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Kinetic Behavior of Fabricated CuO/ZrO₂ Oxygen Carriers for Chemical Looping Oxygen Uncoupling

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Abstract: Chemical looping with oxygen uncoupling (CLOU) is an innovative alternative to conventional combustion. CuO/ZrO₂ oxygen carriers were tested in this system for their effectiveness and resilience. Cupric oxide (CuO) was demonstrated to be a reliable oxygen carrier for oxygen-uncoupling with consistent recyclability even after 50 redox cycles in a thermogravimetric analyzer (TGA). The reduction of CuO to generate Cu₂O and oxygen was observed to be improved markedly for experiments operated at higher temperatures; however, the oxidation of Cu₂O by air to generate CuO was hindered for experiments carried out at elevated temperatures. The reduction rate of fabricated CuO/ZrO₂ particles containing 40% CuO was enhanced with increasing temperature and decreased with increasing particle size for experiments operated in a fixed bed reactor. The geometrical contraction and Avrami-Erofe'ev models were demonstrated to be appropriate for describing the reduction and oxidation of CuO/ZrO₂, respectively. The activation energies for the reduction and oxidation were determined to be 250.6 kJ/mol and 57.6 kJ/mol, respectively, based on experimental results in the temperature range between 850 and 1000 °C.

Keywords: chemical looping; oxygen uncoupling; copper oxide; CuO/ZrO₂

Citation: Ku, Y.; Chang, C.-W.; Shiu, S.-H.; Wu, H.-C.; Moed, N.M. Kinetic Behavior of Fabricated CuO/ZrO₂ Oxygen Carriers for Chemical Looping Oxygen Uncoupling. *Processes* **2021**, *9*, 2156. <https://doi.org/10.3390/pr9122156>

Academic Editor: Hans-Joachim Gehrman

Received: 4 November 2021

Accepted: 24 November 2021

Published: 29 November 2021

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1. Introduction

Chemical looping combustion (CLC) is a novel and effective combustion technique developed to achieve high purity CO₂ in flue gas. The overall energy balance of reactions involved for CLC process is exothermic, and the heat released could be utilized for various applications [1]. The 95% to 99% CO₂ generated by a CLC operation can be inherently captured for utilization or for storage [2,3]. For chemical looping combustion of solid fuels, such as coal and petroleum coke, solid fuel gasification is frequently believed to be the rate-limiting step. Therefore, a chemical looping with oxygen uncoupling (CLOU) process was subsequently suggested to be an alternative to skip solid fuel gasification. Oxygen molecules are uncoupled from metal oxides for experiments conducted in an oxygen-free atmosphere at high temperatures [4], as illustrated by Equation (1). The released oxygen is subsequently combusted with fuels, as described by Equation (2).

Experiments carried out by previous researchers demonstrated that the combustion of several solid fuels by the CLOU process was approximately 3 to 50 times faster than that by typical CLC combustion because of the avoidance of the slow gasification step of solid fuel [4,5]. Copper oxide (CuO), manganese oxide (Mn₂O₃), and cobalt oxide (Co₃O₄) are oxygen carriers commonly employed for the CLOU process to release oxygen at a reasonable rate [6]. Amongst these, Cu-based oxygen carriers are comparatively feasible as

Mn-based and Co-based oxygen carriers are much more expensive and toxic [7,8]. However, the robust operation of Cu-based oxygen carriers at high temperatures is hampered by sintering and attrition due to the low melting point of these copper compounds. Therefore, the coupling of copper compounds with various support materials, such as Al_2O_3 , ZrO_2 , and SiO_2 , is frequently employed to improve their resilience during long-term chemical looping operations [9].

Various kinetic and thermodynamic studies regarding the reactions for chemical looping combustion using Cu-based oxygen carriers were reported, which is helpful for process simulation to design and optimize the system performance. Eyring et al. [10] reported that the activation energy for the reduction of unsupported CuO was determined to be 327 kJ/mol. Sahir et al. [11] reported the activation energy of 280 kJ/mol for the reduction of CuO/ ZrO_2 operated in a fluidized bed reactor. Wang et al. [12] reported that the activation energies for the reduction of CuO/ TiO_2 , CuO/ ZrO_2 , and CuO/ SiO_2 were 155.0, 152.9, and 144.9 kJ/mol, respectively. Song et al. [13] indicated that the activation energy for the reduction of CuO/ SiO_2 was determined to be 315 kJ/mol. Guo et al. [14] indicated that the activation energy was determined to be 343.7 kJ/min for the reduction of the CuO/ CuAl_2O_4 oxygen carrier. The variation among reported activation energies for the reduction of CuO-based oxygen carriers may be mainly due to the different kinetic models adapted by various researchers.

