Chemical-Looping with Oxygen Uncoupling of Different Coals Using Copper Ore as an Oxygen Carrier

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ABSTRACT: Chemical-looping with oxygen uncoupling (CLOU) has been considered as a revolutionary technology for low-energy consumption CO₂ capture. In this work, the performance of copper ore in the CLOU processes for diverse ranks of coal was examined in a batch-scale fluidized-bed at various temperatures. Typical Chinese coals (GaoPing anthracite, FuGu bituminous coal, and ShengLi lignite) were used as fuel. The effects of temperature and coal rank on the redox behavior, carbon conversion rate, and instantaneous rates of char conversion and oxygen generation were first investigated. It was found that both increasing the reactor temperature and decreasing the coal rank had beneficial effects on the carbon conversion rate, instantaneous rates of char conversion, and oxygen generation. In the CLOU processes of coal, the rate-limiting step was the burning of coal char with oxygen of low concentration if the oxygen carrier (OC) was excess to coal. And for higher-rank coals like anthracite, the rate-limitation effect was also greater. Then, two additional CLOU tests of anthracite were conducted to examine the accelerative effect of gasification agents. The results demonstrated that introducing the gasification agent (steam or CO₂) into the fuel-reactor can increase the instantaneous char conversion rate of high-rank coal. Scanning electron microscopy-energy dispersive X-ray spectroscopy results showed that the porous structure of the used copper ore particles was partly blocked by the adhesion of fly ash. To be noted, all used copper ore particles presented a porous structure, and no serious agglomeration phenomenon was detected within the CLOU process, except for high-volatile lignite at 950 °C.

1. INTRODUCTION

According to the analysis of Intergovernmental Panel on Climate Change (IPCC) and International Energy Agency (IEA),1,2 carbon capture, usage, and sequestration has been widely accepted as an important route for reducing anthropogenic emission of greenhouse gas into the atmosphere and would contribute to 10–55% of the cumulative reduction of CO₂ emission globally until 2100. Chemical-looping combustion (CLC) is viewed as a promising candidate for fossil fuel combustion with inherent CO₂ sequestration.3 To settle the issue of the relatively low char gasification rate in the in situ gasification chemical-looping combustion (iG-CLC),4–6 Mattisson et al. first demonstrated the concept of chemical-looping with oxygen uncoupling (CLOU). To address the CLOU process, a special oxygen carrier (OC) material which can release oxygen at appropriate temperatures in the fuel-reactor should be applied, thereby leading the fuel to burn with O₂. Then, the reduced OC is further transported back to be reoxidized with air in the air-reactor and being ready to initiate another cycle. Within a coal-fired CLOU system, the solid fuel reacts directly with gaseous O₂ in the fuel-reactor, which avoids the relatively slow char gasification process to some extent. Consequently, much higher combustion efficiency and CO₂ capture efficiency could be reached.

In the CLOU process, the OC should decompose to release O₂ in the fuel-reactor and regenerate itself in the air-reactor at the interesting temperature window (800–1200 °C). Thus, materials considered as OC mainly include three synthesized metal oxides systems of CuO/Cu₂O, Mn₃O₄/MnO₂ and perovskite-type oxides.8–15 The CLOU concepts have been demonstrated in batch-operating laboratory-scale fluidized-bed reactors10,11,16,17 and continuously operating interconnected fluidized-bed reactors8,12,13,18,19 using these previously mentioned metal oxides systems as OC and methane, kerosene, coal, or petroleum coke as fuel. All of the works about CLOU have been reviewed by Mattisson20 and Qasim et al.21 Among these OCs, Cu-based OC has been considered as one of the most promising candidates since it performs fast oxygen release and appropriate O₂ equilibrium partial pressure within the temperature range of 800–1200 °C. Additionally, Lewis et al.22 demonstrated that the use of CuO could enhance the carbon gasification reaction. Up to now, a number of works were mainly concentrated on four kinds of synthesized Cu-based OCs (CuO/ZrO₂,2,7,11,13 CuO/MgAl₂O₄,8,24–26 CuO/CuAl₂O₄,27,28 and CuO/TiO₂-Al₂O₃30), which were examined to have excellent performance and prospect for using in the CLOU process. Mattisson et al.2,21 first evaluated the performance of CuO/ZrO₂ OC synthesized by freeze granulation with petroleum coke as fuel in a lab-scale fluidized-bed reactor. Abad et al.5 then investigated the reaction between bituminous coal and CuO/MgAl₂O₄ OC in a 1.5 kWth continuously operated CLOU system. Song et al.27 reported a novel coprecipitation route for the preparation of Cu-Al OC from the layered double hydroxides precursor. Xu et al.30 put forward a self-assembled template combustion synthesis (SATCS) method and synthesized CuO/TiO₂-Al₂O₃ OC with hierarchical structure, Cu-rich, micron Al₂O₃-supported and nano TiO₂-stabilized in a core–shell micro-architecture. Eyring et al.31 illustrated the significance of CLOU
by showcasing the relevant engineering considerations, using CuO as OC and coal as fuel.

