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Understanding CuO-support interaction in Cu-based oxygen carriers at a microcosmic level

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Abstract

Oxygen carrier (OC) which is able to release and absorb O_2 repeatedly is the key issue of chemical looping with oxygen uncoupling (CLOU). Active component (typically, metal oxide) is usually supported by inert component to enhance the thermal stability and mechanical strength of OC particle. A clear understanding on the interactions of different phases (active material and support material) in OC particles could help rationalize the design of high-performance OC. In this work, periodical density functional theory (DFT) calculation, thermo-mechanical analysis (TMA), and isothermal decomposition experiments were jointly conducted to gain insight into the effects of different supports (TiO₂, ZrO₂, CuAl₂O₄ and MgAl₂O₄) on the Cu-based OC performance in terms of sintering resistance and decomposition reactivity. CuO nanocluster was positioned on support slab with periodical boundary condition to simulate the impregnation-derived OCs. First, the adsorption energies of CuO nanocluster on four supports, which can be used to assess the sintering resistance characteristics of the supports, were calculated via DFT. It was found that ZrO_2 is most conducive to sintering resistance of OC particles, followed by CuAl₂O₄, MgAl₂O₄, and TiO₂ (in that order). Then, the energy barriers of oxygen release process were examined to evaluate the effect of support on the OC decomposition reactivity. Results showed that the desorption of O₂ molecule formed on the OC surface is the rate-determining step for all supported CuO. The O₂ desorption energy barriers increases in the order of CuO/CuAl₂O₄ < CuO/ZrO₂ < CuO/MgAl₂O₄ < CuO/TiO₂, showing CuAl₂O₄ as support is in best favor of CuO decomposition among four supports. The effects of support on OC performance were explained by the strong interactions between CuO nanocluster and support slab, resulting in significant electron redistribution and microstructure changes of CuO nanocluster. The microcosmic mechanism understandings to sintering resistance and decomposition reactivity were well supported by TMA and isothermal decomposition experiments, respectively.

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Keywords: Density functional theory; Sintering resistance; Reactivity; Chemical looping with oxygen uncoupling; Rational design of oxygen carrier

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1. Introduction

CO₂ emission from fossil fuel combustion has been accepted to be a major factor contributing to the climate change. Several CO₂ capture and storage (CCS) technologies have been developed to reduce the CO₂ emission. Chemical-looping combustion (CLC) is a type of low-cost CO₂ capture technology and becomes a very promising fossil fuels combustion technology [1]. However, because the solid-solid reaction between char and oxygen carrier particles is very slow in CLC of solid fuels (e.g., coal), coal must be gasified (in-situ or exsitu). For in-situ gasification CLC the char gasification is a rate-limiting step, resulting in low combustion efficiency and CO_2 capture efficiency [1]. A more promising CLC process called chemical looping with oxygen uncoupling (CLOU) was proposed [2] as a solution, which takes advantage of some special oxygen carriers being able to release O2 at high temperature (800-1000°C) and oxygendeficient atmospheres. In CLOU, the OC particles are decomposed and release gaseous O₂ in fuel reactor; the presence of O₂ facilitates greatly the fuel conversion, producing CO2 and H2O without N₂; the reduced OC particles are then sent to another reactor (air reactor) and re-oxidized by the air.

The OC material, which is able to release and absorb O₂ repeatedly and bear high temperature without sintering/agglomeration and attrition in redox cycles, is the key issue of CLOU. Previous studies [3–5] have focused on the OC selection and optimization. Copper-based OC has been widely used as the OCs due to its high reactivity, high oxygen transport capacity and relatively low cost. However, the CuO suffers from tendency toward sintering at temperature suitable for CLOU, which may lead to defluidization and low reactivity of the OC particles. Generally, CuO was supported by inert materials to withstand the high temperatures (900-1000°C). To date, a lot of materials including SiO₂, TiO₂, ZrO₂, CuAl₂O₄ and MgAl₂O₄ [6–10] have been studied to use as the support for CuO due to their thermal stability and high melting point. However, previous studies [7,10,11] showed that OCs with various supports present different CLOU characteristics (such as sintering resistance and reactivity). Thus, the selection of support material plays a key role in performance enhancement of the Cu-based OCs. To date, the support selection is mainly based on trial-and-error experiments. However, the microcosmic mechanism of interactions between CuO and support at the atomic level were rarely reported [12]. The fundamental studies on these characteristics of the OCs can be very useful for understanding the key principle determining the performance of Cu-based OCs, and then guiding the best ways for the performance enhancement or rationalizing the design of the high-performance OCs instead of an empirical design. Previous understanding [13] on CuO-support interaction at a microcosmic level is mainly based on the analysis of simplified grain growth equation. The interactions force between CuO and support was simplified as the surface energy of support material in their analysis. As it is very difficult to get the atomic level information by these previous analysis, a density functional theory (DFT) calculation was used in this study.