Although CLOU has been extensively studied, literature on the use of CuO/ ZrO_2 oxygen carriers in this process is limited. In this study, the reduction of pure CuO and fabricated CuO/ ZrO_2 oxygen carriers were investigated through consecutive redox-cycle operations of a thermogravimetric analyzer (TGA). The crystalline phases and surface morphology of both oxygen carriers during the redox operation were identified by X-ray diffraction (XRD) and field-emission scanning electron microscope (FESEM), respectively. The effects of operating temperature and oxygen concentration on the reduction and oxidation of fabricated CuO/ ZrO_2 were investigated in the TGA. The kinetic behavior for the reduction of fabricated CuO/ ZrO_2 with various particle sizes was also examined in a fixed-bed reactor.

2. Materials and Methods

The reactivity and recyclability of oxygen carriers were determined by a thermogravimetric analyzer (TGA, STA 449 F3, NETZSCH). Approximately 50 mg of CuO powder (99%, Aldrich) was loaded in an alumina crucible of the TGA. The temperature of the TGA chamber was raised with a ramping rate of 20 °C/min, and eventually kept at 950 °C. The reduction of CuO was initiated by purging 200 mL/min of N_2 gas into the TGA chamber. After the oxygen was totally released as CuO was entirely reduced to Cu_2O , the oxidation of Cu_2O was started by purging 200 mL/min of air into the TGA chamber.

In this study, CuO and ZrO_2 (99%, Sigma-Aldrich, MO, USA) powders were mixed for the fabrication of CuO/ ZrO_2 composite oxygen carriers. The fractions of CuO and ZrO_2 were predetermined to be 40 and 60 wt%, respectively, as initial tests showed that agglomeration occurred after repeated cycles with a fraction of 80% and 20%, respectively. This did not occur at the chosen ratio (results not reported). The mixed CuO/ ZrO_2 particles were dried and then sieved to acquire those in the size range from 0.3 to 2.8 mm. The CuO/ ZrO_2 particles were subsequently sintered in a muffle furnace (Lindberg BLUE/M UP550) at 1000 °C for 2 h. The redox of these fabricated CuO/ ZrO_2 (labelled as CZ230-S1) particles was studied in the TGA operated at various temperatures and oxygen concentrations in the reaction atmosphere, and the operation was replicated 50 times. The conversions for the reduction (reduction), X_{re} , and oxidation (oxidation), X_{oxi} , of CZ230-S1 oxygen carriers were calculated by Equations (3) and (4), respectively:

$$X_{re} = \frac{m_o - m(t)}{m_o - m_d} \quad (3)$$

$$X_{oxi} = \frac{m(t) - m_d}{m_o - m_d} \quad (4)$$

where m_o is the weight of fully-oxidized oxygen carriers; m_d is weight of fully-reduced oxygen carriers; and $m(t)$ is the weight of the oxygen carriers at period t .

In this study, the temporal behavior and calculated activation energy for reduction of CZ230-S1 was described by the following equation, as used by most researchers on the application of various oxygen carriers for chemical looping [15,16]:

$$\frac{dX_{re}}{dt} = k_1 \times f(X_{re}) \times \left(\frac{P_{O_2,eq} - P_{O_2}}{P_{O_2,eq}} \right)^\alpha \quad (5)$$

where t is reaction time; k_1 is the rate constant for the reduction of oxygen carriers; $f(X_{re})$ is the differential-form kinetic model for the reduction of oxygen carriers; $P_{O_2,eq}$ is the equilibrium oxygen partial pressure in the reaction atmosphere; P_{O_2} is the oxygen partial pressure at reaction time t ; and α is the reaction order with respect to oxygen partial pressure for CZ230-S1 reduction.

Experiments were also conducted in a fixed-bed reactor (FBR) system consisting of a tubular reactor (25.4 mm in ID, 30.48 in OD and 200 mm in high) made of SS310 stainless steel, a temperature control unit, a gas flow control unit, and a gas analysis unit. Approximately 80 g of fabricated CZ230-S1 oxygen carriers were placed in the tubular reactor for experiments operated isothermally at temperatures ranging from 850 to 950 °C. As the temperature was reached, 500 mL/min of nitrogen was then introduced into the reactor. Exhaust gas from the FBR was passed through a cold trap to condense steam and was subsequently analyzed by an O₂ analyzer (Molecular Analysis 6000i).