Obviously, the synthesized Cu-based OC used in the CLOU process has advantages of controllable chemical composition and physical structure. However, these synthesized materials are generally expensive. Furthermore, the OC lifetime is greatly restricted in the industrial CLOU of solid fuels because of OC pollution by coal ash or loss of OC particles when separating the OC from ash or mechanical attrition between OCs and/or reactor wall. Therefore, a cheap OC is highly desired. Copper ore has been considered with advantages of low cost and abundant reserves. Three kinds of copper ore were investigated by Wen et al. in terms of cyclic oxygen release and uptake. It was found that the copper ore with a relatively lower copper content (only 5.82 wt % CuO and 82.8% SiO₂) did not agglomerate during the first 20 cycles at 980 °C. However, serious agglomeration was observed for copper ore particles with higher Cu contents (63.25 wt % and 87.28 wt % CuO). Therefore, a typical issue of agglomeration and sintering of copper ore particles at high temperatures should be urgently overcome. Recently, Zhao et al. utilized a medium Cu content (about 44 wt %) copper ore particles as OCs and investigated their CLOU reactivity with a low-volatile anthracite. It was found that this copper ore OC has high reactivity and cyclic stability in cycling tests, and no serious agglomeration or sintering was found in the used particles. Then, in order to improve the antisintering property of this medium Cu content copper ore, Yang et al. further mixed an iron ore, and this copper ore with a suitable mass ratio and tested them in TGA with syngas as well as in a batch-scale fluidized-bed reactor with coal. It was found that the mixed OC exhibited better reactivity than iron ore and better antisintering than copper ore. Furthermore, Tian et al. used cement-decorated copper ore as OC in the CLOU process. The results showed that copper ore loading with 20 wt % of cement exhibited very good oxygen transport capacity, and no sintering or agglomeration phenomenon occurred within the cyclic redox process at 950 °C.

The CLOU performance for different types of solid fuels is diverse, which mainly depends on the volatiles content and devolatilizing rate of the fuel, the oxygen release rate and oxygen carrying capacity of the OC, and the reaction rate between the char and gaseous oxygen. For example, Leion et al. investigated the oxygen release ability and CLOU reactivity of CuO/ZrO₂ with six different solid fuels. Recently, Adánez-Rubio et al. and Mei et al. investigated the relation between the coal rank and the CLOU performance using CuO/MgAl₂O₄ and CuO/CuAl₂O₄ as OCs, respectively. They both found that an increase of coal rank would contribute to a relatively lower reaction rate.

This work aimed to evaluate the performance of copper ore as OC in the CLOU process for coals of different ranks. The effects of temperature and coal rank on redox behavior, carbon conversion rate, and instantaneous rates of char conversion and oxygen generation were examined in a batch-scale fluidized-bed reactor.

2. EXPERIMENTAL PROCEDURES

2.1. Preparation of Copper Ore and Coal Particles. The used OC particles were prepared from a refined copper ore from Zhongtiaoshan of China. To enhance the crushing strength and eliminate inherent sulfur of the ore, it was first calcined for 5 h at 500 °C and then 10 h at 1000 °C in a muffle oven under air atmosphere. More information about the sulfur behavior of the ore in the calcination process is shown in Section 3.1. Finally, the particles were crushed and sieved to 0.125–0.180 mm to gain the fresh OC. Three Chinese coals with typical ranks, GaoPing anthracite, FuGu bituminous coal, and ShengLi lignite were used as fuels. The coals were first dried under 105 °C for 10 h to remove the apparent water and then crushed and sieved to 0.2–0.3 mm.

2.2. Characterization of Copper Ore and Coal Particles. The ultimate analysis and composition analysis of the raw copper ore particles and the calcined ones are shown in Table 1, which were determined by X-ray fluorescence (XRF) spectrometry (EDAX EAGLE III) together with X-ray diffraction (XRD) analysis (X’PertPRO). It can be seen that quite a lot sulfur was contained in the raw ore before calcination, while it was greatly removed after calcination. The result shows that the copper ore mainly consists of CuO and CuFe₂O₄. Then, the N₂-absorption method (Micromeritics, ASAP2020) was employed to determine the BET specific surface area of the OC. The real density was measured by an automatic true density analyzer (AccuPyc 1330). The crushing strength was determined by measuring the force needed to fracture a particle using a crushing strength apparatus (Shimpo FGI-35), taking as the average value of 20 measurements. The attrition resistance of the OC particles was evaluated by an abrasion tester (DGM-100, made by Dalian intelligent testing machine factory). About 30 g of OC was put into a stainless cylinder (14.5 cm in length and 12.0 cm in diameter) with a 1.5 cm baffle and rotated at a rate of 10 rpm on a ball-mill roller for 50 min. The attrited OC particles were sieved (the size of the sieve is 0.125 mm) and weighted, and then the attrition index was calculated by \[ \delta = \frac{(m_1 - m_2)}{m_1} \times 100\% \], where \( m_1 \) is the weight of the OC before test, and \( m_2 \) is the weight after test. The crystalline phase of the copper ore OC was determined by XRD analysis. Finally, the morphologies of both the fresh and used OC particles were evaluated by an environment scanning electron microscope (ESEM, FEI Quanta 200). The physical and chemical properties of the fresh OC particles are shown in Table 2.

An ultimate analyzer (Vario, EL-2) and a proximate analyzer (Las Navas, TAG2000) were employed to determine the proximate and ultimate analyses of the three pretreated coals, respectively, as shown in Table 3. Note the volatile contents of anthracite (10.69%), bituminous coal (27.19%), and lignite (41.59%), resulting to cover a wide range of coals.

Table 1. Copper Ore Compositional Characteristics

<table>
<thead>
<tr>
<th>samples</th>
<th>component analysis (wt %)</th>
<th>ultimate analysis (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CuO</td>
<td>CuFe₂O₄</td>
</tr>
<tr>
<td>before calcination</td>
<td>21.04</td>
<td>70.05</td>
</tr>
<tr>
<td>after calcination</td>
<td>48.88</td>
<td>45.00</td>
</tr>
</tbody>
</table>

*Measured by XRF together with XRD. Measured by XRF.

