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

Hou-Chuan Wang*, Hsiu-Hsia Lee, Ming-Hui Chang, Hou-Peng Wan, Jui-Yen Cheng, Ting-Yi Wu

Green Energy and Environment Research Laboratories, Industrial Technology Research Institute, Hsinchu 31040, Taiwan

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., ZrO_2 , SiO_2 , and Al_2O_3) 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 ZrO_2 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 ZrO_2 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 $140.2 \text{ kJ mol}^{-1}$ 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/ ZrO_2 ; 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 CO_2 and H_2O . Almost pure CO_2 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 ($> 100 \text{ t d}^{-1}$), and high-purity O_2 (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 $0.3\text{--}0.6 \text{ (kWh)} \cdot (\text{m}^3 \text{ O}_2)^{-1}$ (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 O_2 production ($10\text{--}100 \text{ t d}^{-1}$). The oxygen-specific power of the PSA was approximately $0.4 \text{ (kWh)} \cdot (\text{m}^3 \text{ O}_2)^{-1}$. 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 $700\text{--}900^\circ\text{C}$. The selectivity of O_2 is approximately 100%. Compared to CAS and PAS methods, ITMs are usually applied to small volumes of O_2 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 CO_2 capture without extra energy.

* Corresponding author.

E-mail address: Erichcwang@itri.org.tw

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 Mn₂O₃, 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.

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)·(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 Cu₂MgO₃ 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), coprecipitation (CP), and spray drying (SD), were used to prepare Cu-based OCs. CuO/Al₂O₃ OCs with high CuO loadings were developed through a coprecipitation (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 nanocomposites, 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

at 85°C for 24 h. The precipitate was filtered and repeatedly washed using ethanol. The resulting sample was dried in an oven at 100°C for 4 h and calcined at 600°C for 6 h.

Mesoporous SiO₂ support was synthesized using the spray-drying (SD) method (Wang *et al.*, 2012). Sodium silicate was added to deionized water and 6 N HCl. The mixture was stirred at room temperature for 30 min until a clean solution was obtained. In a separate beaker, Pluronic P123 was added to EtOH (95%) and thoroughly mixed. The Pluronic P123/EtOH solution was added to the sodium silicate mixture to obtain a precursor solution. The precursor was dried in a pilot-scale SD system. The drying temperature of a reaction tower for solvent removal from self-organized particles was 200°C. The resulting SiO₂ particles were collected using a cyclone and bag filter. The collected particles were finally calcined (600°C, 4 h) in a muffle furnace to eliminate the surfactant template.

Mesoporous Al₂O₃ support was prepared through a modified sol-gel method. In a general synthesis, Pluronic P123 and anhydrous ethanol were mixed for 30 min (Solution A). Aluminum isopropoxide, HNO₃ solution, and anhydrous ethanol were mixed for 1 h (Solution B). Solution A was added dropwise into Solution B and the mixture was 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.

Three types of homogeneous Cu-based OCs were prepared through IM using ZrO₂, SiO₂, and Al₂O₃ as supports and Cu(NO₃)₂·3H₂O 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 resulting sample was dried in an oven at 100°C for 12 h and calcined at 900°C for 3 h.

Coprecipitation (CP)

The OC was prepared through CP using Cu(NO₃)₂·3H₂O and ZrOCl₂·8H₂O as materials. Cu(NO₃)₂·3H₂O and ZrOCl₂·8H₂O 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.

Mechanical Mixing (MM)

OCs were prepared through MM using commercial CuO as an active material for releasing O₂ and ZrO₂ 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.

The resulting OCs were denoted as *CuS-P*, where letters *S* and *P* represent support materials, such as ZrO₂ (Zr), SiO₂ (Si), and Al₂O₃ (Al), and the preparation method of the OC, such as MM, IM, and CP. For example, OCs was prepared through IM and ZrO₂ as support, the resulting Cu-based OCs were termed *CuZr-IM OCs*.

