Cycle performance of Cu-based oxygen carrier based on a chemical-looping combustion process

Xiaoming Zheng [a,b], Lixin Che [b], Yanqiong Hao [b], Qingquan Su [a,c,*]

[a] School of Mechanical Engineering, University of Science and Technology Beijing, Beijing 100083, China
[b] Beijing Gas Group Research Institute, Beijing 100011, China
[c] Beijing Engineering Research Center for Energy Saving and Environmental Protection, University of Science and Technology Beijing, Beijing 100083, China

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ABSTRACT

The cycle life of oxygen carrier (OC) is crucial to the practical applications of chemical looping combustion (CLC). Cycle performance of Cu/SiO_2 prepared with a mechanical mixing method was evaluated based on a CLC process characterized with an added methane steam reforming step. The Cu/SiO_2 exhibited high redox reactivity in the initial cycles, while the performance degraded with cycle number. Through characterization of the degraded Cu/SiO_2, the performance degradation was mainly caused by the secondary particles' fragmentation and the fine particles' local agglomeration, which worsened the distribution and diffusion of the reactive gases in the packed bed. A regeneration method of the degraded OC based on re-granulation has been proposed, and its mechanism has been illustrated. With this method, the performance of the degraded OC through 420 redox cycles was recovered to a level close to the initial one.

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1. Introduction

Chemical-looping combustion (CLC) has not only a high thermal efficiency and nearly zero emission of pollutants such as NO_x, but also an inherent advantage of nearly zero energy consumption in capturing CO_2. So, CLC has significant potential in the fields of energy conservation, environmental protection and carbon capture & storage (CCS) [1,2].

Oxygen carrier (OC), as the media of reactions, is the key to CLC. Hossain [3] gave some points to evaluate an OC: oxygen carrying capacity, redox reactivity, mechanical strength, anti-sintering ability, anti-carbon deposition ability, cycle life, cost and environmental impact.

Obviously, the cycle life is one of the important properties of OC for the practical applications of CLC. Until now, the studies on OC's cycle performance have been usually focused on metal oxides. In most cases, the cycle performance as well as reactivity of a single metal oxide declines with cycle number. For Ni-based OC, a dense oxide layer on the particle surface is formed in oxidation of the reduced Ni, which blocks the diffusion of the reactive gases insider the particles, leading to a low oxidation rate [4]. For Cu-based OC, due to the relatively low

melting point of Cu, Cu particles, especially the fine Cu particles easily sinter in the reduction step at a high temperature, leading to a drastic degradation in the cycle performance. Thus, in the preparation of OC, the active component is generally dispersed in a porous inert support, such as Al_2O_3 and SiO_2 [5–7]. The support is helpful to increase the porosity and the specific surface area, and enhance the heat-carrying capacity and the mechanical strength of OC. Ishida et al. [8,9] chose yttria-stabilized zirconia (YSZ) as an inert support and investigated the cycle performance of NiO/YSZ and (NiO+CoO)/YSZ in a Thermogravimetric analyzer (TGA) at 1000 °C for oxidation and at 600 °C for reduction with CH_4. It was found that carbon deposition occurs in reduction for NiO/YSZ and oxidation rate decreases with cycle number for (NiO+CoO)/YSZ. Corbella et al. [10] studied the cycle performance of Fe_2O_3/TiO_2 in a fixed bed at 900 °C. The results showed that $FeTiO_3$ is formed leading to a decrease of oxygen carrying capacity. He et al. [11] conducted an experiment of 20 cycles for Fe_2O_3/Al_2O_3 in a TGA at 900 °C. It was observed that Fe_2O_3 does not react with Al_2O_3, however, the conversion rate of CH_4 to CO_2 and H_2O was only 85% in the reduction step.

Cu-based OCs have high reactivity and oxygen carrying capacity. In addition, Cu or CuO hardly react with inert supports. Its more significant advantage is that the reduction of CuO and the oxidation of Cu are both exothermic reactions [12]. So, for Cu-based OC, the application of a fixed bed reactor with continuous heat supply through reduction and oxidation becomes possible. At present, the experimental studies on the cycle performance of Cu-based OC are mainly carried out in TGA, fixed bed or fluidized bed. Corbella et al. [13]

* Corresponding author at: School of Mechanical Engineering, University of Science and Technology Beijing, Beijing 100083, China. Tel: +86 10 62333542; Fax: +86 10 62333542.
E-mail address: suqingquan@ustb.edu.cn (Q. Su).