Table 2. Physical and Chemical Properties of the Fresh Copper Ore OC

<table>
<thead>
<tr>
<th>oxygen transport capacity, ( R_{OC} ) (wt %)</th>
<th>particle size (mm)</th>
<th>attrition index (%/h)</th>
<th>specific surface area, BET (m²/g)</th>
<th>density (kg/m³)</th>
<th>crushing strength (N)</th>
<th>XRD main phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.44</td>
<td>0.125–0.180</td>
<td>1.74</td>
<td>0.2</td>
<td>5353</td>
<td>1.53</td>
<td>CuO, CuFe₂O₄</td>
</tr>
</tbody>
</table>
2.3. Fluidized-Bed Reactor and Experimental Procedures. A schematic view of the batch-scale fluidized-bed reactor is shown in Figure 1. The reactor system consisted of a fluidized-bed reaction unit, a gas feeding unit, and a gas analyzing unit. The gas feeding unit provided nitrogen or air, which was injected from the bottom of the reactor to simulate the fuel-reactor or air-reactor. The reaction chamber was a straight stainless steel tube of 890 mm in height and 26 mm in diameter, which was heated by an electrical furnace. A stainless porous plate was placed in the tube at the height of 400 mm from the bottom of the reactor, and the temperature within the reactor was measured with K-type thermocouples located at 10 mm above the plate. The exhausted gas from the reactor went through a filter first to remove fine particles as well as an electric cooler to totally eliminate the steam contained in the exhausted gas and finally to an online gas analyzer (Gasboard Analyzer 3100) to determine the concentrations of CO₂, CO, CH₄ (by nondispersive infrared analysis (NDIR)), H₂ (by thermal gas conductivity (TCD)) and O₂ (by electron capture detector (ECD)).

In the CLOU experiments, 40 g of OC was placed on the stainless porous plate, exposing in air for 30 min at a preset temperature to guarantee full oxidation. Then, the reactor was heated in nitrogen atmosphere, and the O₂ partial pressure within the reactor decreased drastically. The OC would decompose and release gaseous oxygen, and the O₂ partial pressure would be close to the equilibrium partial pressure of the OC at the set-point temperature gradually. When the oxygen concentration stabilized, 0.3 g of coal particle was introduced into the reactor from the hopper to start a coal-fired CLOU process. The coal was assumed to be completely converted until no CO₂ was measured in the exhaust gas. Afterward, air was switched as the fluidization gas and the reduced OC was reoxidized.

The CLOU experiments of different coals with copper ore were determined in the fluidized-bed reactor at 850, 900, and 950 °C to evaluate the effects of coal rank and temperature on the thermochemical characteristic of copper ore. In most of the tests, the fluidization gas was nitrogen in reduction periods and air in oxidation periods. Two additional tests using pure CO₂ and gas mixture of nitrogen and steam as fluidization agents and anthracite as fuel in reduction periods were carried out at 900 °C. The gas flow rate in all periods was 800 mL/min (corresponding to the superficial gas velocity u = 0.096 m/s), which led to u/utₐd = 4.4–9.2, where utₐd is the minimum fluidization velocity of the particles.

### Table 3. Proximate and Ultimate Analyses of Three Coals

<table>
<thead>
<tr>
<th></th>
<th>proximate analysis (wt %, ad)</th>
<th>ultimate analysis (wt %, daf)</th>
<th>low heating value (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>moisture</td>
<td>volatiles</td>
<td>ash</td>
</tr>
<tr>
<td>anthracite</td>
<td>2.25</td>
<td>10.69</td>
<td>20.62</td>
</tr>
<tr>
<td>bituminous coal</td>
<td>1.65</td>
<td>27.19</td>
<td>19.62</td>
</tr>
<tr>
<td>lignite</td>
<td>8.62</td>
<td>41.59</td>
<td>35.47</td>
</tr>
</tbody>
</table>

*O₂/O₃ to balance.

2.4. Data Evaluation. In the CLOU process, coal fed into the fuel reactor initially devolatilizes to generate volatiles and char. Subsequently, the volatiles react with gaseous oxygen released from OCs quickly or with OCs directly, whereas char reacts with O₂ relatively slowly. As seen, two consecutive steps are involved in the coal combustion process: volatiles combustion and char combustion. Therefore, in order to better understand the two steps, the evolution of coal, volatiles, and char conversions with time was calculated in this work.

In all experiments, carbon-containing gas was never detected during the oxidation periods. So it was assumed that all of the coal particles have been completely converted, and there was no carbon deposition on the surface of OC samples after the reduction periods. Thus, the carbon conversion, xₐ(t), and char conversion, xₐ,char(t), were calculated as

\[
xₐ(t) = \frac{\int_{t_0}^{t} F_{\text{flus}} (y_{CO} + y_{CO_2} + y_{CH_4}) \, dt}{\int_{t_0}^{\text{total}} F_{\text{flus}} (y_{CO} + y_{CO_2} + y_{CH_4}) \, dt}
\]

(1)

\[
xₐ,char(t) = \frac{\int_{t_0}^{t} F_{\text{flus}} (y_{CO} + y_{CO_2} + y_{CH_4}) \, dt}{\int_{t_0}^{\text{total}} F_{\text{flus}} (y_{CO} + y_{CO_2} + y_{CH_4}) \, dt} (t > t_1)
\]

(2)

where \(y_{CO}, y_{CO_2},\) and \(y_{CH_4}\) are the molar fraction of CO, CO₂, and CH₄ at each second among the exhausted gas, respectively; \(F_{\text{flus}}\) is the outlet gas molar flow rate, determined by \(N_2\) balance between the outlet and the inlet gas flows of the reactor; \(t_0\) and \(t_{\text{total}}\) represent the starting time and the stop time of the CLOU reaction, respectively; and the time \(t_1\) represents the end of coal devolatilization and the beginning of char combustion.