Oxygen Carrier Characterization

The physical properties of the OCs were determined by

N₂ adsorption/desorption at 77 K via a Micromeritics ASAP 2020 volumetric sorption analyzer (Norcross, GA). Before measurement, OCs were degassed under high vacuum at 100°C for 3 h until water vapor and impurities on the surface of the OCs have been desorbed. N₂ adsorption/desorption isotherms were measured at a relative pressure (P_{N_2}/P_0) range of 0.0001–0.99 and employed to determine surface area, pore volume, and average pore diameter via the Barrett-Johnner-Halenda (BJH) equation for pore size of 1.7–100 nm. The particle size and surface morphologies of the OCs were characterized via a field emission scanning electron microscope (SEM, JEOL JSM-6500F/CL (Gatan MonoCL3 plus HSPMT)) and a high-resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy (TEM, JEM-2100F/EDS (Oxford X-MAX 80 mm²)). The crystal phase of the OCs was characterized by a powder X-ray diffractometer (XRD, Mac Science Co., Ltd., Japan) using Cu K radiation (40 kV, 30 mA). The actual CuO content was analyzed via an inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent 5100).

Reactivity Test

Conversion of OCs

Reactivity tests of the oxygen carriers were carried out in a thermogravimetric analyzer (TGA, SETSYS Evolution 24, SETARAM). 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 N₂, 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 (N₂ or CO₂). Therefore, N₂ 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:

$$X_r (\%) = \frac{m_o - m(t)}{m_o - m_r} \times 100\% \quad (3)$$

$$X_o (\%) = \frac{m(t) - m_r}{m_o - m_r} \times 100\% \quad (4)$$

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:

$$\text{OTC} \left(\text{g O}_2 \text{ g}^{-1} \right) = \frac{m_o - m_r}{m_o} \quad (5)$$

$$ROC \left(\% \text{ min}^{-1} \right) = \frac{dX}{dt} \quad (6)$$

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:

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

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 reaction rate constant following the Arrhenius equation; and:

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

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:

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

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

$$G(X) = kt \quad (10)$$

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^2 . 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_2O_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 $37.8 \text{ m}^2 \text{ g}^{-1}$, 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 $1.43 \text{ m}^2 \text{ g}^{-1}$ and $16.8 \text{ mm}^3 \text{ g}^{-1}$, 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 μm , which is larger than that of CuZr-IM OC. The fresh OCs had a BET surface area and pore volume of $1.20 \text{ m}^2 \text{ g}^{-1}$ and $11.3 \text{ mm}^3 \text{ g}^{-1}$, 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 μm . The average BET surface area and pore size of SiO_2 were approximately $250 \text{ m}^2 \text{ g}^{-1}$ and 3–6 nm, respectively. After the IM of copper nitrate, the particle size of CuSi-IM OCs was 3–10 μm . The fresh CuSi-IM OCs had a BET surface area of $6.05 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $35.0 \text{ mm}^3 \text{ g}^{-1}$, 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
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-O ₂ g ⁻¹)	BET surface area (m ² g ⁻¹)	BJH pore volume (mm ³ 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.

Fig. 3. TEM images of ZrO₂ support (left) and CuZr-IM OCs (right).

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

Fig. 4. TEM images and corresponding EDX mapping of CuZr-IM OCs.

Fig. 5. TEM images of mesoporous SiO₂ support (left) and CuSi-IM OCs (right).

that nanosized ZrO₂ may be a good choice as the support material of OC.

Effect of Preparation Method of the OC

Fig. 9 shows the conversions of three 40 wt.% Cu-based OCs using ZrO₂ 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⁻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 ZrO₂ 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.

Fig. 6. TEM images and corresponding EDX mapping of CuSi-IM OCs.

Fig. 7. SEM images of used CuSi-IM OCs after redox reaction.

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	R3	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	0.2543
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	0.5695
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	0.4151
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	0.5117
925	0.725	0.6581	0.5659	0.6274	0.8322	0.4862	0.9764	0.9965	0.934	0.8269	0.8316	0.9311	0.966	0.6566
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	0.7919

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 $140.2 \text{ kJ mol}^{-1}$ and A of $2.82 \times 10^5 \text{ min}^{-1}$ at a temperature of 825–950°C were lower than those of micrometer-sized CuO/SiO₂ 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.

decreasing particle size (Alalwan *et al.*, 2018). This result is consistent with that of a previous study (Pang *et al.*, 2009).

