Experimental Study of Natural Cu Ore Particles as Oxygen Carriers in Chemical Looping with Oxygen Uncoupling (CLOU)

4 AUTHORS, INCLUDING:

Ningsheng Cai

Tsinghua University

138 PUBLICATIONS   **1,793** CITATIONS

Experimental Study of Natural Cu Ore Particles as Oxygen Carriers in Chemical Looping with Oxygen Uncoupling (CLOU)

Yuan-yuan Wen, Zhen-shan Li,* Lei Xu, and Ning-sheng Cai

Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Beijing Municipal Key Laboratory for CO$_2$ Utilization and Reduction, Department of Thermal Engineering, Tsinghua University, Beijing 100084, People's Republic of China

ABSTRACT: The possibility of using three natural Cu ore particles as oxygen carriers in the chemical looping with oxygen uncoupling (CLOU) was investigated. The reaction kinetics of Cu$_2$O with O$_2$ and the decomposition kinetics of CuO in a CO$_2$ atmosphere at different temperatures and oxygen fractions were studied using thermogravimetric analysis (TGA). Both oxygen uptake and oxygen release exhibit a high reaction rate. Multiple oxygen uptake and oxygen release cycles indicated that three natural Cu ore oxygen carriers have high reactivity and cyclic stability. The high-temperature oxygen uptake and oxygen release process for producing O$_2$−CO$_2$ gas mixtures in a fluidized-bed reactor packed with Cu-based oxygen-carrier particles through air separation with carbon dioxide as the purge gas was investigated. Oxygen was absorbed, and heat is stored by the Cu-based oxygen-carrier particles with air being fed. An O$_2$−CO$_2$ stream can be obtained when the fluidized bed was regenerated with carbon dioxide as the fluidizing gas. The O$_2$ fraction in the O$_2$−CO$_2$ gas mixtures can be controlled by adjusting the reaction temperature, depending upon both thermodynamics and kinetics. Among the three natural Cu ore particles, the particles with a high Cu content experienced a serious agglomeration, while for the particles with a low Cu content, agglomeration did not occur after 20 cycles at a very high temperature (980 °C). This natural Cu ore oxygen carrier offers potential for further study and application in the chemical looping combustion and CLOU processes.

1. INTRODUCTION

It is now well-accepted that the release of CO$_2$ from fossil fuel combustion contributes to the enhanced greenhouse effect with the possible disastrous effect on climate change. The emissions of CO$_2$ into the atmosphere have been reported to account for half of the greenhouse effect that causes global warming.[1] An approach to reduce CO$_2$ release from large point sources is CO$_2$ (or carbon) capture and storage (CCS). The estimated costs for CO$_2$ transportation (U.S. $1−3 per ton per 100 km)[2] and sequestration (U.S. $4−8 per ton of CO$_2$)[3] are small compared to the cost for CO$_2$ capture, estimated at U.S. $35−55 per ton of CO$_2$ capture.[4] Therefore, reducing the cost of CO$_2$ capture is absolutely necessary to make CCS more economically attractive. The high cost of CO$_2$ capture stems from the considerable amount of energy required in the separation process.[4]

Among available or proposed techniques involving CO$_2$ separation in the combustion process, chemical looping combustion (CLC) is one of the promising techniques to obtain pure CO$_2$ from a power plant *in situ* allowing for CO$_2$ sequestration.[3,5] The main advantage of CLC compared to the conventional combustion is that CO$_2$ is inherently separated without nitrogen dilution. The majority of studies about CLC have focused on gaseous fuels, such as methane, natural gas, and syngas.[6−10]

Solid fuels are considerably more abundant than gaseous fuels; therefore, the adaptation of CLC to solid fuels would be highly attractive. One means of performing CLC with solid fuel is by first gasifying the solid fuel to the syngas, and then the syngas could be burnt in the CLC unit using oxygen carriers developed for gaseous fuels.[11] The requirement of the air separation unit (ASU) for gasification leads to the added costs

and efficiency reductions. Another option is to directly introduce the solid fuel to the fuel reactor, where the oxygen carrier directly reacts with the fuel.[12−18] Leion et al.[14] performed iron oxide reduction−oxidation experiments with a fluidized-bed reactor using petroleum coke and suggested that the gasification rate was slow compared to both the reaction rate of the gasified products with the iron oxide and the oxidation rate of reduced iron oxide with oxygen; thus, gasification was the rate-limiting step in CLC. As we all know, the reaction rate of solid fuel with gas-phase oxygen is fast; therefore, an alternative option of burning solid fuels is to use an oxygen carrier that can release O$_2$ in the fuel reactor and actually burns the fuel with gas-phase oxygen. This is referred to as chemical looping with oxygen uncoupling (CLOU) and was first proposed by Mattisson et al.[19,20] CLOU provides a novel method of avoiding the gasification step in the fuel oxidation process and, hence, increasing the reaction rates dramatically. The advantage of CLOU as compared to regular CLC is that the slow gasification step is eliminated when employing solid fuels and less oxygen-carrier material is needed in the system, which will also reduce the reactor size and associated costs.[21]

In the concept of CLOU, the reactions in the fuel reactor are complex. Char from coal pyrolysis will react with gases, such as O$_2$ and CO$_2$, and at the same time, char will also interact with the oxygen carrier through the solid−solid reaction. However, the rates of the char gasification reaction and the interaction of char with the oxygen carrier are slower compared to the char

Table 1. Cu Ore Compositional Characteristics (wt %)

	CuO	SiO$_2$	ZnO	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	K$_2$O	others
Cu ore I	87.28	1.73	8.28	1.22	0.50	0.43	0.15	0.41
Cu ore II	63.25	19.64	1.39	9.32	3.24	0.72	1.52	0.91
Cu ore III	5.82	82.83	0.03	5.48	4.95	0.07	0.60	0.22