Thus, the carbon conversion rate, \(xₐ(t)\), and the average apparent conversion rate, \(xₐ,app,CO\), can be determined as

\[
xₐ(t) = \frac{dxₐ}{dt}
\]

(3)

\[
xₐ,app,CO = \frac{0.95}{t_{95,app,CO} - t_0} \times 100\%
\]

(4)

where \(t_{95,app,CO}\) represents the time point when the carbon conversion reaches 95%.

The instantaneous char conversion rate, \(xₐ,char,inst\), was determined on the basis of the remaining nonreacted char, as shown in eq 5.

\[
xₐ,char,inst = \frac{dxₐ,char}{dt} \frac{1}{1 - xₐ,char}
\]

(5)

In order to investigate the oxygen releasing properties of OC, the instantaneous rate of oxygen generation per amount of OC, \(xₐ,char,O₂(t)\), was determined based on the mass balance of the O atoms in the reactor:

\[
xₐ,char,O₂(t) = \frac{M_{O₂}}{m_{OC}} \left[ F_{O₂} + F_{CO_2} + 0.5(F_{CO} + F_{H_2}O) - 0.5F_{char,coal} \right]
\]

(6)

where \(F_i\) is the molar flow rate of gas component \(i\) exiting from the fuel-reactor, which is determined by
where \( y_i \) is the molar fraction of gas component \( i \) (including \( \text{O}_2 \), \( \text{CO}_2 \), \( \text{CO} \), \( \text{CH}_4 \), or \( \text{H}_2 \)) in the product gas. Because of the measurement limitation, the steam content was not determined in the experiment. Therefore, in order to measure the oxygen leaving with \( \text{H}_2\text{O} \) and \( \text{CO} \), the hydrogen generation from hydrogen oxidation in the coal, it was assumed that the hydrogen evolution was proportional to the carbon evolution; i.e., the ratio \( \text{C/H} \) maintained the same value in the gas components as in the coal. Considering the fact that a little methane and hydrogen were detected in the experiment, the \( \text{H}_2\text{O} \) and \( \text{CO} \) concentration ratios were maintained at the same value as in the gas components.

The gas from the reactor was introduced into the air-reactor, where the oxygen was separated using the sulfur release of the copper ore, and \( \text{H}_2\text{O} \) and \( \text{CO} \) were consumed. The oxygen leaving \( \text{H}_2\text{O} \) and \( \text{CO} \) was calculated as the difference between the original oxygen demand of the fuel and the difference of the \( \text{OC} \) transport capacity. Therefore, in order to measure the oxygen leaving with \( \text{H}_2\text{O} \) from the reactor, the minimum solid inventory in the air-reactor and fuel-reactor was determined by the oxygen demand of the fuel and the difference of the \( \text{OC} \) transport capacity.

\[
F_i = F_{\text{in}} y_i
\]  
(7)

\[
F_{\text{O}_2,\text{coal}} = F_{\text{OC/C}} (F_{\text{CO}_2} + F_{\text{CO}} + F_{\text{CH}_4}) - (F_{\text{H}_2} + 2F_{\text{CH}_4})
\]  
(8)

\[
F_{\text{O}_2,\text{coal}} = f_{\text{OC/C}} (F_{\text{CO}_2} + F_{\text{CO}} + F_{\text{CH}_4})
\]  
(9)

where \( f_{\text{OC/C}} \) is the hydrogen to carbon molar ratio in the coals (0.61 for anthracite, 0.61 for bituminous coal, and 1.02 for lignite). Similarly, the oxygen evolution from coal was assumed to be proportional to coal evolution. Therefore, the oxygen flow rate coming from coal was calculated as:

\[
F_{\text{O}_2,\text{coal}} = f_{\text{OC/C}} (F_{\text{CO}_2} + F_{\text{CO}} + F_{\text{CH}_4})
\]  
(10)

where \( F_{\text{O}_2,\text{coal}} \) is the total moles of gaseous \( \text{O}_2 \) that could be generated from copper ore. Then, the average OC conversion rate, \( x_{\text{OC/GS}} \), can be determined as

\[
x_{\text{OC/GS}} = \frac{x_{\text{OC/GS}}}{t_{\text{OC}}} - t_0 \times 100\%
\]  
(11)