DFT calculations have been successfully used to determine the properties (both physical and chemical) of the synthetic material, such as the supported catalyst and the OCs for CLC. Li et al. [14] studied the role of TiO_2 in improving the reactivity of iron oxide in CLC using DFT calculations. They observed that TiO2 can significantly enhance the diffusivity of O^{2-} in the iron oxide. Qin et al. [15] studied the effects of Al₂O₃, ZrO₂ and MgO support on Fe_2O_3 oxygen carrier for the CLC. They found that the presence of support could activate Fe₂O₃ for oxidizing CO into CO₂ and reduce the energy barrier of reaction. All of the studies based on either experiments or DFT calculation suggested the interactions between the active phase materials and the supports in the mixed-metal oxides might result in better comprehensive performance of OC. However, the underlying mechanism has not been comprehensively studied. The objective of this study is to investigate the effect of different supports on the sintering resistance and reactivity of Cu-based OC at a microcosmic level. First, DFT calculation was conducted to clarify the role of support in determining the sintering resistance of CuO. The physical and chemical properties of the supported CuO were discussed. Next, an insight into the oxygen release mechanisms of CuO/TiO₂, CuO/ZrO₂, CuO/CuAl₂O₄ and CuO/MgAl₂O₄ was gained. Meanwhile, the reactivity of CuO on different supports was studied. Last, the thermomechanical analysis (TMA) and isothermal experiments of the four OCs were carried out to testify the DFT calculation result.

2. Computational and experimental details

2.1. DFT model setup and calculation method

The nonlocal generalized gradient approximation (GGA) function was used in the DFT calculation by means of Perdew–Wang (PW91) correlation functional in CASTEP (Cambridge Serial Total Energy Package) [16]. Periodic boundary conditions were applied to the unit cells of TiO₂, ZrO₂, CuAl₂O₄ and MgAl₂O₄ across all three dimensions, and then they were optimized. The Brillouin zone integrations were performed using Monkhorst-Pack type meshes. The energy cutoff (E_{cut}) employed in all calculations was 400 eV together with a k-points separation of 0.04. To accurately describe the strong electron correlation



Fig. 1. Atomic structures of (a) (2×1) TiO₂ (110), (b) (2×2) ZrO₂ (100), (c) (2×1) CuAl₂O₄ (100) and (d) (2×1) MgAl₂O₄ (100) slab.

in Ti, the Hubbard parameter (U) was introduced for the Ti 3d orbitals according to the well-known GGA +U method [17]. We applied U = 4.5 eV to the Ti 3d, as suggested by previous studies [18,19]. These calculation model and parameters were determined via comparative study and convergence test. The calculated lattice parameters of TiO₂, ZrO₂, CuAl₂O₄ and MgAl₂O₄ agreed well with the experimental data (as listed in Table S1 of Supplemental Material (SM)), indicating the validity of parameters setting in this work.

TiO₂ (110), ZrO₂ (100), CuAl₂O₄ (100) and MgAl₂O₄ (100) surfaces were selected as the support surfaces in this work, because they are the stable low-index surfaces and directly comparable. The surfaces were cleaved from the corresponding optimized unit cells of the supports, respectively. Six-layer (2×1) TiO₂ (110) slab, four-layer (2×2) ZrO_2 (100), three-layer (2 × 1) CuAl₂O₄ (100) and (2×1) MgAl₂O₄ (100) slab were built, as can be seen in Fig. 1. The calculated surface energy of each of the four surface cells was converged to a value with an error of $\sim 3\%$, which was acceptable. A total of 20 Å of vacuum gap was used above the surface, and the vacuum gap is large enough to prevent the slab-slab interactions. Subsequently, with the bottom three layers fixed, surfaces were fully relaxed until the threshold values of energy, displacement and force were reached (0.01 meV, 0.001 Å and 0.03 eV/Å, respectively).