oxidation. Therefore, the characteristic of oxygen uptake and release on the oxygen carrier is critical for CLOU. It is required that oxygen carriers can react with oxygen in the air reactor and then also release oxygen through decomposition in the fuel reactor. Commonly, three metal oxide pairs are considered as oxygen carriers for CLOU: CuO/Cu$_2$O, Mn$_2$O$_3$/Mn$_3$O$_4$, and Co$_3$O$_4$/CoO.[20−23] CuO/Cu$_2$O has a larger oxygen capacity than Mn- and Co-based materials; therefore, a Cu-based oxygen carrier is rather appropriate for the solid fuel CLOU and has been given more attention by researchers.[24] The melting point of a Cu-based carrier is low, with 1450 °C for CuO and 1235 °C for Cu$_2$O, and the eutectic minimum melting point for CuO/Cu$_2$O solid−solid mixtures is 1075 °C. They tend to agglomerate more easily because of the high temperature of the oxygen-releasing reaction. The major advancements for avoiding the agglomeration of a Cu-based oxygen carrier in CLC and CLOU were carried out at the Carbochemistry Institute (ICB), Spanish National Research Council (CSIC),[25−28] and a recent excellent review by this group has extensively covered the large volume of literature published to date.[24] There are two methods to deal with the agglomeration. One is to add inert material into the carrier, which is the most commonly used and has been studied widely.[25−28] The other is to manufacture composite to improve the characteristic of the oxygen carrier.[24] Synthetic Cu-based carriers have the advantage of cyclical stability, tolerance of agglomeration, and mechanical stability and are capable of satisfying the working conditions of the fluidized bed. However, synthetic oxygen carriers have the disadvantage of the complex preparation process, which is economically costly and energy-consuming. Also, the preparation process needs a lot of steps and produces pollutants at the same time. The contents of CuO in the Cu-based synthetic carriers in most literature are low,[24] and many kinds of natural Cu ores also have low CuO content. If the Cu ore particles can be used as the oxygen carrier in the CLOU, the complex process of preparing synthetic materials can be eliminated and, therefore, there will be technological and economic advantages. This study deals with some problems in using Cu ore particles as the oxygen carrier in the CLOU.

In this study, the reversible gas−solid reaction

$$Cu_2O + 0.5O_2 \Leftrightarrow 2CuO \tag{1}$$

was used to produce O$_2$−CO$_2$ gas mixtures for the CLOU process. Three natural Cu-contained ore particles have been used as the oxygen carrier and tested in both thermogravimetric analysis (TGA) and the fluidized-bed reactor. Results indicated that these natural Cu ores have high reactivity and stability under the conditions of the multiple oxygen uptake and release cycles. Furthermore, the Cu ore oxygen carrier with low Cu content did not experience a agglomeration problem in the fluidized-bed reactor. The O$_2$ uptake and release characteristic and evolution of the O$_2$ fraction with reaction times at different conditions based on a fluidized bed packed with Cu-based oxygen-carrier particles were also investigated.

2. EXPERIMENTAL SECTION

2.1. Preparation of the Natural Cu Ore Oxygen-Carrier Particles. Three types of Cu ore particles from the Hubei province of China were used in these experiments. The Cu ores were calcined in an air atmosphere for 3 h at 900 °C in a muffle oven and then crashed in a crusher. Finally, the crashed Cu ore paritcles are sieved into size fractions with particle size ranges of 200−500 μm. Table 1 lists the compositional characteristics of the samples. The mass fraction of every component in raw material was determined with X-ray fluorescence (XRF) spectrometry (Shimadzu XRF-1800).

2.2. Oxygen Uptake and Release on a Natural Cu Ore Oxygen Carrier with TGA. TGA (TA SDT Q600) was used to study the oxygen uptake and release processes of the natural Cu ore oxygen carrier. TGA consists of a quartz tube placed in an oven, which can be operated at temperatures up to 1400 °C. A computer continuously records the reaction temperature and sample weight. The reacting gas contains O$_2$, N$_2$, and CO$_2$, and their proportion can be adjusted with mass flow controllers. A small amount of the natural Cu ore oxygen carrier (about <15 mg) was placed in a quartz sample holder and brought to 1000 °C under nitrogen flow for decomposition. After complete decomposition, the temperature was decreased at a rate of 10 °C/min to the oxygen uptake temperature. When approaching the oxidation temperature, the valve was switched to allow for the gas mixture of the reactant to flow over the oxygen carrier. After the oxygen uptake step, the gas stream of N$_2$ was stopped and a gas mixture of O$_2$ and CO$_2$ was introduced to TGA. Then, the temperature was increased to the decomposition temperature at 10 °C/min. The microstructure of the oxygen carrier was investigated by scanning electron microscopy (SEM, JSM-7001F, JEOL). The phase composition of the oxygen carrier was determined by X-ray diffraction (XRD, D/max-2500, Rigaku). The surface area and porosity were measured with a Brunauer−Emmett−Teller (BET) analyzer.

2.3. Experiments in the Fluidized-Bed Reactor. O$_2$ uptake and release cycles using a natural Cu ore oxygen carrier were carried out in a fluidized-bed reactor. The flow rates of CO$_2$ and air from cylinders were controlled using mass flow controllers. The flow rate of fluidizing gases for both oxygen uptake and oxygen release steps is 1 L/min (standard state). The feed gases entered the reactor and were preheated as they flowed upward in the preheater section. The 30 mm quartz tube packed with 50 g of natural Cu ore particles was used as a fluidized-bed reactor. The preheated gas flowed upward through the natural Cu ore oxygen-carrier particle and exited at the top of the reactor. The product gases were analyzed using an oxygen and carbon dioxide gas analyzer. The progress of the oxygen uptake and release steps was followed by monitoring the O$_2$ content in the product gases. Complete oxygen release was achieved in all cycles for all tests.

3. RESULTS AND DISCUSSION

3.1. Kinetics and Thermodynamic Characteristic of Oxygen Uptake and Release of Oxygen on the Cu-Based Oxygen Carrier. The reaction kinetics of Cu$_2$O with O$_2$ at different temperatures was depicted in Figure 1. Conversion, X, was defined as

$$X = \frac{M_{Cu_2O}}{0.5M_{O_2}} \frac{m_t - m_0}{m_0 x_{Cu_2O}} \tag{2}$$

where M_{Cu_2O} and M_{O_2} are the molecular weights of Cu$_2$O and O$_2$, respectively, m_t is the sample mass at time t, m_0 is the initial sample mass, and x_{Cu_2O} is the Cu$_2$O mass fraction.
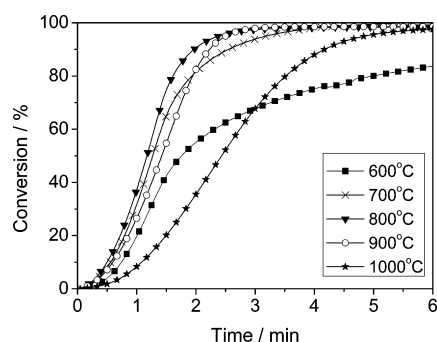
Figure 1. Cu_2O conversion as a function of time for different reaction temperatures (79% N_2 and 21% O_2).

