion on the transition metal surfaces. In Fig. 9, we can see oxygen ion diffusion barrier for Co, Mn and Ni surfaces are relatively low (<1 eV). However, the diffusion barrier for Ni surface are higher 1 eV, which results in lower oxygen mobility compared with Co, Mn and Ni. However, because Ni surface can be easily oxidized to NiO due to high activity of Ni for \( \text{O}_2 \) dissociation, it is necessary to investigate the oxygen vacancy formation in Ni oxide. Also, we investigate the vacancy formation in CoO, \( \text{Co}_2\text{O}_4 \), CuO, \( \text{Cu}_2\text{O} \), MnO, \( \text{Mn}_2\text{O}_4 \) for understanding the oxygen role in the morphological evolution of these transition metal surface.

One oxygen vacancy was created in the transition metal oxide slab and the vacancy formation energy with structural relaxation evaluated at depths of oxygen vacancy to the outmost surface. The vacancy formation energy on the surface and on the subsurface as a function of depth for transition metal oxides are plotted as shown in Fig. 11. From Fig. 11, we found that the formation energies increase with the depth. In the outermost surface, the oxygen vacancy formation energy is lower than 5 eV for all these transition metal oxides. For CuO, \( \text{Co}_2\text{O}_4 \) and \( \text{Mn}_2\text{O}_4 \), the vacancy formation energy is lower than 4 eV even the depth is larger than 7 Å. The low vacancy formation energy makes them feasible CLOU oxygen carrier materials.

For \( \text{Cu}_2\text{O}, \text{MnO} \) and \( \text{CoO} \), the vacancy formation energy of larger than 4.5 eV occurs predominantly when the depth is larger than 5 Å. However, for NiO, the vacancy formation energy is higher than 4.5 eV even the vacancy is close to the outmost surface. It indicates it is unfavorable for NiO to form surface defect during redox reaction. This is consistent with SEM observation in Fig. 6(c) and (d). Therefore, to apply Ni as oxygen carrier material, it is necessary to
add suitable support which can facilitate the oxygen vacancy formation. We notice that the vacancy formation energy in higher oxidation states is lower than the lower oxidation states. The vacancy formation energy in Co$_3$O$_4$ is lower than in CoO, thus the reduction from Co$_3$O$_4$ to CoO is more energy favorable than from Co to Co, this is consistent with our XRD results in Fig. 2. Similarly, the vacancy formation energy in CuO is lower than in Cu$_2$O, which suggests CuO reduction in CLOU process is more likely to result in Cu$_2$O rather than Cu, this explains our XRD data in Fig. 3. In Mn system, the vacancy formation energy in Mn$_3$O$_4$ is lower than in MnO, consequently MnO, instead of Mn, becomes the reducing product in chemical looping reactions, as seen in Fig. 5.

4. Conclusions

In this work, we compared the structural changes in transition metal oxide particles at a nanoscale during redox reactions, which affect their performance on a macroscopic level. This study focused on the cyclic oxidation-reduction reactions of Co, Cu, Ni and Mn systems that are transition metals used in chemical looping technology applications. Upon oxidation, dense Co microparticles converted to Co$_3$O$_4$ with the morphology changed to a porous structure. This was ascribed to processes associated with ion transport, diffusion, and volume expansion. The Co microparticles were oxidized to Co$_3$O$_4$ upon cyclic oxidation with increasing CoO impurity. CuO is desired to be reduced to Cu$_2$O during reduction and oxidized to CuO within technology interest. The atomistic thermodynamics methods and density functional theory calculations show Cu activity is weaker than Mn, Co and Ni. Mn microparticles were oxidized to a mixed phases of MnO and Mn$_3$O$_4$, which causes severe delamination during oxidation. This delamination can be self-healed during reduction. Ni microparticles can promptly react with air to form NiO crystals on the surface. These crystals had very little oxygen defects due to high oxygen diffusion barrier, which leads to dense Ni surface. Consequently, Ni microparticles in CLC applications are mostly limited to surface activities. The O$_2$ adsorption study indicates that the early transition metals tend to have stronger interaction with O$_2$ than the late transition metals. 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 to form defective nanostructures. These findings together with the morphological changes during the redox reactions in transition metal systems provide an insight into the reaction mechanism at atomic level. They also form a fundamental basis for understanding transformations occurring during the redox process for transition metal oxide materials that are of value to metal oxide material selection and design for chemical looping applications.

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References


