The Effect of the Support Structure and Size of Cu-based Oxygen Carriers on the Performance of Chemical Looping Air Separation

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ABSTRACT

Chemical looping air separation (CLAS) is a novel and efficient method of producing high-purity oxygen because of its low-energy demands. Cu-based materials are suitable oxygen carriers (OCs) for CLAS. In the current study, Cu-based OCs in different particle sizes were prepared using various methods (viz., through mechanical mixing, impregnation, and coprecipitation) and different supporting materials (viz., ZrO₂, SiO₂, and Al₂O₃) and porosities (viz., in the mesopore range). This study evaluated the reactivity, reaction kinetics, and recyclability of these OCs by measuring their conversion rates for reduction (oxygen release) and oxidation (regeneration) in a thermogravimetric analyzer. CuO OCs on ZrO₂ nanoparticles prepared through impregnation (CuZr-IM) exhibited almost complete conversion and the fastest reaction rates of all the OCs for reduction and oxidation. These characteristics are primarily attributable to the fine particles (100–250 nm) of the OCs. Furthermore, the CuO on the surface of the ZrO₂ particles was distributed in a uniform pattern, as these fine particles displayed greater oxygen mobility and more rapid diffusion than the micrometer-sized particles paired with bulk materials. Kinetic analysis revealed that Avrami-Erofe’ev random nucleation and the subsequent growth reaction model with \( n = 2 \) (A2), with an observed activation energy of 140.2 kJ mol \(^{-1}\) in our study, is the optimal fitting for CuZr-IM OC conversion during reduction, and a long-term-stability test indicated that this OC is an appropriate candidate for CLAS.

Keywords: Chemical looping; Oxygen carrier; Oxygen; CuO/ZrO₂; Kinetics mechanism.

INTRODUCTION

Oxy-fuel combustion is used for thermal power generation and as one of the carbon capture and storage technologies (Scheffknecht et al., 2011). Oxy-fuel combustion is the process of burning fuel using pure oxygen instead of air. It produces exhaust, which primarily comprises CO₂ and H₂O. Almost pure CO₂ can be obtained by condensing water vapor. In the oxy-fuel combustion process, the required oxygen is produced through air separation (Smith and Klosek, 2001). A cryogenic air separation (CAS) process is the most common and commercially available method for large-scale, high-volume (> 100 t d\(^{-1}\)), and high-purity O₂ (99.5–99.8%). However, the CAS method is complicated and highly energy-consuming because it involves the liquefaction of air and distillation of liquid air. The oxygen-specific power of the CAS process is 0.3–0.6 (kWh) (m\(^3\) O₂)\(^{-1}\) (Fan and Zhu, 2015). Moreover, it may cause an explosion resulting from rough handling in the CAS process. The other methods of producing oxygen are pressure swing adsorption (PSA) and membrane separation. The former method, which absorbs nitrogen by using adsorbent materials, such as zeolite or carbon molecular sieves, produced approximately 95% oxygen (Delavar and Nabian, 2015). PSA process is appropriate for small to medium volumes of O₂ production (10–100 t d\(^{-1}\)). The oxygen-specific power of the PSA was approximately 0.4 (kWh) (m\(^3\) O₂)\(^{-1}\). Membrane separation is another favorable technology for oxygen separation from air. Some advanced membranes, such as ion transport membranes (ITMs) for air separation, are currently available (Dyer et al., 2000). Oxygen ions are diffused through vacancies of ceramic membranes fabricated from metal oxides at high temperatures of 700–900°C. The selectivity of O₂ is approximately 100%. Compared to CAS and PAS methods, ITMs are usually applied to small volumes of O₂ production (approximately 20 t d\(^{-1}\)) and generate extremely high-purity oxygen (> 99%). However, the inability to produce nitrogen and high cost of membrane materials are disadvantages of ITMs.

Chemical looping process (CLP) has been developed over the past few years (Fan, 2010; Chen et al., 20188; Chiu and Ku, 2012). CLP is a novel oxy-fuel combustion technology in which metal oxide is used in place of air to offer oxygen for fuel combustion. Through a cyclic loop in between fuel and air reactors, the system can output heat for power generation with inherent CO₂ capture without extra energy.