Figure 2. Oxygen release on CuO at different temperatures and oxygen partial pressures with CO_2 as the purge gas.

Theoretically, 160 g of pure CuO oxygen carrier should release 16 g of O_2, corresponding to a maximum O_2 release capacity of 0.10 g of O_2/g of CuO at 100% CuO decomposition.

From Figure 1, it can be seen that the surface chemical reaction, with a fast reaction rate, dominated the initial stage and was followed by a slow product layer diffusion stage. The transition between the fast and slow reaction stages was attributed to the formation of a CuO product layer, which limits the oxygen contact with Cu_2O. This behavior has been observed for oxidation of Cu_2O at a low temperature of 600 °C; however, this decrease in the oxidation rate did not take place at high temperatures. It can be seen that the reaction of Cu_2O with O_2 in the range of 700−900 °C was very fast. At the same time, Figure 1 also shows that the rate of conversion decreases at higher temperatures (800−1000 °C); for example, when the reaction temperature was increased to 1000 °C, there was an obvious decrease in the reaction rate. In the literature, different models have been used to describe the oxidation/reduction kinetic behavior, i.e., the shrinking core model, grain model, pore model, or nucleation and growth model, and more details can be found in the recent review paper.[24] The thickness of the product layer formed on the free surfaces of the solid reactant is a critical parameter to mark the end of the fast reaction period. The assumption of a critical product layer thickness has to be used almost in all of the above models to explain the "maximum" conversion. From Figure 1, it can be seen that the critical product layer thickness depends upon the temperature; i.e., it increases with the increase in the temperature. It is well know that the chemical reaction rate coefficient increases with the temperature; therefore, the conversion rates at 700 and 800 °C are faster than that at 600 °C. The oxidation rate is controlled by not only the kinetics but also the thermodynamics, $C_{O_2} - C_{O_2,e}$, where C_{O_2} is the gas-phase oxygen concentration and $C_{O_2,e}$ is the O_2 equilibrium concentration. When the temperature is greater than 800 °C, $C_{O_2,e}$ increases more quickly, as shown in eq 3 and Figure 3, resulting in the value of $C_{O_2} - C_{O_2,e}$ to decrease rapidly, and therefore, the oxygen uptake rate begins to drop in the higher temperature range of 800−1000 °C (Figure 1).

When the oxygen uptake step was completed, the flow of air was stopped and CO_2/O_2 gas mixtures were introduced into the TGA apparatus. The sample was then heated over a temperature range, and the conversion was determined, as shown in Figure 2. From Figure 2, the decomposition rate of CuO strongly depends upon the temperature and oxygen partial pressure. For example, CuO start to decompose at 800 °C in a pure CO_2 atmosphere, but the decomposition rate is
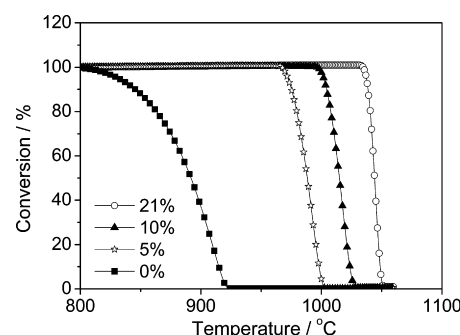
very slow, as shown in Figure 2. When the O_2 fraction was increased to 5−21 vol %, the starting temperature of CuO decomposition increases, while the decomposition rate was fast, as shown in Figure 2. At a certain oxygen partial pressure in the gas phase, both the decomposition rate coefficient and $C_{O_2,e}$ increase with the increase of the temperature, resulting in a faster oxygen release rate. As the oxygen partial pressure in the gas-phase increases, it is expected that the oxygen release rate will decrease. This phenomenon was validated by the experimental results, as shown in Figure 2. Because the reverse reaction should be applied to oxygen carrier regeneration, its rate represents a significant feature of the overall process. Thus, an optimum temperature for regeneration of the Cu-based oxygen carrier should be higher than 950 °C if the O_2 fraction in the O_2/CO_2 mixture is higher than 4.21% by volume.

The O_2 equilibrium pressure for the Cu-based oxygen carrier is important for the oxygen uptake and release kinetics, as calculated from thermodynamic data. A reaction can only proceed if the Gibbs free-energy change is less than zero, at the equilibrium O_2 partial pressure, when oxygen uptake and release are balanced and the Gibbs free-energy change is zero. The values of Gibbs free energy for CuO, Cu_2O, and O_2 at various temperatures can be obtained from the literature;[29] therefore, the equilibrium O_2 partial pressure, $P_{O_2,e}$, can be calculated and a correlation can be obtained. Consequently, the O_2 equilibrium pressure for the CuO oxygen carrier as a function of the temperature (600 < T < 950 °C) was estimated as

$$\frac{P_{O_2,e}}{P^0} = \exp\left[-9.383\left(\frac{1000}{T}\right)^4 + 47.54\left(\frac{1000}{T}\right)^3 \right.$$
$$\left. - 86.30\left(\frac{1000}{T}\right)^2 + 48.45\left(\frac{1000}{T}\right) - 2.473\right] \quad (3)$$

The unit of $P_{O_2,e}$ is Pa. Thermodynamic calculations are compared to experimental results in Figure 3. The experimental data shown in Figure 3 correspond to the starting point of CuO decomposition of each curve in Figure 2. From Figure 3, it can be seen that eq 3 agrees with the experimental results well. Thus, eq 3 can be used to determine the appropriate oxygen uptake and release temperature at different O_2 partial pressures.