3. Results and Discussion

3.1. Reduction of CuO Oxygen Carriers

Experimental results for the reduction of CuO conducted in a TGA during various redox cycles under nitrogen atmosphere at 950 °C are shown in Figure 1. It can be observed that aging occurred over the process, with the oxidized weight of the oxygen carrier slightly but steadily decreasing between the cycles. This was most pronounced after the first cycle, where the oxidized oxygen carrier weight was only 94.5% that of the original weight. Regardless of this reduction in oxidization efficiency, CuO exhibited excellent oxygen uncoupling even after a 50-cycle operation, corresponding to the results reported by previous researchers [10]. As shown in Figure 2, the XRD patterns of reduced CuO sampled after various redox cycles were rather similar, and all samples demonstrated the presence of Cu₂O. The surface morphology and crystalline size of CuO sampled after various redox cycles were also observed to be comparable by examining the SEM images, as illustrated in Figure 3. While the size of particles varied between figures, the pore size and structure seemed to be rather constant, indicating that CuO is feasible as an oxygen carrier for CLOU operations because of its stability and recyclability.

3.2. Performance of Fabricated CuO/ZrO₂ Oxygen Carrier

Based on thermodynamic calculation, reduction of CuO would take place at temperatures above 800 °C in an oxygen-free atmosphere [17]. Therefore, the reactivity and recyclability of fabricated CZ230-S1 oxygen carriers for reduction were evaluated in the TGA for 50 redox cycles at 950 °C. As depicted in Figure 4, relatively high reduction (typically close to 100%) was maintained for CZ230-S1 during continuous redox cycles. The reduction rate for CZ230-S1 particles of various sizes was studied in the fixed bed reactor conducted at various temperatures, the calculated reduction rates are shown in Figure 5. Reduction rates for experiments conducted at temperature of 950 °C were observed to be almost 10 times higher than those conducted at 850 °C. More oxygen was uncoupled for experiments conducted at higher reaction temperatures, similar to the reported studies that reduction was observed at operating temperatures higher than 800 °C for silica-supported

CuO [17]. Therefore, the application of CZ230-S1 oxygen carriers for CLOU is preferred at higher temperatures; however, the operating temperature should not be higher than the melting temperature of CuO (around 1060 °C) to avoid serious sintering of these Cu-based oxygen carriers.

As also shown in Figure 5, the reduction rate was fairly enhanced for experiments conducted with CZ230-S1 particles of smaller sizes, comparable to the observations reported by several previous researchers for various CLP operations [15,18,19], indicating that reduction rate is appreciably affected by internal mass transfer within the oxygen carrier, which is more significant for experiments operated at higher temperatures. In addition, an increase in active site surface area is also expected to have an influence on reaction rates. Hence, operating temperature and particle size are both essential parameters to be considered for utilizing copper-based oxygen carriers for a CLOU process.

Figure 1. Conversion for the oxygen uncoupling of CuO in the TGA during various redox cycles under nitrogen atmosphere at 950 °C.

Figure 2. XRD patterns of decomposed CuO during 1, 2, 3, 10, and 50 redox cycles under nitrogen atmosphere at 950 °C.

Figure 3. SEM images of CuO oxygen carriers after 1, 2, 3, 10, and 50 redox cycles under nitrogen atmosphere at 950 °C.

Figure 4. Conversion for oxygen uncoupling of CZ230-S1 in the TGA under nitrogen atmosphere at 950 °C.

Figure 5. Oxygen uncoupling rate for CZ230-S1 of various particle sizes operated at temperature ranging from 850 to 950 °C.

3.3. Reduction and Oxidation Kinetics of CuO/ZrO₂ Oxygen Carriers

Reduction and oxidation kinetics of CZ230-S1 particles were investigated in the TGA operated between 850 and 1000 °C. As demonstrated in Figure 6, the reduction conversion (X_{re}) of CZ230-S1 particles was found to be accelerated markedly for experiments conducted at higher temperatures.

Figure 6. Conversion for oxygen uncoupling of CZ230-S1 in the TGA operated at various temperatures.

Experimental results for the reduction of CZ230-S1 were regressed with various kinetic models in this study. The geometrical contraction (R2) model was demonstrated to be appropriate for describing the reduction of CZ230-S1 particles, which assumes that the nucleation of Cu₂O occurs rapidly on the surface of particles, and the reduction rate of CZ230-S1 is essentially controlled by the formation of the Cu₂O layer [20]. The reduction of CZ230-S1 based on the geometrical contraction model (R2) for experiments operated at various temperatures was calculated and demonstrated in Figure 7, which was highly related to the operating temperature. Based on Arrhenius's law, the activation energy (E_{a1})

for the reduction of CZ230-S1 was determined to be about 250 kJ/mole, comparable to the reported results listed in the Introduction section of this paper. Figure 8 shows that the reduction of CZ230-S1 was inhibited for experiments conducted with O₂/N₂ mixtures containing higher oxygen concentrations, the reaction order (α) with respect to oxygen partial pressure for Equation (5) was evaluated to be 0.86.