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Chemical looping with oxygen uncoupling (CLOU) is one operating mode of CLP (Mattisson et al., 2009; Imtiaz et al., 2013). The gas-phase oxygen produced by some specific metal oxides, such as CuO or MnO2, is directly reacted with solid fuels in order to produce nearly pure CO2 in the reducer. Chemical looping air separation (CLAS), which is another operating mode of CLP, is a novel alternative for oxygen production proposed by Moghtaderi (2010). In the CLAS process, oxygen carriers (OCs) containing metal oxides are circulated between an oxidation reactor (oxidizer) and a reduction reactor (reducer). In the reducer, OCs were reduced to produce gas-phase oxygen (Eq. (1)). In order to obtain higher-purity oxygen, steam or CO2 can be used as carrier gas in the reducer. The reduced OCs are then transported to an oxidizer. Fresh air is provided to the oxidizer to regenerate reduced OCs (Eq. (2)). CLAS is a cost-effective and energy-efficient method to produce oxygen compared with CAS. The average oxygen-specific power of CLAS is approximately 0.04 (kWh) (m3 O2)–1.

\[
\text{MeO}_y \leftrightarrow \text{MeO}_2 + O_2(g) \quad (1)
\]

\[
\text{MeO}_y + O_2(g) \leftrightarrow \text{MeO}_3(g) \quad (2)
\]

The selection of suitable OCs is the key issue in CLAS. In previous thermodynamic evaluation, some metal oxides, such as Cu-, Mn-, Os-, and Co-based oxides, could release gas-phase oxygen at high temperatures (1100–1400 K) and were used as OCs for CLAS (Wang et al., 2013b). Among these metal oxides, CuO was the most suitable material for CLAS because of its higher oxygen transport capacity (0.1 (g O2)–1(g CuO)–1) and higher reaction rates. However, the low melting point of Cu (1085°C) caused sintering and agglomeration, thus limiting its application at high temperature (Ku et al., 2017). Therefore, some inert materials, such as Al2O3, SiO2, TiO2, ZrO2, YSZ, and MgAl2O4, were used as supports for Cu-based OC for increasing the reactivity, stability, mechanical strength, and sinter resistance. SiO2 is an appropriate support for CuO because SiO2 does not react with CuO at the oxygen-releasing temperature (Shah et al., 2012). However, agglomeration is the main problem of SiO2 support. Therefore, CuO/MgO-SiO2 OCs were synthesized (Song et al., 2014a). The results revealed that MgO addition on SiO2 support may suppress the agglomeration and increase the reactivity and stability during redox cycles due to the formations of Cu-MgO-SiO2 stabilizing the structure of OCs. Kinetics of Cu-based OCs prepared with different support materials (ZrO2, TiO2, and SiO2) for CLAS was studied by using thermogravimetry (TG) (Wang et al., 2013a). The results show that reaction rates of Cu-based OCs with different supports were as follows: ZrO2 > TiO2 > SiO2. It may be attributed to the fact that a higher surface area of ZrO2 facilitates gas diffusion and heat transfer, thus increasing the reaction rate.

Different methods, such as mechanical mixing (MM), freeze granulation (FG), sol-gel (SG), impregnation (IM), co-precipitation (CP), and spray drying (SD), were used to prepare Cu-based OCs. CuO/Al2O3 OCs with high CuO loadings were developed through a co-precipitation (CP) method (Imtiaz et al., 2012). It shows that the pH value influences the oxygen-carrying capacity and reactivity of OCs. CuO/Al2O3 OCs synthesized at a high pH value (i.e., 12.5) resulted in OCs with a higher CuO content (87.8 wt.%) and possessed a higher oxygen capacity. CuO/MgO-SiO2 OCs prepared using dry IM exhibit a higher stability than CuO/SiO2 (Song et al., 2014a). The addition of MgO to CuO/SiO2 and OCs prepared through IM method may suppress agglomeration.

Most studies on the preparation of Cu-based OCs for CLAS have focused on the MM method because scaling up for the production of OCs is simpler and easier compared to the other methods. However, the particle size of most OCs has been on the micrometer scale (Wang et al., 2014; Ku et al., 2018). Some researches have been conducted on the effect of support microstructure and the particle size of OCs for CLAS. The relationship between the conversion rate and the open porosity of supports was also studied (Liu et al., 2016). It has been reported that the high open porosity of the support is beneficial for gas transfer, thus increasing the reaction rate. CuO/Al2O3 OCs derived from layered double hydroxide (LDH) precursors were prepared through CP method, and the OC was a two-dimensional (2D) nanostructured matrix (Song et al., 2013). It shows that the CuO nanocrystals (30–50 nm) were well dispersed in porous LDH supports. The reaction rates were faster in both reduction and oxidation reaction because of CuO nano-composites, and porous structures. Moreover, agglomeration was not observed for this nanostructured OC.