3.2. Multiple Cycles of Oxygen Uptake and Release of the Cu-Based Oxygen Carrier. Because the oxygen carrier is repeatedly used in the CLOU process (that is, after the oxygen uptake step, the oxygen carrier must be regenerated in the subsequent cyclic reaction to release O_2 for fuel combustion),
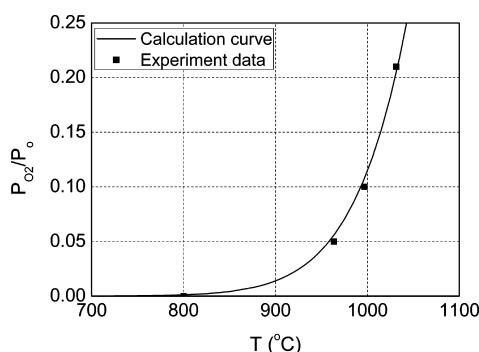
Figure 3. O_2 equilibrium pressure of Cu_2O-CuO.

the oxygen uptake and release characteristics of the oxygen carrier are very important for practical application. Figure 4
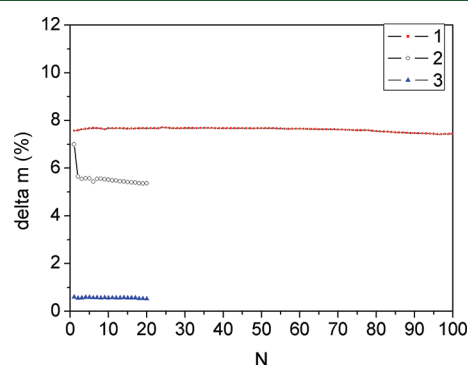

Figure 4. Multiple oxygen uptake and release cycles of three Cu ore oxygen carriers (oxygen uptake, 900 °C, 21 vol % O_2, and 79 vol % N_2; oxygen release, 950 °C and pure CO_2).

shows the O_2 uptake in air and O_2 release in a CO_2 atmosphere quantified as the mass variation for three natural Cu ore particles. Extended testing of sample 1 over 100 cycles at 950 °C was carried out. From Figure 4, it can be seen that the oxygen uptake capacity for three Cu ore particles did not decrease with an increasing cycle number and the stability of the natural Cu-based oxygen carrier is high. From these data, a conclusion is that the cyclic reactivity of natural Cu ore particles is not a problem for CLOU application.

The effect of the cyclic number on the cyclic reaction rate is shown in Figure 5. The shape of the oxygen uptake curve for different cycles shows that the reaction of Cu_2O with O_2 can also be divided into two different stages. The first stage is a
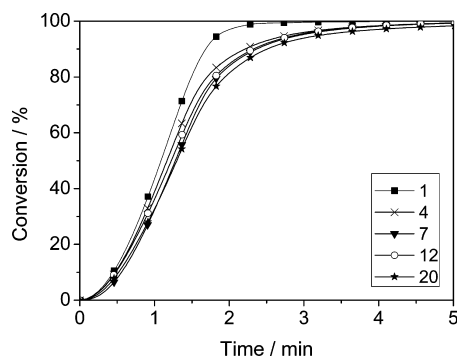

Figure 5. Oxygen uptake rate of the sample I oxygen carrier for different cycle numbers, N (900 °C, 21 vol % O_2, and 79 vol % N_2).

rapid, chemically controlled reaction period that is followed by a much slower product diffusion stage. In comparison to cycle 1, the conversion value for cycle 4 at a time value of approximately 2 min is significantly different (around 95% for cycle 1 and 84% for cycle 4). However, there was no big decay for oxidation kinetics for cycles from 4 to 20. At the same time, almost all Cu_2O can be converted to CuO within 4 min for all cycles, as shown in Figure 5. This is because Cu has a rather high solid-state diffusion coefficient, so that bulk Cu should be accessible at higher temperatures.

To understand the reaction mechanism during the high-temperature cycles on the Cu-based oxygen carrier, samples from oxygen uptake and release stages were studied by XRD, as shown in Figure 6. It was observed that only Cu_2O exists in the
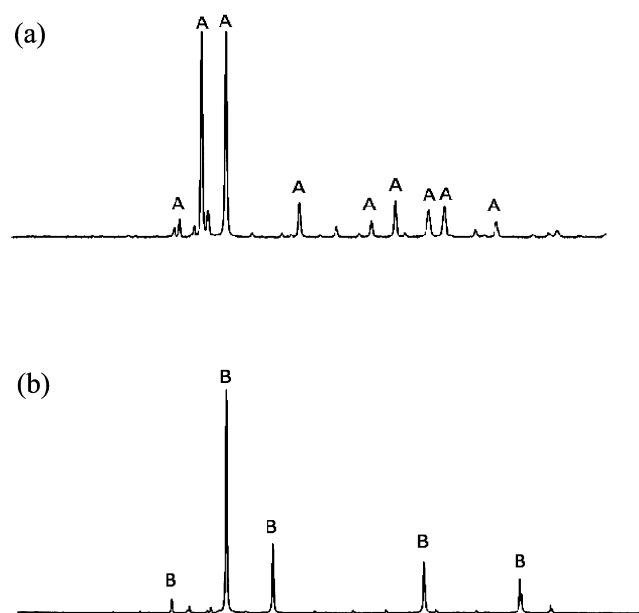

Figure 6. XRD results of the sample I oxygen carrier after and before the sorption stage (A, CuO; B, Cu_2O): (a) after oxygen uptake and (b) before oxygen uptake.

regenerated sample. These results indicated that Cu_2O reacts with O_2 in the air step to form CuO, while CuO decomposes to Cu_2O and O_2, and O_2 is released into the gas atmosphere during the oxygen release step.

In the process of oxygen uptake and release, solid particles are heated to certain high temperatures well below the melting point. Cu_2O or CuO sintering may occur, possibly resulting in particle structure changes. While small solid grains may coalesce and sinter, the surface and porosity may decrease with the increase of the residence time. Table 2 shows the comparison of the pore structure at different cycles for Cu ores I and II, from the information of specific surface area, pore