where \( x_{\text{OC/GS}} \) represents the point in OC conversion when the 

3. RESULTS

3.1. Sulfur Behavior of Copper Ore in Calcinations Process. From the XRD result of the copper ore sample before calcination, this copper ore mainly consists of \( \text{CuFe}_2\text{S}_4 \), \( \text{CuS} \), and \( \text{SiS}_2 \), while \( \text{CuO} \) or \( \text{Fe}_2\text{O}_3 \) is not found. In fact, the original copper ore, which generally contains very low copper content and is difficult for flotation, usually undergoes the sulfuration reaction before the flotation process, which changes copper oxide in the original ore to copper sulfide as well as improves the surface hydrophobicity. In order to gain insight into the sulfur release in the calcination process in the muffle oven, we carried out some experiments in the laboratory-scale fixed-bed reactor (see Figure 1) with quite low superficial velocity to simulate the calcination process. First of all, the original massive copper ore was dried at 105 °C for 24 h to obtain the sample before calcination. In the experiment, the reactor was first heated to 500 °C under air atmosphere with a flow rate of 200 mL/min. Then 10 g of copper ore was introduced into the reactor by the hopper to investigate the sulfur release property at 500 °C. The off gas from the reactor was introduced into the online gas analyzer for measuring the \( \text{SO}_2 \) and \( \text{O}_2 \) concentrations. When the concentration of \( \text{SO}_2 \) decreased to zero, the sulfur release process was assumed to be finished. The sample was taken out when the temperature decreased to room temperature. Afterward, a similar experiment was carried out at 1000 °C using the same sample in the previous experiment to detect if there was still some residual sulfur in the sample.

Figure 2 shows the gas concentration profiles during the sulfur release of copper ore at 500 °C and 1000 °C. As the \( \text{SO}_2 \) concentration detected in the test was above the measurement limit of the equipment, the presented maximum concentration of \( \text{SO}_2 \) was 10 000 vppm. At 500 °C, the concentration of \( \text{SO}_2 \) increased rapidly from 0 vppm to above 10 000 vppm and the \( \text{O}_2 \) concentration decreased rapidly from 21% to almost 0% after the copper ore sample was added into the reactor. After about 180 min, the \( \text{SO}_2 \) concentration decreased to zero. However, when the further calcination experiment was carried out under 1000 °C, it was found from the curve of \( \text{SO}_2 \) concentration in Figure 2b that there was still residual sulfur in the sample. But the total amount of the released sulfur at 1000 °C was much less than that at 500 °C.
The result suggests that this copper ore cannot release sulfur completely at 500 °C, and it needs a higher temperature for the sulfur removal from the copper ore. On the basis of these understandings, in the calcination process the copper ore was first calcined for 5 h at 500 °C and then 10 h at 1000 °C in an air-atmosphere muffle oven.

3.2. CLOU Behavior. The exit gas composition in the reduction stage has been measured for each experimental condition. As an example, the time-dependent gas concentrations in the CLOU combustion process of bituminous coal at 900 °C are shown in Figure 3. In the reduction period, the oxygen concentration decreased sharply from about 1.5% to lower than 0.2% after the coal particles were introduced into the reactor, which was attributed to the oxygen consumption through the combustion of volatiles. Then, the oxygen concentration gradually increased to about 0.7%, which was because of the lower oxygen consumption rate through the combustion of char. A peak of CO, CH₄, or H₂ was observed at the start of the reduction stage, which was because of the coal devolatilization. These reducible gases had insufficient residence time to be reduced by gaseous oxygen or OCs before exiting from the reactor. When compared with the other two coals (not shown here), the reaction for lignite had the largest amount of unreacted combustible gases and then followed by bituminous coal and anthracite. To be noted, it has been proven that the volatiles in the coals could be completely combusted in a real CLOU system.18 As for the CO₂ concentration, it increased rapidly to a peak concentration of 40% (lignite), 24% (bituminous coal), and 6% (anthracite) within 30 s, which clearly demonstrated that the reaction rate of the fuels decreased in the order lignite > bituminous coal > anthracite. Obviously, the different CLOU characteristics of the three coals were attributed to the coal rank (mainly the volatiles and char contents). Additionally, we mention here that the effects of coal ranks on the CLOU process with various types of coal also have been examined by Adanez Rubio et al.,18 Mei et al.,36 and Song et al.39

3.3. Effect of Temperature and Coal Rank. In order to unveil the effects of reaction temperature and coal rank on the carbon conversion rate in the CLOU process, the carbon conversion rate, Xₚ, was calculated for each experiment, as shown in Figure 4. The time t₁ (corresponding to a constant Xₚ for each coal) represents the end of coal devolatilization and the beginning of the char combustion, which was determined by the method introduced in the ref 40. Before t₁, it was assumed that the main reactions were the combustion of volatiles. Subsequently, the main reactions were changed to the combustion of char, which was much slower. Obviously, due to the higher reactivity for all reactions involved at higher temperatures, the carbon conversion rate for all the three coals had an obviously increasing trend with the temperature, except for an anomalous curve for lignite at 950 °C. This was likely due to the slight defluidization (a detailed explanation will be shown in Section 3.5) of the OC particles at 950 °C, at which a drastic bed pressure drop decrease in the reactor was detected. Figure 5 shows the instantaneous char conversion rate with the evolution of char conversion. As shown in Figure 5a, the temperature effect on instantaneous char conversion rate for bituminous coal was similar with the carbon conversion rate, as well as anthracite and lignite (not shown). With regard to the effect of the coal rank, as illustrated in Figure 4, the carbon conversion rate of the three coals had an order of lignite > bituminous coal > anthracite at each temperature. The reason might be 2-fold: on the one hand, low rank coals contained higher volatiles content and lower char content, and the combustion of more volatiles would lead to a greater local temperature rise and then faster OC decomposition, which helps faster conversion of coal char. On the other hand, the combustion of low-rank coal char might be easier than that of high-rank coal,41 which is partly relevant to the porosity of char particles. As shown in Figure 5b, the instantaneous char conversion rate also had an order of lignite > bituminous coal > anthracite at 900 °C, which can support this statement.

Figure 3. Typical concentration profile (dry basis) for bituminous coal at 900 °C in the reduction period.