The objective of the current study is to prepare the Cu-based OCs for CLAS operation. Cu-based OCs with different support materials (e.g., ZrO2, SiO2, and Al2O3), pore structures, and particle sizes were prepared using various methods, such as IM, CP, and MM. The reactivity, kinetics, and recyclability of these Cu-based OCs for CLAS reaction has been analyzed from the TGA results. It may lead to a better understanding of the correlation between the conversion rate and the particle size and porosity of supports.

**EXPERIMENTAL**

**Preparation of Oxygen Carrier**

In this study, Cu-based OCs with different structures and particle sizes were prepared using the following methods: IM, CP and MM. The content of CuO in the OCs is 40 wt.% in this study.

**Impregnation (IM)**

In this study, three Cu-based OCs were prepared using ZrO2, SiO2, and Al2O3 as support materials. ZrO2 support was prepared through modified sol-gel methods (Mokhtar et al., 2013). Zr precursors were prepared using an aqueous solution of ZrOCl2·8H2O (Solution A). Ammonia solution (28%) was mixed with cetyltrimethylammonium bromide and homogeneously stirred for 30 min (Solution B). Solution B was added dropwise into Solution A and the mixture was stirred in an ultrasonic bath for 2 h. NaOH was then slowly added to the solution until pH reached 9.0. The formed precipitate was transferred to an autoclave and heated.
Cu(NO$_3$)$_2$·3H$_2$O as the copper precursor. In the IM (Si), and Al$_2$O$_3$ (Al), and the preparation method of the OC, in an oven at 80°C overnight and calcined at 900°C.

Mechanical Mixing (MM)

Three types of homogeneous Cu-based OCs were prepared through IM using ZrO$_2$, SiO$_2$, and Al$_2$O$_3$ as supports and Cu(NO$_3$)$_2$·3H$_2$O as the copper precursor. In the IM procedure, the copper precursor solution was dissolved in deionized water and slowly added in the aforementioned support materials. The solution was then stirred for 1 h. The mixed sample was aged for 20 h at room temperature. The resulting sample was dried in an oven at 100°C for 4 h and calcined at 600°C for 6 h.

Oxygen Carrier Characterization

Mechanical Mixing (MM)

OCs were prepared through MM using commercial CuO as an active material for releasing O$_2$ and ZrO$_2$ powders as support materials (Ku et al., 2018). The particle sizes of these metal oxide materials were 1–10 µm. CuO powder was mixed with water and support materials, and 10 wt.% binder was added and mixed. OC samples were dried at 80°C for 12 h and calcined at 900°C for 3 h.

Coprecipitation (CP)

The OC was prepared through CP using Cu(NO$_3$)$_2$·3H$_2$O and ZrOCl$_2$·8H$_2$O as materials. Cu(NO$_3$)$_2$·3H$_2$O and ZrOCl$_2$·8H$_2$O were added in water and stirred for 1 h. Aqueous NaOH was gradually added until pH reached 9.0 and precipitation occurred. The resulting sample was dried in an oven at 80°C overnight and calcined at 900°C.

Reactivity Test

Conversion of OCs

Reactivity tests of the oxygen carriers were carried out in a thermogravimetric analyzer (TGA, SETSYS Evolution 24, SETARMA). The temperature of TGA chamber was elevated with a ramping rate of 10°C min$^{-1}$ from room temperature to 900°C. The carry gas used for oxygen release in the reducer was pure N$_2$, and the gas used for the regeneration of OCs in the oxidizer was air. Previous study (Song et al., 2014b) indicated that no obvious difference was observed in the reactivity of oxygen carriers with different inert reducing environments (N$_2$ or CO$_2$). Therefore, N$_2$ was usually used as the regeneration gas. The flow rate of the reacting gas was controlled at 200 mL min$^{-1}$. The OC (20–40 mg) was loaded in a platinum basket and heated to 900°C. The duration was set at 60 min for reduction and oxidation. The data of weight changes can be used for the conversion of OCs using the following equations:

$$X_r \, (\%) = \frac{m_o - m(t)}{m_o - m_r} \times 100\%$$

(3)

$$X_o \, (\%) = \frac{m(t) - m_r}{m_o - m_r} \times 100\%$$

(4)

where $X_r$ and $X_o$ are the conversions of OCs during reduction and oxidation, respectively; and $m_o$, $m(t)$, and $m_r$ are the masses of the sample in a completely oxidized state, during the test, and in a completely reduced state, respectively.