Table 2. Pore Surface Area Analysis of Samples I and II

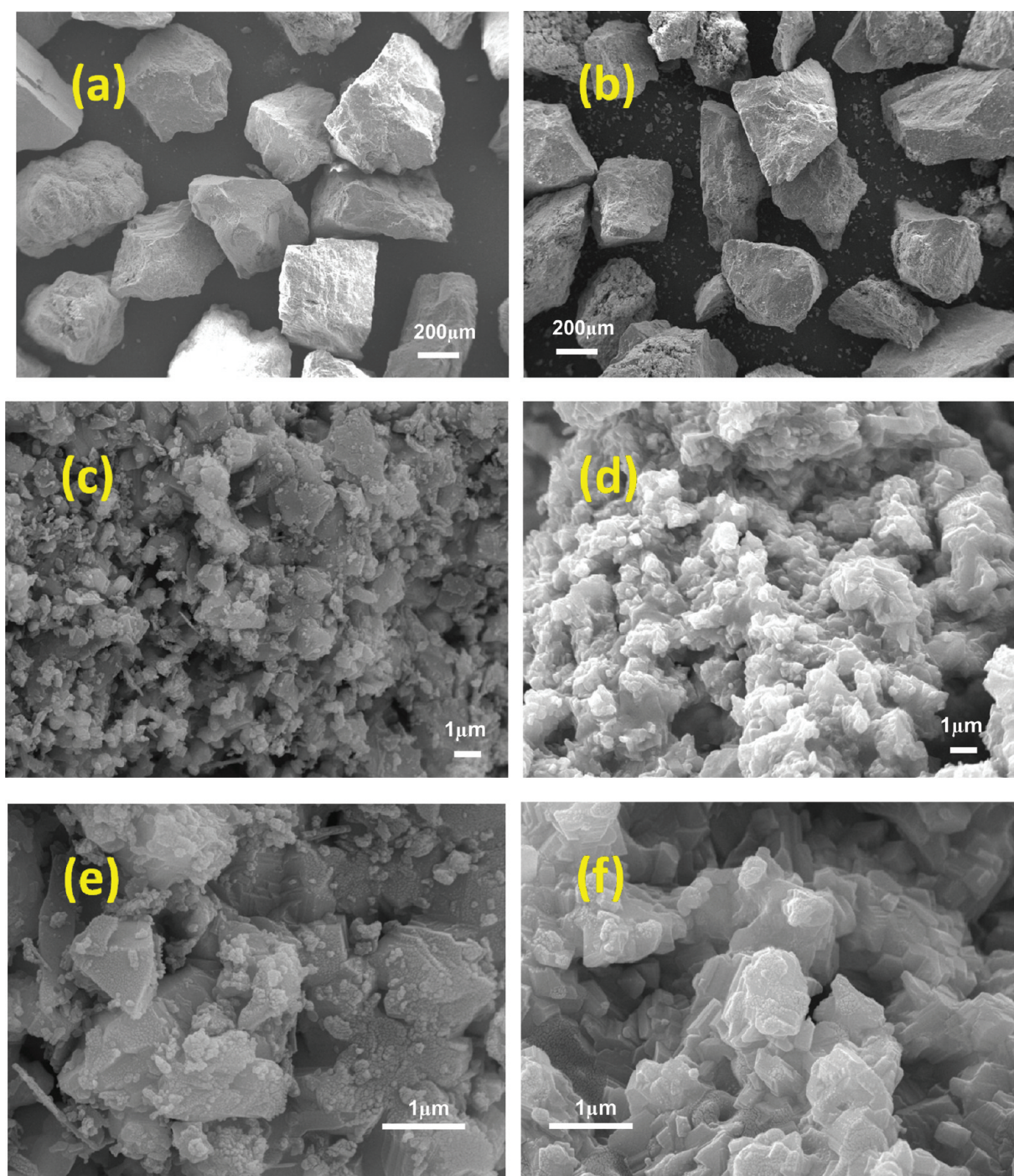|	BET surface area (m²/g)		BJH adsorption average pore diameter (nm)		BJH adsorption total pore volume (cm³/g)	
	before the first cycle	after the first cycle	before the first cycle	after the first cycle	before the first cycle	after the first cycle
Cu ore I	3.292	0.108	2.076	1.955	0.08	0.02
Cu ore II	15.368	3.687	2.469	2.754	0.137	0.047

Figure 7. SEM results of the Cu ore III oxygen carrier (a, c, and e, sample of the first cycle before oxygen uptaken; b, d, and f, sample of the 20th cycle after oxygen uptake).

diameters, and total pore volumes. There was also an obvious change for these parameters before and after cycling, indicating a serious sintering for the high Cu content of the oxygen carrier. Figure 7 shows SEM of Cu ore III, which has a very low Cu content. It can be seen that there was a significant degree of "smoothing" of the particle surfaces, but the agglomeration of oxygen-carrier particles did not occur with an increase of the cyclic number.

3.3. Experimental Results in the Fluidized-Bed Reactor. Because the sample used for the above TGA test was small (<15 mg) and dispersed, it is difficult to study the sintering and agglomeration problems. At the same time, the O_2

fraction in the oxygen release step is also an important parameter for CLOU, but only mass changing signals can be obtained with TGA. Therefore, a fluidized-bed reactor was used to study both O_2 release characteristics at different temperatures and Cu ore sintering and agglomeration problems. During the experiment, the Cu-based oxygen carrier in the fluidized-bed reactor was first heated to 950 °C in a pure CO_2 atmosphere to make CuO decompose completely. Then, the temperature of the fluidized-bed reactor was decreased, and CO_2 was switched to air stream after the reactor temperature was stable. The evolutions of the O_2 concentration, CO_2 concentration, and reaction temperature with the reaction

time for the Cu-based oxygen carrier during the O_2 uptake tests were shown in Figure 8. The outlet O_2 concentrations were not
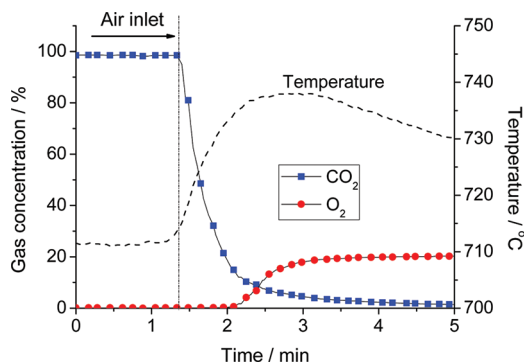

Figure 8. Curves of oxygen uptake (sample III).

higher than 1% for a stable period, and these experimental results showed that O_2 in air can be absorbed effectively by a natural Cu ore oxygen-carrier particle in the fluidized bed. After the stable period, the O_2 uptake capacity of Cu_2O was nearly exhausted and a large part of active Cu_2O was converted to CuO. The gradual increase in the O_2 concentration occurred because of the depletion of Cu_2O in the oxygen carrier. Figure 8 shows the temperature as a function of the reaction time. It can be seen that the reactor temperature increases. This is because oxygen uptake on the Cu-based oxygen carrier is exothermic, and the released heat results in a higher reactor temperature.