Figure 7. Kinetic regression results based on the geometrical contraction model (R2) for the reduction of CZ230-S1 conducted with various operating temperatures.

Figure 8. Effect of oxygen concentration on the conversion of CZ230-S1 reduction in a TGA.

As illustrated in Figure 9, the oxidation (oxygen recoupling) of reduced CZ230-S1 was almost completed within 2 min for experiments conducted at temperatures ranging from 850 to 900 °C; longer times were required for experiments performed at higher temperatures, probably due to the fact that the driving force for oxygen transfer was decreased by the higher equilibrium partial pressures of oxygen at higher temperatures. The temporal behavior for the oxidation of reduced CuO/ZrO₂ is described by the following equation, which is similar to Equation (5):

$$\frac{dX_{re}}{dt} = k_1 \times f(X_{re}) \times \left(\frac{P_{O_2,eq} - P_{O_2}}{P_{O_2,eq}} \right)^\alpha \quad (6)$$

where k_2 is the rate constant for the oxidation of reduced oxygen carriers; $f(X_{oxi})$ is the differential-form kinetic model for the oxidation of reduced oxygen carriers; and β is the reaction order with respect to oxygen partial pressure for the oxidation of reduced CZ230-S1 with air.

Figure 9. Conversion for oxidation of reduced CZ230-S1 conducted at various operating temperatures.

Among various reaction models employed to describe the oxidation of reduced CZ230-S1 conducted with various temperatures under air atmosphere, the Avrami-Erofev'ev (A2) model is assumed to be most suitable as depicted in Figure 10. The reaction order (β) with respect to oxygen partial pressure for the oxidation of reduced CZ230-S1 with air was determined to be 0.5, whereas the reaction order for reduction was determined to be 0.37. The activation energy (E_{a1}) for the oxidation of reduced CZ230-S1 was calculated to be about 57 kJ/mole based on Arrhenius's law, much lower than that (about 250 kJ/mole) for the reduction of CZ230-S1, indicating that oxygen-recoupling was less temperature-dependent than oxygen-uncoupling for CZ230-S1. The difference of determined activation energies, 193 kJ/mol, is considered as the enthalpy for CuO uncoupling (ΔH_{CLOU}).

Figure 10. Kinetic regression results based on the Avrami-Erofev'ev (A2) model for the oxidation of decomposed CZ230-S1 conducted with various temperatures under air atmosphere.

4. Conclusions

Cupric oxide (CuO) demonstrated sound recyclability for oxygen-uncoupling in the TGA even after 50 redox cycles and was validated by XRD and SEM characterization without obvious changes in morphology and crystalline. The reduction rate of CuO increased markedly with increasing operating temperature, whereas the oxidation rate of Cu₂O decreased with increasing operating temperature. CZ230-S1 oxygen carriers were fabricated and were examined for their reduction and oxidation behavior in the TGA. The reduction rate determined by experiments carried out with fabricated zirconia supported CuO (CZ230-S1) pellets in a fixed bed reactor. The concentration of O₂ was increased for experiments conducted at higher reaction temperatures and was decreased for experiments conducted with larger particles. The geometrical contraction (R2) model and Avrami-Erofe'ev (A2) model were demonstrated to be appropriate to describe the reduction and oxidation of the CZ230-S1 oxygen carrier, respectively. The activation energies for the reduction and oxidation of CZ230-S1 were determined to be 250.6 and 57.6 kJ/mol, respectively. The difference of E_{a1} and E_{a2} can be considered as the enthalpy of CuO uncoupling. Recommendations for future research are an optimization of the CuO/ZrO₂ ratios, the use of pore-forming agents other than starch, application in a fluidized moving bed reactor, the use of solid fuels, and the effect of H₂S, commonly released by gasification of coal, on the reactivity of the oxygen carrier.

Author Contributions: Conceptualization, Y.K., C.-W.C., S.-H.S.; methodology, Y.K.; validation, C.-W.C., S.-H.S.; formal analysis, Y.K.; investigation, C.-W.C., S.-H.S.; resources, Y.K.; data curation, C.-W.C., S.-H.S.; writing—original draft preparation, C.-W.C., S.-H.S.; writing—review and editing, Y.K., H.-C.W., N.M.M.; visualization, Y.K., H.-C.W., N.M.M.; supervision, Y.K.; project administration, Y.K.; funding acquisition, Y.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by Grant MOST 105-3113-E-007-001- and MOST 103-2221-E-011-002-MY3 from the Ministry of Science and Technology, Taiwan.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are openly available on request.

Acknowledgments: The authors would like to express gratitude to the Ministry of Science and Technology, Taiwan for their funding.

Conflicts of Interest: The authors declare no conflict of interest.

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