In addition to conversion, the oxygen transport capacity (OTC) and reaction rate of solid conversion (ROC) could be determined (Song et al., 2014b). The OTC and ROC of OCs were defined as follows:

$$\text{OTC (g O}_2\text{ g}^{-1}) = \frac{m_o - m_r}{m_o}$$

(5)


\[ \text{ROC} \left( \% \text{ min}^{-1} \right) = \frac{dX}{dt} \tag{6} \]

**Reaction Kinetics in Reduction**

The reduction kinetics of Cu-based OCs for CLAS were calculated using the procedure reported by the previous study (Song et al., 2014c; Wang et al., 2016). In this study, the reaction rate for reduction of Cu-based OCs was evaluated using the following equations:

\[ \frac{dX}{dt} \left( \% \text{ min}^{-1} \right) = kf(X)\left(C - C_{eq}\right)^n \tag{7} \]

where \( X, f(X), \) and \( t \) are the conversion of OCs during reduction, kinetic mechanism functions, and reaction times, respectively; \( C \) and \( C_{eq} \) are oxygen concentrations used for oxidation and equilibrium oxygen concentration used for CuO decomposition, respectively; \( n \) and \( k \) are the reaction order and rate constant following the Arrhenius equation; and:

\[ k \left( \text{min}^{-1} \right) = A \exp\left(\frac{E_a}{RT}\right) \tag{8} \]

where \( A, E_a, R, \) and \( T \) represent the pre-exponential factor, activation energy, gas constant, and reaction temperature, respectively.

The value of \( n \) is zero because the reduction of CuO is a thermal decomposition process and oxygen is not present in the reactive gas (N\(_2\) as the carrier gas). Therefore, Eq. (7) can be simplified as follows:

\[ \frac{dX}{dt} \left( \% \text{ min}^{-1} \right) = kf(X) \tag{9} \]

The integral form of Eq. (9) is as follows:

\[ G(X) = kt \tag{10} \]

where \( G(X) \) is a kinetic mechanism function, which can be obtained from different gas-solid reaction mechanisms. Table 1 summarizes \( G(X) \) equations for different reaction mechanisms (Song et al., 2014c). For example, \( G(X) \) under the D1 reaction mechanism is determined by the value of \( X \). Therefore, the reaction rate constant \( (k) \) can be calculated using the slope of the fitting line in the plots of \( G(X) \) of \( X^2 \) versus reaction time.

**RESULTS AND DISCUSSION**

**Characterization of OCs**

The OCs comprising 40 wt.% CuO on various support materials (ZrO\(_2\), SiO\(_2\), Al\(_2\)O\(_3\)) were prepared in this study. Table 2 lists the oxygen transport capacity, BET surface area, and pore volume of the OCs. For CuZr-IM OC, the precursor solution of copper was impregnated on the surface of ZrO\(_2\) particles. The particle size and BET surface area of ZrO\(_2\) supports were 15–25 nm and 37.8 m\(^2\) g\(^{-1}\), respectively. After IM, the size of CuZr-IM OCs was 100–250 nm. Therefore, CuZr-IM OCs can be classified as fine particles. Fig. 1 shows SEM images of OCs in general. The fresh OCs had a BET surface area and pore volume of 1.43 m\(^2\) g\(^{-1}\) and 16.8 mm\(^3\) g\(^{-1}\), respectively. A crystalline phase from the XRD analysis shows CuO and ZrO\(_2\).

For CuZr-CP, the OC was prepared through CP. It reported that pH affects the reactivity and crushing strength of OCs (Imtiaz et al., 2012). In this study, the pH of 9.0 was selected because the OCs had high reactivity and mechanical strength. The particle size of the CuZr-CP was 20–50 \( \mu \)m, which is larger than that of CuZr-IM OC. The fresh OCs had a BET surface area and pore volume of 1.20 m\(^2\) g\(^{-1}\) and 11.3 mm\(^3\) g\(^{-1}\), respectively. The crystalline phase showed CuO and ZrO\(_2\) in XRD analysis.