For the oxygen release step, the post-breakthrough period of the O_2 uptake step was stable for a period of 10−20 min. Then, the flow of air was stopped, and only CO_2 was introduced into the reactor. The temperature of the reactor was increased to 960 °C and kept stable for some time to make CuO decompose completely and reactivate the oxygen carrier. When the O_2 concentration from the gas analyzer approaches zero, the process of CuO decomposition was considered to finish. The decomposition rate of CuO in the temperature range from room temperature to 760 °C is very little; therefore, the progress of CuO decomposition below 760 °C is considered to have no effect on the O_2 released amount during the oxygen release step. Figure 9 showed the O_2 fraction and reacton temperature during the O_2 release step as a function of time. From eq 3, CuO would not decompose until the reactor temperature reached its thermodynamic equilibrium temperature. When the temperature in the reactor reached the CuO
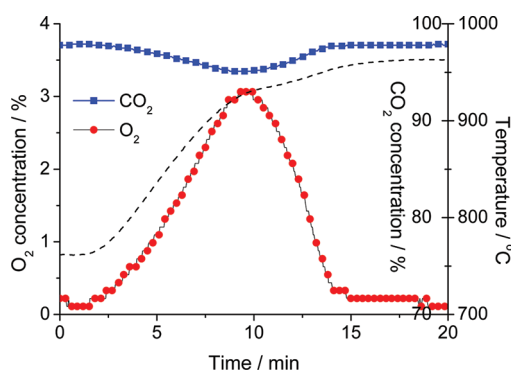
decomposition temperature, CuO began to decompose and the CuO decomposition rate increased with an increasing reactor temperature, resulting in the O_2 fraction gradually increasing with time, as seen in Figure 9. When the reactor temperature approached 930 °C, the decomposition rate of CuO was accelerated largely and the O_2 fraction approached a maximum. With the increase of the regeneration time, the fraction of CuO undecomposition in the reactor decreased and the O_2 fraction began to decrease with time. When all CuO was decomposed, no O_2 was released and the O_2 concentration approached zero at this time.

The effect of the reaction temperature on oxygen uptake was investigated experimentally. Figure 10 shows the experimental
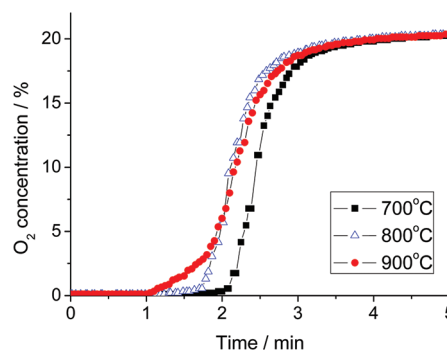

Figure 10. Oxygen uptake at different temperatures (sample III).

results of O_2 uptake on the natural Cu ore oxygen carrier (sample III) at different temperatures. It can be seen that O_2 from air can be absorbed effectively by the Cu-based oxygen carrier in the temperature range of 700−900 °C. The oxygen release temperature for CuO decomposition in the CLOU system is critical and governed by the thermodynamics of the regeneration system. At 101 325 Pa, temperatures ranging from 920 to 980 °C with 2−3.7% O_2 during oxygen release are required. It is required for the CLOU system that O_2 absorbed by the oxygen carrier can be released effectively in the fuel reactor in a pure CO_2 atmosphere. With the release of O_2 from the oxygen carrier, the O_2-CO_2 gas mixture can be obtained and the solid fuel can be burnt with O_2. Figure 11 shows the experimental results of O_2 release on the Cu-based oxygen carrier at different temperatures. It can be seen from Figure 11 that the O_2 fraction in the gas mixture increases with an increasing reaction temperature. When the reaction temperature is 920 °C, the O_2 fraction is only 2%. With a further increase of the reaction temperature, the O_2 fraction can also

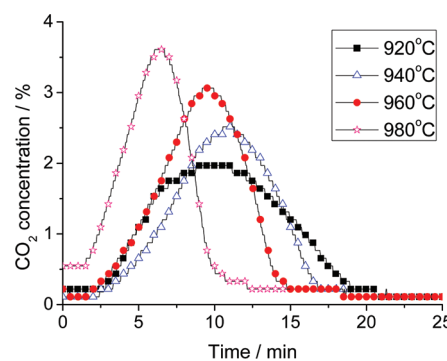**Figure 9.** Curves of oxygen release (sample III).

Figure 11. Oxygen release at different temperatures (sample III).

increase, as shown in Figure 11. It can be concluded that the O_2 fraction in the gas mixture can be controlled by adjusting the reaction temperature.

From the above TGA and fluidized-bed tests, it can be seen that the natural Cu ore particles had attractive features, but there are still some problems for the use of natural Cu ore particles as an oxygen carrier. The critical issue for the Cu-based oxygen carrier is the agglomeration problem occurring at high temperatures because of the rather low melting temperature of copper material. To avoid the agglomeration, the use of low CuO content (less than 20 wt %) oxygen carriers[30] and lower operating temperatures (800−850 °C)[31,32] was suggested to avoid agglomeration. However, for the CLOU, a high temperature in the fuel reactor must be required to obtain a reasonable O_2 partial pressure because of the restriction of thermodynamic equilibrium between Cu_2O and O_2, as shown in eq 3 and Figure 3. Therefore, the agglomeration occurring in the fluidized-bed reactor and the long-term validation of natural Cu ore use are needed. A total of 20 cycles of oxygen uptake by Cu_2O (800 °C with air) and oxygen release from CuO (980 °C with CO_2) were investigated, and the results were shown in Figure 12. Figure 13 showed the agglomeration tendency of
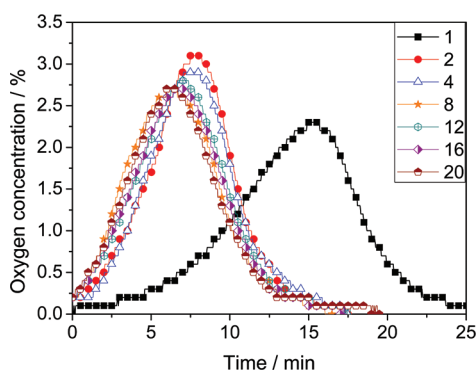

Figure 12. Oxygen fraction from the reactor outlet for different cycles during the oxygen release step (Cu ore III; oxygen uptake at 800 °C with air and oxygen release at 980 °C with CO_2).

three natural Cu ore particles after different cycles. It was found that samples I and II experienced a serious agglomeration during the oxygen release step in the fluidized bed, as shown in panels a and b of Figure 13. However, there was no agglomeration for sample III during 20 cycles, as shown in

Figure 13c. At the same time, the reactivity of sample III was stable, as shown in Figure 12. These results indicated that the agglomeration is dependent upon the Cu content in the Cu ore sample.