Complete LST/QST approach (linear/quadratic synchronous transit) [20] was used in the work to calculate the energy barriers (ΔE_b) of different oxygen release steps and further to determine the oxygen release reactivity of OC. The value of ΔE_b could be calculated as below [12]:

$$\Delta E_b = E(\mathrm{TS}) - E(\mathrm{IS}) \tag{1}$$

where E(TS) and E(IS) are the energies of the transition state (TS) and the initial states (IS), respectively.

For more details on DFT parameter selection and accuracy verification, see Section S1, SM.

2.2. Materials and experiments

To ensure the experiment materials in correspondence with the DFT calculation models, the OCs (CuO/TiO₂, CuO/ZrO₂, CuO/CuAl₂O₄ and CuO/MgAl₂O₄) with CuO loading of ca. 10 wt.% were synthesized by impregnation method. A detailed description of the impregnation preparation method can be found in Section S2, SM.

To study the effects of the supports on the sintering properties of OCs, TMA experiments were performed (SETSYS EVO TMA 18). The OCs lay 2 mm thick in the ceramic crucible, then pressed by the probe with a 2 g load. The sample was first heated to 600° C at 20° C / min, then the heating rate was changed to 10° C / min to observe the sintering process.

To study the effects of the supports on the reactivity of OCs, isothermal decomposition experiments were performed in a thermogravimetric analyzer (TGA, WCT-1D). To evaluate reaction kinetics, it was important to ensure that all transport limitations (heat and mass) were absent. For our TGA, when the gas flow rate was higher than 60 ml/min and loading mass less than 28 mg, it is considered that the heat and mass transport limitations were eliminated. So, during the isothermal experiments, twenty milligrams of OCs were first heated from room temperature to 900°C, 925°C and 950°C under an air flow of 70 ml/min, respectively. When the temperature was stable, the atmosphere was switched to a N₂ (99.999 %) flow of 70 ml/min for oxygen release. The sample weight and the reaction temperature were recorded continuously during the TGA experiment. The oxygen release rate dX/dt (mg O₂/(min·mg OC)) was used to evaluate the reactivity of OC and it was calculated on the basis of the relationship between the sample conversion and reaction time:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{\mathrm{d}m}{m_{\mathrm{ox}}\mathrm{d}t} \times 60 \times 100\% \tag{2}$$

where m_{ox} is the total mass of OC (fully oxidized) before reaction, and *m* was the instantaneous mass at time *t* of OC in reaction.



Fig. 2. A schematic view for the oxygen release of supported CuO (a) and the atomic structure of the Cu_4O_4 nanocluster (b). The bond lengths are presented in Å.

Sections S2 and S3 (in SM) presented the detailed experimental processes in the TMA and TGA, respectively.

3. Results and discussion

3.1. Adsorption of Cu_4O_4 nanocluster on the supports

Figure 2a shows the schematic view for the oxygen release of supported CuO. The high temperature and low oxygen partial pressure provide the driving force for oxygen release. A cubic Cu_4O_4 nanocluster [12] was used to simulate the active phase that adheres to the support.

Figure 2b shows the Cu_4O_4 nanocluster, which was optimized in a large cubic box of 20 Å × 20 Å × 20 Å to eliminate the effect of periodicity. This structure is complex enough for our study to compare the impact of different support, and greater number of atoms will create too much work without much benefits for the focus of our research. The calculated length of the Cu-O bond in the Cu₄O₄ nanocluster is 1.952 Å, which agrees with the experimental result (1.95 Å) [21].