Figure 4. Carbon conversion rate as a function of carbon conversion for all coals at different temperatures.
The average carbon conversion rate within the reduction stage, $x_{0.95,C}$, was calculated for each test, as shown in Figure 6. $x_{0.95,C}$ for bituminous coal and anthracite had an obviously increasing trend with the temperature, while for lignite it first increased slightly from 850 to 900 °C and then decreased slightly from 900 to 950 °C, which was attributed to slight defluidization of copper ore particles at 950 °C. It can be concluded that a higher temperature had an enhanced effect on the combustion rate for different types of coals and increased the combustion rates of high-rank coal to a greater extent. Furthermore, $x_{0.95,C}$ for the three coals had an order of lignite > bituminous > anthracite at all temperatures. In addition, the gaps of conversion rate for the three coals were reduced with the temperature elevating from 850 to 950 °C.

In order to better understand the reactivity of copper ore OC with different coals, the instantaneous oxygen generation rate with the evolution of the carbon conversion at various temperatures was calculated, as shown in Figure 7. As seen, the effect of temperature and coal rank on the instantaneous rate of oxygen generation was similar to that on the carbon conversion rate. The instantaneous oxygen generation rate had a consistent trend with the carbon conversion rate. Table 4 shows the average instantaneous oxygen generation rates for volatiles combustion, $x_{O_2,vol}$ ($0 < t < t_1$), and char combustion, $x_{O_2,char}$ ($t > t_1$), and average OC conversion rate, $x_{OC,0.95}$ (between carbon conversion from 0 to 0.95). Obviously, both increasing the temperature and decreasing the coal rank had beneficial effects on the OC conversion rate. Moreover, the $O_2$ concentration was still above zero during the whole process (from the concentration files), which indicated that the oxygen release of copper ore was not the rate-limiting step. So, it was considered that the oxygen generation rate depended mainly on the combustion rate of coal with gaseous oxygen. As shown in Table 4, the $x_{O_2,char}$ for char combustion was much smaller than $x_{O_2,vol}$ for volatiles combustion, which showed that the
combustion of volatiles was much faster than the solid–gas reaction between char and \( \text{O}_2 \)\textsuperscript{42}. It is noted that the volatile matter in coal may react directly with copper ore, especially for low-rank coals, which can increase the oxygen generation rate as well.

Adanez-Rubio et al.\textsuperscript{25} found that the rate-limiting step in CLOU depends on the ratio of OC to coal used. If the OC to coal ratio is low enough, the rate-limiting step in CLOU is the oxygen release step. But, if the oxygen carrier is in excess to coal (like this work, also in real CLOU processes), the rate-limiting step in CLOU is the oxidation of volatiles and coal char under low-concentrated \( \text{O}_2 \). The oxidation of volatiles and coal char with the help of \( \text{H}_2\text{O} \) and/or \( \text{CO}_2 \). It will need further research to study the competitive and cooperative relations between the reaction rates of oxygen release and char combustion, which are our main work in the next stage.

### 3.4. Redox Cyclic Test

Successive redox cycles were conducted at 900 °C to investigate the potential cyclic stability of copper ore in the CLOU process with different coals. Figure 8 shows the \( \text{CO}_2 \) concentration curves for five reduction cycles using anthracite as fuel. As shown, in the reduction period, the peak \( \text{CO}_2 \) concentration of copper ore was stabilized at about 6% with the cycle number, and the time consumed for each reduction process was nearly 40 min. Furthermore, a small amount of \( \text{CO} \) (<1%) and \( \text{H}_2 \) (<0.3%) was detected in the beginning of each reaction period, which is not shown in the figure. The gas concentration profiles when using bituminous coal and lignite as fuels were similar (not shown here), while with higher peak \( \text{CO}_2 \) concentration as well as shorter reaction time. Figure 8 also shows the average OC conversion rate, \( x_{\text{OC,0.95}} \), as a function of cycle number. As seen, the average OC conversion rate remained stable at all five reduction periods, being a value of about 2.8% per min. In conclusion, these results demonstrated that copper ore particles are potentially suitable for the CLOU process with coals. However, a long-term test is highly required, which will be addressed in the next stage.

### 3.5. Pore Structure and Surface Morphology Analysis

The BET specific surface area measured for both the fresh used OCs was very small. The specific surface area of the fresh OC was 0.2 m\(^2\)/g, which was higher than those of used OCs (all lower than 0.1 m\(^2\)/g). This was because of the slight sintering of the OC particles or the blocking of coal fly ash, which probably resulted in slight reactivity decrease of copper ore particles. The reason for blocking of fly ash generated was verified by EDX analysis, as shown in Figure 9. It can be seen that nearly no Na or K element was found on the surface of the fresh copper ore particles. However, for the copper ore particles after reacting with different coals, both of the Na and K elements increased significantly on the surface, which was caused by the adhesion of fly ash. The SEM images of higher magnification for the fresh OC and used OCs are shown in Figure 10. It was found that the surfaces of all the particles presented a porous structure, but for used OCs, the pores were smaller than that of fresh particles and slight sintering of the used particles was found. It was emphasized that no serious agglomeration phenomenon of the used OC particles occurred in the CLOU of almost all tests, except slight defluidization was found when combusting lignite at 950 °C, which led to a decrease in the combustion rate of coal obviously (see Figure 4). Moreover, some small agglomerates of the copper ore particles were found after testing with lignite at 950 °C, which verified the slight defluidization once again. Factually, the reduction between copper oxide and fuel was exothermic, resulting in an increase of local temperature that favors more serious sintering of copper ore particles. Since the volatiles content of lignite was the maximum among the three coals, the combustion of lignite released more heat than the other two coals, resulting in a higher local temperature around the ore particles. Thus, the copper ore particles with lignite agglomerated more seriously, and then the defluidization of OC particles appeared.