The critical idea of CLOU is the transport of O_2 from the air to the fuel reactor by means of a carrier. Normally, the carrier consists of an active component and inert material, and the active component content has a big effect on the solid recirculation rate and inventory of a CLOU system. The recirculation rate ($\dot{m}_{ox}$) of the oxygen carrier can be calculated from a mass balance[33]

$$\dot{m}_{ox} = b_r M_{CuO} F_C \Delta X_C / x_{CuO} \qquad (4)$$

where b_r is the stoichiometric factor (4 for the reaction of C with CuO to form CO_2 and Cu_2O), F_C is the moles of char entering into the fuel reactor, ΔX_C is the char conversion in the fuel reactor, and x_{CuO} is the mass content of CuO in the oxygen carrier.

The solid inventories in the air reactor and fuel reactor are[3]

$$m_{bed,ox} = \frac{\dot{m}_{ox}}{C_{ox}\frac{dX}{dt}\Big|_{ox}}, \qquad m_{bed,red} = \frac{\dot{m}_{ox}}{C_{red}\frac{dX}{dt}\Big|_{red}} \qquad (5)$$

where C is a measure of how much oxygen the carrier is able to transfer for a given change in conversion.

From eqs 4 and 5, it can be clearly seen that both the solid recirculation rate and solid inventory in the air and fuel reactor increase with the decrease in the CuO content in the oxygen carrier. For the Cu ore particles with ∼5% CuO content, a very large solid recirculation rate and solid inventories are required, resulting in some problems in the reactor design and operation, as well as economic issues. Therefore, the method of increasing the CuO content in natural Cu ore particles and avoiding the agglomeration will be required in future studies.

4. CONCLUSION

The properties of the oxygen uptake and release processes of three natural Cu ore oxygen carriers were studied in its application for the production of an O_2-CO_2 stream for the CLOU process. These three natural Cu ore oxygen carriers gave high conversion and high cyclic oxygen uptake and release rates. In particular, this material had excellent regeneration capacity in cyclic use, which was one of the key factors for CLOU. The oxygen uptake and release processes for the production of the O_2-CO_2 gas mixture in a fluidized-bed
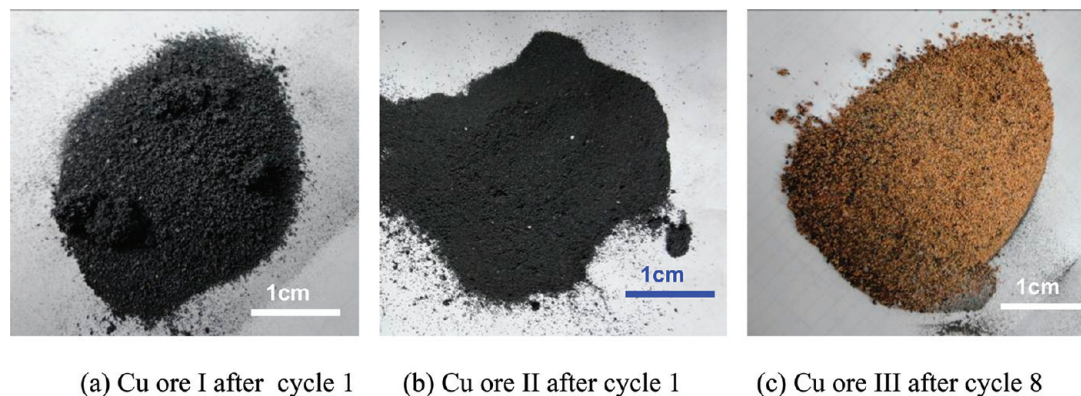
(a) Cu ore I after cycle 1   (b) Cu ore II after cycle 1   (c) Cu ore III after cycle 8

Figure 13. Natural Cu ore particle sample after fluidized-bed oxygen uptake and release cycles (oxygen uptake at 800 °C with air and oxygen release at 980 °C with CO_2).

reactor with carbon dioxide as the purge gas were investigated. The experimental results indicated that O_2 in air can be absorbed effectively by the Cu-based oxygen carrier. In the O_2 release step, the O_2 fraction in O_2-CO_2 stream increases with an increase of the temperature. This step was governed by both thermodynamics and kinetics. Among three natural Cu ore particles, the particles with a high Cu content experienced a serious agglomeration, while for the particle with a low Cu content, agglomeration did not occur for 20 cycles at a very high temperature (980 °C). This natural Cu ore oxygen carrier offers potential for further study and application in the CLC and CLOU processes.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone: 86-10-62789955. Fax: 86-10-62770209. E-mail: lizs@tsinghua.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Houghton, J. T.; Meira Filho, L. G.; Callander, B. A.; Harris, N.; Kattenberg, A.; Maskell, K. Climate change 1995: The science of climate change. *Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: Cambridge, U.K., 1996.

(2) Freund, P. Making deep reductions in CO_2 emissions from coal-fired power plant using capture and storage of CO_2. *Proc. Inst. Mech. Eng.* **2003**, *217* (1), 1−7.

(3) Lyngfelt, A.; Leckner, B.; Mattisson, T. A fluidized-bed combustion process with inherent CO_2 separation: Application of chemical-looping combustion. *Chem. Eng. Sci.* **2001**, *56* (10), 3101−3113.

(4) Singh, D.; Croiset, E.; Douglas, P. L.; Douglas, M. A. Techno-economic study of CO_2 capture from an existing coal-fired power plant: MEA scrubbing vs. O_2/CO_2 recycle combustion. *Energy Convers. Manage.* **2003**, *44* (19), 3073−3091.

(5) Ishida, M.; Jin, H.; Okamoto, T. Kinetic behaviour of solid particle in chemical-looping combustion: Suppressing carbon deposition in reduction. *Energy Fuels* **1998**, *12* (2), 223−229.

(6) Jin, H.; Ishida, M. Reactivity study on natural gas-fueled chemical-looping combustion by a fixed-bed reactor. *Ind. Eng. Chem. Res.* **2002**, *41* (16), 4004−4007.

(7) Mattisson, T.; Lyngfelt, A.; Cho, P. The use of iron oxide as an oxygen carrier in chemical-looping combustion of methane with inherent separation of CO_2. *Fuel* **2001**, *80* (13), 1953−1962.

(8) Cho, P.; Mattisson, T.; Lyngfelt, A. Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion. *Fuel* **2004**, *83* (9), 1215−1225.

(9) Adanez, J.; de Diego, L. F.; Garcia-Labiano, F.; Gayan, P.; Abad, A.; Palacios, J. M. Selection of oxygen carriers for chemical-looping combustion. *Energy Fuels* **2004**, *18* (2), 371−377.