The models of supported CuO nanoclusters were also periodic, as can be seen in Fig. 3. Adsorp-

tion energies (ΔE_{ads}) of the CuO nanocluster on the supports, which reflects the stability of the cluster on the support surface, were calculated according to Eq. (3) below

$$\Delta E_{\rm ads} = E_{\rm CuO-surf} - (E_{\rm surf} + E_{\rm CuO}) \tag{3}$$

where E_{surf} and E_{CuO} are the total energies of the bare support surfaces and the free CuO cluster, and $E_{CuO-surf}$ is the total energy of the CuO cluster supported on the surface. Four supported CuO models (CuO/TiO2, CuO/ZrO2, CuO/CuAl2O4 and $CuO/MgAl_2O_4$) were built through the following procedure. First, the Cu₄O₄ nanocluster is deposited on the optimized support surface. Next, the obtained systems were optimized again, keeping cell volume, shape and axes fixed. Figure 3 shows the atomic structure of the Cu₄O₄ supported on the four supports. It was found that the Cu_4O_4 cluster makes new bonds with the support surfaces, where two Cu atoms from the cluster make bonds with two O atoms on the support surface, and two O atoms from the cluster bind with the two metal atoms on the support surface (Ti, Zr and Al for the corresponding surfaces, respectively).

3.2. Effect of CuO-support interactions on sintering resistance

Figure 4 shows the electron density of the CuO/TiO₂, CuO/ZrO_2 , $CuO/CuAl_2O_4$ and CuO/MgAl₂O₄. It can be seen that some electrons accumulated around the O_{c-3} and O_{c-4} atoms. This is mainly ascribed to the effects of the surface metal sites (Ti, Zr and Al) of supports. Meanwhile, some electron density depletion is visible near the cluster Cu_{c-1} and Cu_{c-2} atoms, which make bonds with surface O atoms (front view of the structures in Fig. 4). The charges exchanges between the atoms in CuO cluster or support surface result in significant electron redistribution and microstructure changes of CuO nanocluster, indicating a strong interaction between CuO and support. The lengths of the new formed Cu-O or O-Me_s



Fig. 3. The atomic structure of the Cu_4O_4 nanocluster supported on (a) TiO_2 (110), (b) ZrO_2 (100), (c) $CuAl_2O_4$ (100) and (d) $MgAl_2O_4$ (100) slab.



Fig. 4. Front view and side view of the calculated electron density profiles for the Cu_4O_4 supported on (a) TiO₂ (110), (b) ZrO₂ (100), (c) $CuAl_2O_4$ (100) and (d) MgAl₂O₄ (100). The blue and red regions represent the electron gain and depletion, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(Ti_s, Zr_s, Al_s) bonds between Cu₄O₄ nanocluster and supports are listed in Table 1. From Table 1, CuO/TiO₂ has a longer new formed bond compared to these of CuO/ZrO₂, CuO/CuAl₂O₄ and CuO/MgAl₂O₄, indicating that the interactions between CuO and TiO₂ are relatively weaker. The interaction between CuO and support can also be evaluated by ΔE_{ads} of CuO on support.

The calculated ΔE_{ads} were -2.96 eV, -5.14 eV, -4.25 eV and -5.42 eV for CuO/TiO₂, CuO/ZrO₂, CuO/CuAl₂O₄ and CuO/MgAl₂O₄, respec-

tively. ΔE_{ads} has the order of CuO/TiO₂<CuO/ CuAl₂O₄<CuO/ZrO₂<CuO/MgAl₂O₄. Larger negative ΔE_{ads} strengthens the adsorption of CuO nanoclusters on the support surface and prevents the migration and aggregation of the small CuO nanoclusters on the support surface, which limits the CuO nanoclusters growth and agglomeration, and then eventually enhances the sintering resistance of the particle. As shown in the DFT calculation results, MgAl₂O₄, ZrO₂ and CuAl₂O₄ as support show better sintering resistance than TiO₂. This can be confirmed by the previous experiment results [7] and our TMA experiment results.

Xu et al. [22] used the surface energy of support materials to assess the effect of various support materials on the sintering resistance. They found that $MgAl_2O_4$ and ZrO_2 show higher surface energies and better sintering resistance than TiO_2 . In fact, we found that ΔE_{ads} is also related to the calculated surface energies of the supports (0.84, 1.69, 1.36 and 2.14 J/m², respectively for TiO₂, ZrO₂, CuAl₂O₄ and MgAl₂O₄). Factually, higher surface energy of support results in higher ΔE_{ads} . Compared to the surface energy of support materials, the adsorption strength between CuO and support materials can give a more intuitive reflection to their sintering resistance. Therefore, ΔE_{ads} can be an indicator to assess the sintering resistance characteristic, and can be used to reasonably select the high performance OCs.