The attrition index of fresh OC particles and used OC particles was tested in an abrasion tester for 50 min. The result showed that the attrition index was 1.74%/h for fresh copper ore particles. However, the attrition indexes for the three kinds of used particles (2.03%/h for anthracite, 2.89%/h for bituminous coal, and 2.46%/h for lignite) were all larger than that for the fresh particles, although the differences were very limited. This means that the attrition resistance for this copper ore particles will decrease slightly with an increase of reaction time.

### Table 4. Average Instantaneous Oxygen Generation Rate for Volatiles Combustion, \( x_{\text{O}_2,\text{vol}} \), and Char Combustion, \( x_{\text{O}_2,\text{char}} \), Average OC Conversion Rate, \( x_{\text{OC,0.95}} \), between Carbon Conversion from 0 to 0.95.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( x_{\text{O}_2,\text{vol}} \times 10^4 ) (g/s per g OC)</th>
<th>( x_{\text{O}_2,\text{char}} \times 10^4 ) (g/s per g OC)</th>
<th>( x_{\text{OC,0.95}} ) (g/s per g OC)</th>
<th>( x_{\text{OC,0.95}} ) (% per min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>0.23</td>
<td>0.06</td>
<td>1.07</td>
<td>0.45</td>
</tr>
<tr>
<td>900</td>
<td>0.46</td>
<td>0.22</td>
<td>2.82</td>
<td>1.20</td>
</tr>
<tr>
<td>950</td>
<td>0.72</td>
<td>0.44</td>
<td>7.48</td>
<td>1.52</td>
</tr>
</tbody>
</table>
4. DISCUSSION

In the conventional CLC process, steam and CO₂ are usually used as gasification agents reacting with solid fuel to improve the reaction rate, especially the char conversion rate. According to the previous analysis, the coal char (especially for high rank coals) conversion rate was much slower than the OC decomposition rate, which limited the overall reaction rate.

In order to solve this problem, it is feasible to introduce an appropriate content of steam or pure CO₂ into the fuel-reactor to promote the gasification of the char in the CLOU process to achieve a relatively higher overall reaction rate, as well as to attain a high-concentration CO₂ steam exiting from the fuel-reactor. So, we have carried out two additional tests using steam content of 40% in nitrogen and pure CO₂ as fluidization gas to...
before being fully converted. The fuel-reactor is within a high-pressure gasification environment, undergoing plenty of complicated reactions in the fuel-reactor of CLOU. As known, within a CLOU process, the fuel is converted before it is fully char converted at 900 °C. Obviously, when introducing the gasification agents into the fuel-reactor, the instantaneous char conversion rate was higher than that with pure nitrogen. The reasons may be very complicated, relating to very complicated reactions in the fuel-reactor before being fully converted. The fuel-reactor is within a high-temperature and oxygen-deficient environment, and the OC in the oxidized state first decomposes to release gaseous O2:

$$2\text{MeO}_x \leftrightarrow 2\text{MeO}_{x-1} + \text{O}_2(g) \quad (R1)$$

And the coal devolatilizes to char and volatiles simultaneously:

$$\text{coal} \rightarrow \text{char} + \text{volatiles}(g) + \text{H}_2\text{O}(g) \quad (R2)$$

Thus, these combustible gases are oxidized rapidly as in the normal combustion process:

$$\text{volatiles}(g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(g) \quad (R3)$$

Also, it is possible for volatiles to perform the CLC reduction reactions directly:

$$\text{volatiles}(g) + \text{MeO}_x \rightarrow \text{MeO}_{x-1} + \text{CO}_2(g) + \text{H}_2\text{O}(g) \quad (R4)$$

On the other side, the char particles will also react with gaseous O2 generated from the OC as in a normal CLOU process.

$$\text{char} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad (R5)$$

Simultaneously, as the oxygen concentration was much lower than the concentration of gasification agents (H2O and/or CO2) around the char particles, H2O (as an example of gasification agents) also could diffuse into the pores and prompt char gasification without influencing the combustion reaction of char with O2:

$$\text{char} + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + \text{H}_2(g) \quad (R6)$$

Then, the gasification products (H2 and CO) reacted with O2 outside the char particles (CLOU mode, like R3) or directly reacted with oxygen carriers (CLC mode, like R4) to form CO2 and H2O.

When using CO2 as a gasification agent, a similar process can be predicted. Because these gasification products could more easily react with O2 or OCs than char, a higher overall reaction rate was achieved. This accelerative effect shown in Figure 11 was most likely caused by the char gasification reactions. Using CO2 as gasification agent is preferred in a real CLOU system, as producing a large amount of steam will consume much energy. It is possible to use the condensed flue gas (i.e., the recycled flue gas, containing mainly CO2) as the fluidization gas and gasification agent.