(10) Abad, A.; Mattisson, T.; Lyngfelt, A.; Johansson, M. The Use of iron oxide as oxygen carrier in a chemical-looping reactor. *Fuel* **2007**, *86* (7−8), 1021−1035.

(11) Jin, H.; Ishida, M. A new type of coal gas fueled chemical-looping combustion. *Fuel* **2004**, *83* (17−18), 2411−2417.

(12) Cao, Y.; Casenas, B.; Pan, W. P. Investigation of chemical looping combustion by solid fuels. 2. Redox reaction kinetics and product characterization with coal, biomass, and solid waste as solid fuels and CuO as an oxygen carrier. *Energy Fuels* **2006**, *20* (5), 1845−1854.

(13) Gupta, P.; Velazquez-Vargas, L. G.; Li, F.; Fan, L. S. Chemical looping combustion of coal. *Proceedings of the 2005 American Institute of Chemical Engineers (AIChE) Annual Meeting and Fall Showcase*; Cincinnati, OH, Oct 30−Nov 4, 2005; pp 7620−7625.

(14) Leiona, H.; Mattisson, T.; Lyngfelt, A. The use of petroleum coke as fuel in chemical-looping combustion. *Fuel* **2007**, *86* (12−13), 1947−1958.

(15) Scott, S. A.; Dennis, J. S.; Hayhurst, A. N.; Brown, T. In situ gasification of a solid fuel and CO_2 separation using chemical looping. *AIChE J.* **2006**, *52* (9), 3325−3328.

(16) Dennis, J. S.; Scott, S. A.; Hayhurst, A. N. In situ gasification of coal using steam with chemical looping: A technique for isolating CO_2 from burning a solid fuel. *J. Energy Inst.* **2006**, *79* (3), 187−190.

(17) Shen, L. H.; Zheng, M.; Xiao, J.; Xiao, R. A mechanistic investigation of a calcium-based oxygen carrier for chemical looping combustion. *Combust. Flame* **2008**, *154* (3), 489−506.

(18) Shen, L. H.; Wu, J. H.; Gao, Z. P.; Xiao, J. Reactivity deterioration of NiO/Al_2O_3 oxygen carrier for chemical looping combustion of coal in a 10 kW_{th} reactor. *Combust. Flame* **2009**, *156* (7), 1377−1385.

(19) Mattisson, T.; Leion, H.; Lyngfelt, A. Chemical-looping with oxygen uncoupling using CuO/ZrO_2 with petroleum coke. *Fuel* **2009**, *88* (4), 683−690.

(20) Mattisson, T.; Lyngfelt, A.; Leion, H. Chemical-looping with oxygen uncoupling for combustion of solid fuels. *Int. J. Greenhouse Gas Control* **2009**, *3* (1), 11−19.

(21) Leiona, H.; Mattisson, T.; Lyngfelt, A. Using chemical-looping with oxygen uncoupling (CLOU) for combustion of six different solid fuels. *Energy Procedia* **2009**, *1*, 447−453.

(22) Zhang, T.; Li, Z. S.; Cai, N. S. Continuous O_2-CO_2 production using a Co-based oxygen carrier in two parallel fixed-bed reactors. *Korean J. Chem. Eng.* **2009**, *26* (3), 845−849.

(23) Li, Z. S.; Zhang, T.; Cai, N. S. Experimental study of O_2-CO_2 production for the oxyfuel combustion using a Co-based oxygen carrier. *Ind. Eng. Chem. Res.* **2008**, *47* (19), 7147−7153.

(24) Adanez, J.; Abad, A.; Garcia-Labiano, F.; Gayan, P.; de Diego, L. F. Progress in chemical-looping combustion and reforming technologies. *Prog. Energy Combust. Sci.* **2012**, *38* (2), 215−282.

(25) Adanez-Rubio, A. A.; Gayán, P.; García-Labiano, F.; de Diego, L. F.; Adánez, J.; Abad, A. Development of CuO-based oxygen carrier materials suitable for chemical-looping with oxygen uncoupling (CLOU) process. *Energy Procedia* **2011**, *4*, 417−424.

(26) Adanez-Rubio, A. A.; Gayán, P.; García-Labiano, F.; de Diego, L. F.; Adánez, J. Demonstration of chemical-looping with oxygen uncoupling (CLOU) process in a 1.5 kW_{th} continuously operated unit using a Cu-based oxygen carrier. *Int. J. Greenhouse Gas Control* **2012**, *6*, 189−200.

(27) de Diego, L. F.; Garcia-Labiano, F.; Gayan, P.; Celaya, J.; Palacios, J. M.; Adanez, J. Operation of a 10 kW_{th} chemical-looping combustor during 200 h with a $CuO-Al_2O_3$ oxygen carrier. *Fuel* **2007**, *86* (7−8), 1036−1045.

(28) Garcia-Labiano, F.; Gayan, P.; Adanez, J.; De Diego, L. F.; Forero, C. R. Solid waste management of a chemical-looping combustion plant using Cu-based oxygen carriers. *Environ. Sci. Technol.* **2007**, *41* (16), 5882−5887.

(29) *Thermochemical Data of Pure Substances*, 3rd ed.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2008.

(30) de Diego, L. F.; Gayan, P.; García-Labiano, F.; Celaya, J.; Abad, A.; Adanez, J. Impregnated CuO/Al_2O_3 oxygen carriers for chemical-looping combustion: Avoiding fluidized bed agglomeration. *Energy Fuels* **2005**, *19* (5), 1850−1856.

(31) Gayan, P.; Forero, C. R.; Abad, A.; de Diego, L. F.; García-Labiano, F.; Adanez, J. Effect of support on the behavior of Cu-based oxygen carriers during long-term CLC operation at temperatures above 1073 K. *Energy Fuels* **2011**, *25* (3), 1316−1326.

(32) Forero, C. R.; Gayan, P.; García-Labiano, F.; de Diego, L. F.; Abad, A.; Adanez, J. High temperature behaviour of a $CuO/\gamma Al_2O_3$

oxygen carrier for chemical-looping combustion. *Int. J. Greenhouse Gas Control* **2011**, *5* (4), 659−667.

(33) García-Labiano, F.; de Diego, L. F.; Adanez, J.; Abad, A.; Gayan, P. Reduction and oxidation kinetics of a copper-based oxygen carrier prepared by impregnation for chemical-looping combustion. *Ind. Eng. Chem. Res.* **2004**, *43*, 8168−8177.