The conversion of CuZr-IM OCs during reduction can be obtained using kinetic parameters according to Eq. (10). Fig. 12 shows the prediction results, which indicated that the predicted value (line) was close to the experimental values (dot points) at reaction temperatures of 825–950°C.

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

Fig. 13. (a) Weight fraction and (b) conversion of CuZr-IM OCs during 20 consecutive redox cycles.

Fig. 14. SEM images of used CuZr-IM OCs after 20 redox cycles.

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 $140.2 \text{ kJ mol}^{-1}$ 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.

ACKNOWLEDGMENT

This study was supported by the Bureau of Energy, Ministry of Economic Affairs of Taiwan.

REFERENCES

- Abad, A., Adanez-Rubio, I., Gayan, P., Garcia-Labiano, F., de Diego, L.F. and Adanez, J. (2012). Demonstration of chemical-looping with oxygen uncoupling (CLOU) process in a 1.5 kW_{th} continuously operating unit using a Cu-based oxygen-carrier. *Int. J. Greenhouse Gas Control* 6: 189–120.
- Alalwan, H.A., Mason, S.E., Grassian, V.H. and Cwierny, D.M. (2018). $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles as oxygen carriers for chemical looping combustion: An integrated materials characterization approach to understanding oxygen carrier performance, reduction mechanism, and particle size effects. *Energy Fuels* 32: 7959–7970.
- Chen, C., Lee, H.H., Chen, W., Chang, Y.C., Wang, E., Shen, C.H. and Huang, K.E. (2018). Study of an iron-based oxygen carrier on the moving bed chemical looping system. *Energy Fuels* 32: 3660–3667.