Table 5 shows the minimum fuel-reactor solid inventory and the circulation rate for different OCs used in CLOU. The circulation rate for copper ore and CuO/CuAl2O4 was calculated with ΔX = 0.65; i.e., it was assumed that the conversion difference of the OC within the air-reactor and fuel-reactor was 0.65. The results about CuO/CuAl2O4 and CuO/MgAl2O4 are also presented here as comparison. The experiments conditions and used coals for CuO/CuAl2O4 were the same as the conditions in this work. For the copper ore and CuO/CuAl2O4, the effects of coal rank were both significant. From Table 5, the CLOU of anthracite required the largest solid inventory for all the OCs, and then followed by bituminous coal and lignite. Obviously, the solid inventory for copper ore was larger than that for CuO/CuAl2O4 at 900 °C (especially for anthracite), which was attributed to the slower oxygen generation rate. Part of the reason for the lower oxygen generation rate was because of the lower copper content for copper ore. Because of the relatively low oxygen carrying capability of copper ore, the circulation rate of CuO/CuAl2O4 was smaller than that of copper ore. It also can be found that increasing reactor temperature can reduce the copper ore solid inventory to some extent, especially for anthracite. On the other hand, the circulation rate had an order of lignite > anthracite > bituminous coal for both of the OCs. Furthermore, the effects of coal rank on solid inventory and circulation rate for copper ore and CuO/CuAl2O4 were similar with that for CuO/MgAl2O4. In addition, when adding 40% steam into the fluidization gas or using CO2 as fluidization gas, the solid inventory to some extent, especially for anthracite.
CuO/CuAl2O4, CuO/MgAl2O4
gasi
CLOU process could be a good solution, and sometimes a
extremely low. At this point, applying a high rank coal to a
at high temperatures, while for a high rank coal, when applied
which sintering occurs easily for the copper-based OCs (which
the low rank coal, lignite as an example, since it exhibits
observed in the CLOU process, except for the case when
and no serious agglomeration of the used particles was
ash. All used copper ore particles presented a porous structure,
into the fuel-reactor can indeed increase the instantaneous rate
of carbon conversion. SEM-EDX results showed that the used
fication agent (CO2 or steam) could also be introduced if
With all the coals used, it was found that both an increase in
the temperature and a decrease of coal rank generally had an
obvious beneficial effect on the rates of carbon conversion and
oxygen carrier conversion, and instantaneous rates of char conversion
and oxygen generation were
for the real CLC and CLOU process. For
important for the related experimental analysis.
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| Table 5. Solid Inventory, m_{OC,FR} and Circulation Rate, m_{OC} for Copper Ore (Using N2, Steam or CO2 as Fluidizing Agents), CuO/CuAl2O4, CuO/MgAl2O4 with Different Ranks of Coals |
|---|---|---|---|---|
| | anthracite | bituminous | lignite |
| copper ore (850 °C) | 2472 | 2.91 | 450 | 2.46 | 294 | 4.43 |
| copper ore (900 °C) | 1750 | 2.91 | 296 | 2.46 | 226 | 4.43 |
| copper ore (950 °C) | 955 | 2.91 | 286 | 2.46 | |
| CuO/CuAl2O4 (900 °C) | 356 | 1.67 | 164 | 1.41 | 155 | 2.54 |
| CuO/MgAl2O4 (950 °C) | 490 | 1.34 | 140 | 1.00 | 45 | 1.45 |
| copper ore (900 °C+40%H2O) | 1585 | 2.91 | |
| copper ore (900 °C + 100% CO2) | 1595 | 2.91 | |

"The coals used in their work were not the same as ours.

5. CONCLUSIONS
A copper ore with medium copper content has been evaluated as OC for CLOU using different coal at different operation conditions in a batch-scale fluidized-bed reactor. The effects of coal rank and temperature on redox behavior, carbon conversion rate, and instantaneous rates of char conversion and oxygen generation were first examined.

With all the coals used, it was found that both an increase in the temperature and a decrease of coal rank generally had an obvious beneficial effect on the rates of carbon conversion and oxygen carrier conversion, and instantaneous rates of char conversion and oxygen generation. However, when using lignite as fuel at 950 °C, the enhancing effect was restrained due to the agglomeration problem caused by the drastic temperature increase. For the coal CLOU process, the rate-controlled step is the burning of carbon with oxygen if OC is excess. And for higher ranks of coal, the rate-limitation effect is also greater. Moreover, introducing the gasification agents (CO2 or steam) into the fuel-reactor can indeed increase the instantaneous rate of carbon conversion. SEM-EDX results showed that the used copper ore particles were indeed blocked by the adhesion of fly ash. All used copper ore particles presented a porous structure, and no serious agglomeration of the used particles was observed in the CLOU process, except for the case when using lignite as fuel at 950 °C.

The experimental results revealed above could have profound guiding significance for the real CLC and CLOU process. For the low rank coal, lignite as an example, since it exhibits relatively fast carbon conversion rate in the iG-CLC process, there is no urgent need applying it to a CLOU process, during which sintering occurs easily for the copper-based OCs (which are also more expensive than, e.g., iron-based OCs for iG-CLC) at high temperatures, while for a high rank coal, when applied to a CLC process, the carbon conversion rate could be extremely low. At this point, applying a high rank coal to a CLOU process could be a good solution, and sometimes a gasification agent (CO2 or steam) could also be introduced if necessary. For midrank coal, either a CLOU or iG-CLC process could be employed. By applying different coal to different CLC process, high energy utilization efficiency could be obtained.

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REFERENCES
(12) Ryden, M.; Lyngfelt, A.; Mattisson, T. CaMn0.875Ti0.125O3 as oxygen carrier for chemical-looping combustion with oxygen uncoupling (CLOU) - experiments in a continuously operating fluidized-bed reactor system. Int. J. Greenhouse Gas Control 2011, 5, 356–366.