For CuSi-IM, the precursor solution of copper was impregnated into the mesoporous SiO\(_2\) particle. The particle size of the SiO\(_2\) support was 1–10 \( \mu \)m. The average BET surface area and pore size of SiO\(_2\) were approximately 250 m\(^2\) g\(^{-1}\) and 3–6 nm, respectively. After the IM of copper nitrate, the particle size of CuSi-IM OCs was 3–10 \( \mu \)m. The fresh CuSi-IM OCs had a BET surface area of 6.05 m\(^2\) g\(^{-1}\) and a pore volume of 35.0 mm\(^3\) g\(^{-1}\), which were larger than

**Table 1. \( G(X) \) equations for different reaction mechanisms.**

| Reaction mechanism model | \( G(X) \) equation |
|--------------------------|----------------------|
| One-dimensional diffusion (D1) | \( X^2 \) |
| Two-dimensional diffusion (D2) | \( (1 - X)\ln(1 - X) + X \) |
| Three-dimensional diffusion, Jandar function (D3) | \( [1 - (1 - X)^{1/3}]^2 \) |
| Three-dimensional diffusion, G-B function (D4) | \( 1 - 2X/3 - (1 - X)^2/3 \) |
| First-order chemical reaction (C1) | \( -\ln(1 - X) \) |
| Second-order chemical reaction (C2) | \( (1 - X)^{1 - 1} \) |
| Avrami-Erofe’ev random nucleation and subsequent growth reaction model with \( n = 2 \) (A2) | \( [-\ln(1 - X)]^{1/2} \) |
| Avrami-Erofe’ev random nucleation and subsequent growth reaction model with \( n = 3 \) (A3) | \( [-\ln(1 - X)]^{1/3} \) |
| Phase boundary reaction with \( n = 2 \) (R2) | \( 1 - (1 - X)^{1/2} \) |
| Phase boundary reaction with \( n = 3 \) (R3) | \( 1 - (1 - X)^{1/3} \) |
| Mampel power law with \( n = 1 \) (P1) | \( X^1 \) |
| Mampel power law with \( n = 2 \) (P2) | \( X^{1/2} \) |
| Mampel power law with \( n = 3 \) (P3) | \( X^{1/3} \) |
| Mampel power law with \( n = 4 \) (P4) | \( X^{1/4} \) |
Table 2. Properties of Cu-based OCs.

| Oxygen carrier | Theoretical CuO loading (%) | Actual CuO loading (%) | Oxygen transport capacity (g-O₂ g⁻¹) | BET surface area (m² g⁻¹) | BJH pore volume (mm³ g⁻¹) |
|----------------|-----------------------------|------------------------|-------------------------------------|---------------------------|--------------------------|
| CuZr-MM        | 40.0                        | 41.5                   | 0.42                                | 1.36                      | 5.16                     |
| CuZr-IM        | 40.0                        | 39.9                   | 0.40                                | 1.43                      | 16.8                     |
| CuZr-CP        | 40.0                        | 38.2                   | 0.38                                | 1.20                      | 14.1                     |
| CuSi-IM        | 40.0                        | 38.8                   | 0.39                                | 6.05                      | 35.1                     |

Fig. 1. SEM images of (a) CuZr-MM, (b) CuZr-IM, (c) CuZr-CP, and (d) CuSi-IM OCs.

those of CuZr-IM and CuZr-CP. The crystalline phase showed CuO and SiO₂ in the XRD analysis.

Reactivity of OCs

Effect of Support Material

In this study, three materials (i.e., ZrO₂, SiO₂, and Al₂O₃) with different particle sizes and pore structures were used as a support for Cu-based OCs. All Cu-based OCs were prepared through IM because OCs have high reactivity and satisfactory mechanical strength (de Diego et al., 2004). Fig. 2 presents the effect of the support material on the reactivity of Cu-based OCs for CLAS. The reaction temperature of reduction and oxidation was controlled at 900°C. CuZr-IM exhibited superior conversion and faster reaction rate during reduction. This result may be attributed to the particle size of the ZrO₂ support. The ZrO₂ supports used for CuZr-IM were prepared through a modified sol-gel method. ZrO₂ supports were nanoparticles with a particle size of 15–25 nm (Fig. 3). After the IM of nano-sized ZrO₂, the particle size of CuZr-IM OC was 100–250 nm, which is considerably smaller than that of other OCs. Fig. 4 shows TEM images and the corresponding EDX mapping of CuZr-IM; a high degree of dispersion of CuO was observed on the surface of ZrO₂ supports. The oxygen mobility, diffusion, and heat transfer of fine particles were superior to those of bulk materials with micrometer-sized particles, thus facilitating OC reactivity. These findings are consistent with those of a previous study (Song et al., 2013).