- Chiu, P.C. and Ku, Y. (2012). Chemical looping process - A novel technology for inherent CO₂ capture. *Aerosol Air Qual. Res.* 12: 1421–1432.
- de Diego, L.F., Garcia-Labiano, F., Adanez, J., Gayan, P., Abad, A., Corbella, B.M. and Palacios, J.M. (2004). Development of Cu-based oxygen carriers for chemical-looping combustion. *Fuel* 83: 1749–1757.
- Delavar, M. and Nabian, N. (2015). An investigation on the oxygen and nitrogen separation from air using carbonaceous adsorbents. *J. Eng. Sci. Technol.* 10: 1394–1403.
- Dyer, P.N., Richards, R.E., Russek, S.L. and Taylor, D.M. (2000). Ion transport membrane technology for oxygen separation and syngas production. *Solid State Ionics* 134: 21–33.
- Fan, J. and Zhu, Lin. (2015). A novel technique based on coal gasification integrated with chemical looping air separation. *J. Fundam. Renewable Energy Appl.* 5: 150.
- Fan, L.S. (2010). *Chemical looping systems for fossil energy conversions*. John Wiley & Sons, Inc., Hoboken, NJ.
- Imtiaz, Q., Kierzkowska, A.M., Broda, M. and Muller, C.R. (2012). Synthesis of Cu-rich, Al₂O₃-stabilized OCs using a coprecipitation technique: Redox and carbon formation characteristics. *Environ. Sci. Technol.* 46: 3561–3566.
- Imtiaz, Q., Hosseini, D. and Müller, C.R. (2013). Review of oxygen carriers for chemical looping with oxygen uncoupling (CLOU): Thermodynamics, material development, and synthesis. *Energy Technol.* 1: 633–647.
- Ku, Y., Shiu, S.H., Liu, Y.C., Wu, H.C., Kuo, Y.L. and Lee, H.Y. (2017). Liquid sintering behavior of Cu-based oxygen carriers for chemical looping process. *Catal. Commun.* 92: 70–74.
- Ku, Y., Wu, H.C., Chang, C.W. and Shiu, S.H. (2018). Chemical looping with air separation (CLAS) in a moving bed reactor with CuO/ZrO₂ oxygen carriers. *Int. J. Greenhouse Gas Control* 70: 225–235.
- Liu, Y., Kirchesch, P., Remhof, A., Graule, T., Liersch, A. and Clemens, F. (2016). Development of oxygen carriers for chemical looping combustion: Effect of support microstructure on the performance of oxygen carriers. *Microporous Mesoporous Mater.* 232: 264–272.
- Mattisson, T., Lyngfelt, A. and Leion, H. (2009). Chemical-looping with oxygen uncoupling for combustion of solid fuels. *Int. J. Greenhouse Gas Control* 3: 11–19.
- Moghtaderi, B. (2010). Application of chemical looping concept for air separation at high temperatures. *Energy Fuels* 24: 190–198.
- Mokhtar, M., Basahel, S.N. and Ali, T.T. (2013). Effect of synthesis methods for mesoporous zirconia on its structural and textural properties. *J. Mater. Sci.* 48: 2705–2713.
- Pang, J.M., Guo, P.M., Zhao, P., Cao, C.Z. and Zhang, D.W. (2009). Influence of size of hematite powder on its reduction kinetics by H₂ at low temperature. *J. Iron Steel Res. Int.* 16: 7–11.
- Scheffknecht, G., Al-Makhadmeh, L., Schnell, U. and Maier, J. (2011). Oxy-fuel coal combustion—A review of the current state-of-the-art. *Int. J. Greenhouse Gas Control* 5S: S16–S35.
- Shah, K., Moghtaderi, B. and Wall, T. (2012). Selection of suitable oxygen carriers for chemical looping air separation: A thermodynamic approach. *Energy Fuels* 26: 2038–2045.
- Smith, A.R. and Klosek, J. (2001). A review of air separation technologies and their integration with energy conversion processes. *Fuel Process. Technol.* 70: 115–134.
- Song, H., Shah, K., Doroodchi, E. and Moghtaderi, B. (2014a). Development of a Cu–Mg-based oxygen carrier with SiO₂ as a support for chemical looping air separation. *Energy Fuels* 28: 163–172.
- Song, H., Shah, K., Doroodchi, E., Wall, T. and Moghtaderi, B. (2014b). Reactivity of Al₂O₃- or SiO₂-supported Cu-, Mn-, and Co-based oxygen carriers for chemical looping air separation. *Energy Fuels* 28: 1284–1294.
- Song, H., Shah, K., Doroodchi, E., Wall, T. and Moghtaderi, B. (2014c). Analysis on chemical reaction kinetics of CuO/SiO₂ oxygen carriers for chemical looping air separation. *Energy Fuels* 28: 173–182.
- Song, Q., Liu, W., Bohn, C.D., Harper, R.N., Sivaniah, E., Scott, S.A. and Dennis, J.S. (2013). A high performance oxygen storage material for chemical looping processes with CO₂ capture. *Energy Environ. Sci.* 6: 288–298.
- Wang, H.C., Lu, C., Bai, H., Hwang, J.F., Lee, H.H., Chen, W., Kang, Y., Chen, S.T., Su, F., Kuo, S.C. and Hu, F.C. (2012). Pilot-scale production of mesoporous silica-based adsorbent for CO₂ capture. *Appl. Surf. Sci.* 258: 6943–6951.
- Wang, K., Yu, Q. and Qin, Q. (2013a). Reduction kinetics of Cu-based oxygen carriers for chemical looping air separation. *Energy Fuels* 27: 5466–5474.
- Wang, K., Yu, Q. and Qin, Q. (2013b). The thermodynamic method for selecting oxygen carriers used for chemical looping air separation. *J. Therm. Anal. Calorim.* 112: 747–753.
- Wang, K., Yu, Q., Duan, W., Qin, Q. and Xie, H. (2014). The adaptability of Cu/Zr oxides as oxygen carrier used for chemical looping air separation (CLAS). *J. Therm. Anal. Calorim.* 115: 1163–1172.
- Wang, W., Zhang, B., Wang, G. and Li, Y. (2016) O₂ release of Mn-based oxygen carrier for chemical looping air separation (CLAS): An insight into kinetic studies, *Aerosol Air Qual. Res.* 16: 453–463.

Received for review, June 16, 2019

Revised, November 26, 2019

Accepted, January 9, 2020