3.3. Effect of CuO-support interactions on the CuO decomposition reactivity

Previous study [7] found that CuO supported with different supports performed various reactivity, though they were prepared by the same method. It indicated the CuO-support interactions might also affect the CuO decomposition reactivity. To elaborate the effect of CuO-support interactions on the CuO decomposition reactivity, the oxygen release mechanism of CuO nanoclusture supported on TiO₂, ZrO₂, CuAl₂O₄ and MgAl₂O₄ slab was investigated by the DFT calculation.

We have found that the formation and desorption processes of O_2 are the rate-limiting steps for CuO decomposition, but the diffusion of the O

Table 1

Bond lengths of Cu-O bonds in the CuO nanoclusters supported on different materials; O_c and Cu_c are the O and Cu atoms in the CuO cluster. Me_s (Ti_s, Zr_s, Al_s), Cu_s and O_s are the corresponding atoms at the support surfaces.

	CuO/TiO ₂	CuO/ZrO ₂	CuO/CuAl ₂ O ₄	CuO/MgAl ₂ O ₄
$O_{c-1}-Me_s(Å)$	1.900	1.872	1.896	1.870
O _{c-2} –Me _s (Å)	1.912	1.873	1.896	1.870
O _s –Cu _{c-3} (Å)	2.004	2.042	1.894	1.925
O _s –Cu _{c-4} (Å)	2.004	2.043	1.893	1.925
$\Delta E_{\rm ad} \ ({\rm eV})$	-2.96	-5.14	-4.25	-5.42



Fig. 5. The structures of the IS – initial states, TS – transition states, IM – intermediate states and FS – final states for the O₂ formation and O₂ desorption processes of CuO supported on TiO₂, ZrO₂, CuO/CuAl₂O₄ and MgAl₂O₄. The bond lengths are presented in Å.

anion from lattice to surface in the CuO slab is not [12]. Therefore, the study only focuses on the formation and desorption processes of O_2 from CuO supported by different supports.

In the calculation, the possible oxygen release process of CuO/support was determined. Taken CuO/TiO_2 as an example, the optimized Cu_4O_4/TiO_2 structure (see Fig. 3a or Fig. 5-IS) was used as the initial state (IS) of process. The outmost O atoms (O_{c-1} and O_{c-2}) in the Cu₄O₄/TiO₂ were regarded as the most possible released O atoms, because they can migrate more easily than the other O atoms. First, O_{c-1} and O_{c-2} were removed from the IS system. Second, an O₂ molecule was located above the Cu₄O₂/TiO₂. Different locating positions of the O_2 molecule were tested (9 points from 2 Å to 10 Å above the Cu₄O₂/TiO₂). It was found that if the initial distance is shorter than about 5 Å, the O₂ molecule tends to be adsorbed on Cu₄O₂ nanocluster and then stabilizes after the structure was optimized. Yet if the initial distance is longer than 5 Å, the O_2 molecule does not have this trend. Therefore, we located O_2 molecule about 3 Å above the Cu₄O₂/TiO₂ to initiate the calculation and obtain chemisorbed O2 molecule model, as shown in Fig. 5-IM. In Fig. 5-IM, the O₂ molecule is bonded with two Cu atoms in Cu_4O_2 cluster with bond lengths of 1.821 A and 1.821 A, forming a bridging adsorbed O_2 molecule with bond length of 1.408 A. The adsorption energy of the O_2 molecule is as high as 3.42 eV, indicating the O_2 molecule is chemisorbed on the cluster. The structure was set as the intermediate state (IM) of the oxygen release process. Next, the chemisorbed O_2 molecule in IM system was removed and then placed 7 Å above the Cu_4O_2/TiO_2 (ensuring the O_2 molecule has little interaction with the Cu_4O_2/TiO_2). The structure was then optimized and set as final state (FS), as in Fig. 5-FS. It was found that the bond length of the O_2 molecule gets shortened to 1.248 Å, which is similar to the bond lengths in free O_2 molecules (1.225 Å). Thus, in FS, the O_2 molecule escapes to gas phase.