For the CuSi-IM OC, the mesoporous SiO₂ support was prepared through SD. The particle size of the prepared SiO₂ was 1.0–10.0 µm. The pore size and BET surface area of the SiO₂ support were 3–6 nm and approximately 250 m² g⁻¹, respectively. After IM of the copper precursor, the particle size of CuSi-IM was 3–15 µm. Although the BET surface...
Fig. 2. Effect of support material on the conversion of Cu-based OCs in reduction and oxidation.

area of porous SiO₂ support was 250 m² g⁻¹. However, CuO will impregnate into the porous SiO₂ and then full up the pores due to high loading (40 wt.%). Moreover, the OC will be calcined at high temperature of 900°C. The surface area of CuSi-IM OC was therefore decreased dramatically.

Fig. 5 shows TEM images of mesoporous SiO₂ support and CuSi-IM OCs; the particle size of CuO on the surface of the SiO₂ support ranged from 6–13 nm. The TEM images indicate a fine dispersion of copper oxide on the SiO₂ support (Fig. 6). The porosity of the SiO₂ support and CuO nanoparticles may enhance reactivity performance and provide high conversion and a fast reaction rate during reduction. However, the particle size of CuSi-IM OCs was 3–15 µm. The reactivity of CuSi-IM was slightly less than that of CuZr-IM. Moreover, the regeneration of CuSi-IM OC was incomplete during oxidation because of the slight agglomeration of CuSi-IM OCs during redox (Fig. 7).

The CuO supported on the mesoporous Al₂O₃ support (CuAl-IM OC) showed lower conversion (approximately 25%) during the reduction process compared with CuZr-IM and CuSi-IM. This result can be attributed to the formation of copper aluminate (CuAl₂O₄) between the CuO and Al₂O₃ support during calcination (Eq. (11)), which significantly reduced the oxygen release of the OC. Fig. 8 shows XRD patterns of CuAl-IM, indicating that copper aluminate (CuAl₂O₄) was present. This finding is in accordance with the results of previous studies (Abad et al., 2012; Song et al., 2014a). CuAl₂O₄ is a very stable substance with a reduction temperature of about 900–1000°C. CuAl₂O₄ will decomposed slowly to form Al₂O₃ and O₂ in the anoxic environment (reduction reaction, Eq. (12)), but also CuAlO₂ is formed at the same time, so CuAl₂O₄ can only be partially regenerated into CuO. Therefore, the amount of CuO capable of releasing oxygen reduced, which means Al₂O₃ is not a suitable support material for the oxygen-releasing carrier despite having a mesoporous structure. The aforementioned analysis indicates
that nanosized ZrO\textsubscript{2} may be a good choice as the support material of OC.

\[
\text{CuO} + \text{Al}_2\text{O}_3 \rightarrow \text{CuAl}_2\text{O}_4 \quad (11)
\]

\[
4\text{CuAl}_2\text{O}_4 \rightarrow 4\text{CuAlO}_2 + 2\text{Al}_2\text{O}_3 + \text{O}_2 \quad (12)
\]

**Effect of Preparation Method of the OC**

Fig. 9 shows the conversions of three 40 wt.% Cu-based OCs using ZrO\textsubscript{2} as supports obtained through various preparation methods in one reduction and oxidation (redox) cycle in CLAS. The reaction temperature of redox was controlled at 900°C. OCs prepared through IM were more reactive than those prepared through CP and MM. CuZr-IM OC had a high conversion rate of nearly 100%. Furthermore, the average ROC was the fastest in the reduction process (7.40% min\textsuperscript{-1}) (Table 3). This result may be attributed to the particle size of the OCs. The aforementioned analysis indicates high conversion of CuZr-IM results from the CuO homogeneously dispersed on the nanosized ZrO\textsubscript{2} supports. Although CuZr-CP OCs have higher crushing strength, the particle size was larger than that of CuZr-IM. The particle size determines reactivity performance, including conversion and reaction rate, in CLAS.
For the regeneration of reduced OCs during oxidation in air at a temperature of 825–950°C, the average rates of solid conversion were 16.58%, 11.57%, and 5.78% min⁻¹ for CuZr-IM, CuZr-CP, and CuZr-MM, respectively. CuZr-IM OC exhibited the fastest kinetics. Moreover, this result may be attributed to the particle size of OCs. Furthermore, the oxidation rate of the OC was considerably faster than the reduction rate. These results are consistent with previous study (Song et al., 2014c). CuZr-IM OCs exhibited the highest conversion and fastest reaction rate during redox in CLAS.

Kinetic Analysis of OCs during Reduction

As stated previously, CuZr-IM was the most suitable Cu-based OC for CLAS because of its high conversion and reaction rate during redox. Therefore, CuZr-IM was selected as an OC for the determination of chemical kinetics during reduction in CLAS.

Table 1 summarizes \( G(X) \) equations of different gas-solid reaction mechanisms. The reaction rate constant \( (k) \) can be calculated from the slope of the fitting line in a plot of \( G(X) \) versus time. Table 4 presents the results of \( R^2 \) values for fitting different reaction mechanisms based on CuZr-IM
Fig. 8. XRD patterns of CuAl-IM OCs. The major reflection peaks are annotated as: CuO (-), Al2O3 (o), CuAl2O4 (x).

Fig. 9. Conversion of Cu-based OCs during reduction and oxidation reaction for CLAS.

Table 3. Rates of conversion for Cu-based OCs during reduction and oxidation.

| Cu-based oxygen carrier | Rate of conversion (ROC) in reduction (% min⁻¹) | Rate of conversion (ROC) in oxidation (% min⁻¹) |
|-------------------------|-----------------------------------------------|-----------------------------------------------|
| CuZr-IM                 | 7.40                                          | 16.58                                         |
| CuZr-CP                 | 5.35                                          | 11.57                                         |
| CuZr-MM                 | 5.14                                          | 5.78                                          |
| CuSi-IM                 | 7.17                                          | 16.30                                         |

OCs during reduction at a temperature of 825–950°C. It indicated that Avrami-Erofe’ev random nucleation and the subsequent growth reaction model with $n = 2$ (A2) are the optimal fit for CuO-based OC conversion during reduction in CLAS. Therefore, the oxygen release of OCs was determined using the rates of nucleation, nuclei growth, and nucleus formation.

The kinetic mechanism function $G(X)$ under the A2 reaction model is determined by the value of $[-\ln(1-X)]^{1/2}$. Fig. 10 shows the results of the fitting curves of $G(X)$ versus reaction time at different reduction temperatures. Table 5 presents linear correlation coefficient ($R^2$) values of the least-squares linear fitting and rate constants for temperatures from 825 to 950°C. Rate constants were 0.0636, 0.0831, 0.1271, 0.1820, 0.23, and...
Table 4. $R^2$ for fitting different reaction mechanisms based on CuZr-IM conversion during reduction.

| T (°C) | D1     | D2     | D3     | D4     | C1     | C2     | A2-1   | A2-2   | A3     | R2     | P1     | P2     | P3     |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 825    | 0.6789 | 0.6592 | 0.6384 | 0.6523 | 0.7534 | 0.8294 | 0.9929 | 0.992  | 0.6912 | 0.8998 | 0.8297 | 0.9194 | 0.882  |
| 850    | 0.6746 | 0.6405 | 0.6023 | 0.6276 | 0.7567 | 0.7348 | 0.9964 | 0.9848 | 0.8407 | 0.8735 | 0.8604 | 0.9084 | 0.9543 |
| 875    | 0.6989 | 0.6592 | 0.614  | 0.6439 | 0.8021 | 0.7287 | 0.9933 | 0.9896 | 0.7663 | 0.8930 | 0.878  | 0.9319 | 0.9233 |
| 900    | 0.7182 | 0.6605 | 0.5884 | 0.6363 | 0.845  | 0.6007 | 0.9894 | 0.9954 | 0.8535 | 0.8818 | 0.8576 | 0.9386 | 0.9408 |
| 925    | 0.725  | 0.6581 | 0.5659 | 0.6274 | 0.8322 | 0.4662 | 0.9764 | 0.9965 | 0.934  | 0.8269 | 0.8316 | 0.9311 | 0.966  |
| 950    | 0.7345 | 0.6825 | 0.5929 | 0.653  | 0.878  | 0.4845 | 0.9647 | 0.9990 | 0.9817 | 0.8571 | 0.8272 | 0.9190 | 0.9778 |

Fig. 10. Plots of $G(X)$ versus reaction time of CuZr-IM at different temperatures during reduction.