TS (transition state) search calculation was performed to obtain the TS structures and the corresponding energy barriers. From Fig. 5, we obtained the whole CuO oxygen release process, which includes the formation (IS \rightarrow IM) and desorption of O_2 (IM \rightarrow FS). When beginning with the IS, two O atoms of the Cu₄O₄ cluster break two of the Cu-O bonds with bond lengths of 1.889 A. The O atoms then migrate from the initial sites and approach to each other. The TS structure is shown in Fig. 5-TS. Subsequently, a chemisorbed O2 complex is formed in IM. In O₂ desorption process, the chemisorbed O₂ complex breaks the bonds with the Cu_4O_2 cluster, and gradually moves away from the surface and forms a free O_2 molecule. The calculated energy barrier of O₂ formation is 1.78 eV and the corresponding reaction energy is -0.04 eV. Meanwhile, the required O_2 desorption energy is 3.45 eV, which is equal to the corresponding O_2 desorption energy barrier. The energy barrier of O_2 desorption is higher than that of O₂ formation, indicating that the O₂ desorption is the rate limiting step in the CuO oxygen release. It should be mentioned that the energy barrier of O_2 desorption for free Cu₄O₄ cluster is higher than the pure CuO bulk surface [12], which may be the reason why Cu_4O_4 cluster losing oxygen is much harder than CuO bulk.

For comparison, we studied the oxygen release processes of the CuO/ZrO₂, CuO/CuAl₂O₄ and the CuO/MgAl₂O₄. Similar to the case of CuO/TiO₂, the oxygen release also proceeded in two steps, that is the formation and desorption of O_2 , as seen in Fig. 5. The corresponding potential energy profiles are presented in Fig. 6. From Fig. 6, we observed that in the O_2 formation process, the reactions are unfavorable endothermic for the CuO/ZrO₂, CuO/CuAl₂O₄ and CuO/MgAl₂O₄. The corresponding reaction energies are 0.61 eV, 0.71 eV and 1.01 eV, respectively. However, it is exothermic for CuO/ TiO₂, and the reaction energy is -0.04 eV. The O₂ formation energy barriers are 1.78 eV (with the support of TiO₂), 2.09 eV (with ZrO_2), 2.21 eV (with $CuAl_2O_4$) and 2.25 eV (with $MgAl_2O_4$). In the O_2 desorption process, the energy barriers are 3.45 eV, 3.33 eV, 3.28 eV



Fig. 6. Potential energy profiles of oxygen release processes of CuO/TiO₂, CuO/ZrO₂, CuO/CuAl₂O₄ and CuO/MgAl₂O₄, and corresponding energy barriers of O₂ formation and of O₂ desorption.

and 3.41 eV, respectively for CuO/TiO₂, CuO/ZrO₂, CuO/CuAl₂O₄ and CuO/MgAl₂O₄. These results showed the same rule that the energy barrier of O₂ desorption is higher than that of O₂ formation, indicating that the O₂ desorption is the rate-limiting step for all these four OCs during their oxygen release processes. It should be mentioned that this rate-limiting step is an ab initio simulation result at the molecular level. The macroscopic oxygen release process of OCs particles also include a complex kinetics process of mass transport, this process after the O₂ desorption is not in the consideration of this paper.

Comparing the energy barriers in the rate-limiting O_2 desorption process, the values increased in the order of CuO/CuAl₂O₄ (3.28 eV) < CuO/ZrO₂ (3.33 eV) < CuO/MgAl₂O₄ (3.41 eV) < CuO/TiO₂ (3.45 eV). The lower energy barrier implies that the reaction requires a lower thermodynamic driven force. Therefore, CuO/CuAl₂O₄ will have relatively higher decomposition reactivity while the CuO/TiO₂ will be relatively lower.

3.4. Transformation temperature of the supported OCs by TMA experiments

We performed TMA experiments to determine the transformation temperature of different OCs (For further TMA experimental data see Section S2, SM). From Fig. 7, the transformation temperature of CuO/TiO₂ is relatively lower than the others, which means that the intense surface change of CuO/TiO₂ will happen in a relatively lower temperature. Meanwhile, the sintering temperature of CuO/CuAl₂O₄, CuO/ZrO₂ and CuO/MgAl₂O₄ will be relatively higher than that of CuO/TiO₂. The result was approximately consistent with the DFT calculation results.