Table 5. Fitting results of OC conversion during reduction at different temperatures.

| Reaction temperature (°C) | $R^2$ values for fitting linear | The reaction rate constant ($k$) |
|---------------------------|--------------------------------|--------------------------------|
| 825                       | 0.9929                         | 0.0636                         |
| 850                       | 0.9964                         | 0.0831                         |
| 875                       | 0.9933                         | 0.1271                         |
| 900                       | 0.9894                         | 0.1820                         |
| 925                       | 0.9764                         | 0.230                          |
| 950                       | 0.9647                         | 0.2859                         |

0.2859 for 825, 850, 875, 900, 925, and 950°C, respectively. The rate constant increased with the reduction temperature, indicating that high temperature is advantageous for thermal decomposition and oxygen release of CuZr-IM OCs.

The activation energy can be calculated according to the Arrhenius equation. Fig. 11 shows the fitting lines of $\ln(k)$ versus $1000/T$ for the reduction of CuZr-IM OCs. The values of activation energy ($E_a$) and pre-exponential factor ($A$) can be obtained by calculating the slope and intercept of the fitting line. The $E_a$ of 140.2 kJ mol$^{-1}$ and $A$ of $2.82 \times 10^5$ min$^{-1}$ at a temperature of 825–950°C were lower than those of micrometer-sized CuO/SiO$_2$ OCs (176 kJ mol$^{-1}$) at temperatures higher than 900°C (Song et al., 2014c). CuZr-IM OC with lower activation energy may be attributed to the
Fig. 11. Plots of ln($k$) versus 1000/$T$ of CuZr-IM OCs at different temperatures during reduction.

Fig. 12. Conversion of CuZr-IM OCs during reduction at 825–950°C.

**Stability of OCs**

Based on the aforementioned analysis, CuZr-IM OCs are better for CLAS. In addition to a high conversion and fast reaction rate, long-term recyclability and durability are necessary for OCs. These can reduce the fine-particle purging, thereby reducing the fresh OC makeup rate. To determine the long-term reaction stability, a 20-cycle redox test was performed on CuZr-IM OCs at 900°C using a TGA. The OTC of an OC is defined as the difference in the mass fraction between the completely oxidized and reduced forms. This can be a critical index to determine the favorability for oxygen transport (Song et al., 2014b). Fig. 13 shows the weight fraction of CuZr-IM OCs during 20 consecutive redox cycles, indicating CuZr-IM OCs with a stable OTC in CLAS. The reduced OCs were completely reoxidized during oxidation. Furthermore, the CuZr-IM was converted over 20 redox cycles. The CuZr-IM OCs maintained relatively stable conversion. Comparison of the fresh and used OCs after 20 redox cycles in CLAS revealed no evident agglomeration for the used OCs (Fig. 14).

**CONCLUSION**

In this study, the reactivity and conversion rates of novel Cu-based OCs prepared with various methods and different supporting materials for CLAS were studied. Cu-based OCs impregnated with supporting ZrO$_2$ nanoparticles (CuZr-IM OCs) exhibited excellent performance and can be employed in CLAS to produce oxygen at temperatures of 825–950°C. This result can be attributed to the small particle size of the OCs. The CuO nanoparticles on the surface of the nano-ZrO$_2$ supports were distributed in a uniform pattern and displayed...
greater oxygen mobility and faster diffusion than micrometer-sized particles and bulk materials. The reaction kinetics of the CuZr-IM OCs during reduction were studied, and Avrami-Erofe’ev random nucleation and the subsequent growth reaction model with $n = 2$ (A2) were found to be the optimal fit for OC conversion during this reaction. Additionally, an activation energy of 140.2 kJ mol$^{-1}$ for this OC indicates that reducing the particle size decreases the activation energy. Recyclability and durability tests also reveal that the CuZr-IM OC is suitable for CLAS reactions. In the future, the fluidized-bed process should be used to evaluate the real-time oxygen concentration during reduction. A series of parametric tests will also be conducted.

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