Fig. 7. Transformation temperature of CuO/TiO_2 , $CuO/CuAl_2O_4$, CuO/ZrO_2 and $CuO/MgAl_2O_4$.



Fig. 8. Conversion rate of CuO for CuO/TiO₂, CuO/CuAl₂O₄, CuO/ZrO₂ and CuO/MgAl₂O₄ at 925°C.

3.5. Oxygen release rates of the supported OCs by isothermal decomposition experiments

We performed isothermal decomposition experiments to determine the oxygen release rates of CuO with different supports. Figure 8 shows the oxygen release rates at 925 °C as an example (for other temperatures see Section S3, SM). As can be seen from Fig. 8, at the beginning of the reaction, the oxygen release rates of CuO with different supports were very close to each other. The explanation for this phenomenon is that the decomposition of CuO mainly occurs on the particle surface where the support effect was relatively weak in the initial conversion period. In the next conversion period, the support effect was highlighted, with the different oxygen release rates. CuO/CuAl₂O₄ performs the highest conversion rate, followed by CuO/ZrO₂, CuO/MgAl₂O₄ and CuO/TiO₂. It implies that when supported by CuAl₂O₄, CuO shows higher reactivity. The results agree well with the DFT calculation results, which concluded that CuO cluster supported by CuAl₂O₄ had lower oxygen release energy barriers. During the final

conversion period, the conversion rate of $CuO/CuAl_2O_4$ still retained a small value, which may be attributed to the quite slower release oxygen of $CuAl_2O_4$ at high temperatures [23].

4. Conclusions

In this work we have investigated the interaction between CuO and four supports (TiO₂, ZrO₂, CuAl₂O₄ and MgAl₂O₄) at the microcosmic level via DFT calculation. The adsorption energies of CuO nanocluster on the four supports were -2.96, -5.14, -4.25 and -5.42 eV, respectively. DFT calculations indicated that the adsorption energy of CuO nanocluster on the TiO₂ is the lowest, which determines it easily suffering from sintering. While CuO nanocluster has strong interaction with the ZrO₂, CuAl₂O₄ and MgAl₂O₄, which is in favor of the stability of CuO and improves the sintering resistance of the OC particles. The calculation results were in consistent with the previous experiments and our TMA results.

We further investigated the microcosmic oxygen release mechanisms of CuO supported on different supports. It was found that energy barrier of O₂ desorption is higher than that of O₂ formation, indicating that O₂ desorption is the rate-limiting step of CuO decomposition. For the OCs with different supports, the O₂ desorption energy barriers increases in the order of CuO/CuAl₂O₄ < CuO/ZrO₂ < CuO/MgAl₂O₄ < CuO/TiO₂. The energy barriers were 3.28, 3.33, 3.41 and 3.45 eV, respectively. The isothermal experiment results were consistent with the DFT predictions, which showed that the oxygen release rates of CuO/CuAl₂O₄ is highest, followed by CuO/ZrO₂, CuO/MgAl₂O₄ and CuO/TiO₂.

The effect of support on the sintering resistance and decomposition reactivity of Cu-based OCs is attributed to the strong interaction of CuO and support, which results in the electron redistribution and microstructure changes of CuO. Our atomic understanding on CuO-support interaction and its effect to CuO decomposition reactivity add a well supplement to previous experimental studies [13]. These studies will help us rationalize the selection of support materials to achieve high performance of Cu-based OC. However, it should be noted that the present DFT calculation cannot consider the friction and wear properties which may be relative to mechanical strength of materials. And it is also difficult to consider the oxygen release properties evolution after repeated redox cycles which are affected by the physic-chemical property and microstructure change at high temperatures. In our future work, we will consider changing the DFT calculation model to set the CuO as periodic slab and setting the support materials as nanocluster to access a high content ratio of CuO. The similar content ratio between CuO and support materials is also in our consideration. Also, it is possible to investigate the effect of CuO clusters on the OC performance. By then, it is possible to guide the customization of OC particles by optimal preparation processes. Using this methodology on compounds having the tendency of forming spinel structures (Fe₂O₃, Mn₃O₄, MgO and Al₂O₃) is also in our consideration for our future work.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.proci.2016.06.195, http://ees.elsevier. com/proci/.

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