prepared CuO/SiO$_2$ and CuO/TiO$_2$ with impregnation, and conducted 20 cycles in a fixed bed reactor at 800 °C. They reported that partial CuO decomposes to Cu$_2$O, which means a decrease of oxygen carrying capacity, and CuO/TiO$_2$ sinters seriously. Adanez et al. [14] prepared CuO/Al$_2$O$_3$ (CuO, 14 wt%; Al$_2$O$_3$, 86 wt%) with dry impregnation, and studied its cycle performance in fluidized-bed reactors using methane as fuel. They showed that CuO/Al$_2$O$_3$ was durable, no carbon deposition and agglomeration was observed, and meanwhile, the attrition rate was low and constant during 200 h operation. de Digeo et al. [15,16] prepared CuO/SiO$_2$ with an impregnation method and evaluated its cycle performance in TGA at 800 °C. They observed that CuO/SiO$_2$ (CuO, 20 wt%; SiO$_2$, 80 wt%) does not degrade substantially in 100 redox cycles, however, sintering and degradation occurred when CuO content was over 20 wt%. Obviously, the cycle performance of Cu/SiO$_2$ was maintained at a cost of reducing the active component content, that is, at a cost of reducing OC's oxygen carrying capacity. On the other hand, for Cu-based OC with a high active component content, Chuang SY et al. [17] prepared CuO/Al$_2$O$_3$ (CuO, 82.5 wt%; Al$_2$O$_3$, 17.5 wt%) with mechanical mixing, and its performance was evaluated in a fluidized bed at 800 °C using CO as fuel. They found that particles sintered and low yields of CO$_2$ occur only in six redox cycles.

So, for a Cu-based OC, the key to improve its cycle performance is to lower the reaction temperatures in reduction and oxidation to an extent sufficient to suppress sintering and carbon deposition. Accordingly, the authors [18] have presented a CLC process based on a fixed bed with adding a step of CH$_4$ steam reforming ahead of the reduction step, in which CH$_4$ is converted into H$_2$ and CO, whose reduction ability is much stronger than that of CH$_4$, so the required reduction temperature is greatly reduced. Furthermore, based on this process, the authors [19] have conducted a study on the influence of the preparation method, inert support, Ni component, particle size and GHSV on the performance of Cu-based OC at the initial stage. The results showed that Cu/SiO$_2$ has a high oxygen carrying capacity as well as good reactivity. Certainly, compared to the CLC in a fluidized bed reactor at high temperature, the applicable GHSV for this CLC is limited, due to the heat and mass transfer being slow in a fixed bed reactor at relatively low temperature.

As a whole, the previous studies on the cycle life of Cu-based OC were conducted in a lower CuO content with fewer cycles, and it was far from the requirements for CLC's practical applications. Therefore, it is necessary to investigate Cu-based OC's cycle life with a high enough CuO content and cycle number.

In this study, the cycle performance of Cu/SiO$_2$ was conducted in a fixed bed reactor at 500 °C based on the CLC process characterized with an added methane steam reforming step in a long term. In order to elucidate the mechanism of degradation, the fresh and the degraded OCs were characterized with XRD and SEM. Furthermore, a regeneration method of the degraded OC was proposed and applied, and its mechanism was illustrated. The results of this study are also useful for the CLC using other fuels including H$_2$ or CO.

2. Experimental

2.1. Oxygen carrier preparation

A Cu-based OC was prepared with a mechanical mixing method. Cu powders with a diameter range of 38–52 μm were used as the active component, and SiO$_2$ particles with a size range of 48–75 μm, which were prepared by grinding spherical SiO$_2$ (Qingdao Haiyang Chemical Co.,Ltd), were used as inert support. Cu powder was mixed with SiO$_2$ powder in a Cu to SiO$_2$ mass ratio of 4:1. A 2% aqueous polyvinyl alcohol solution was used as binder in a mass content of 20%. Then, the mixture was pressed with a tablet machine at 10 MPa for 2 min. The pressed flakes were dried at 120 °C in a drying chamber overnight and calcined at 550 °C for 5 h in a muffle oven. The calcined

flakes were crushed and screened to a particle size of 1–3 mm, which was used as the Cu-based OC of Cu/SiO$_2$.

2.2. Experimental apparatus

The schematic of the experimental apparatus for evaluating the cycle performance of Cu/SiO$_2$ is shown in Fig. 1.

30 mL OC was packed in the thermostatic section of a stainless steel tube reactor with a diameter of 25 mm and a height of 550 mm. Corundum spheres of 20 mL were packed on the top of OC as a distributer and corundum spheres of 24 mL were packed at the bottom of OC as a support. The temperature was measured by a K-type thermocouple with a diameter of 1.2 mm installed just on the top of the OC layer.

The experimental apparatus ran automatically under PLC control. Before the cycle experiment, the initial redox performance of Cu/SiO$_2$ was measured to determine the required time for complete reduction and oxidation. The measurement was carried out in the following steps:

The OC layer was heated to 500 °C with a heating rate of 10 °C/min in flowing air of 225 mL/min to ensure that the particles were fully oxidized before the reduction step. Then, CO$_2$ of 500 mL/min was introduced to the reactor for 0.5 h to replace the air in the reactor. After that, the reducing gas of 80% H$_2$ in CO$_2$ at 125 mL/min was fed to the reactor. The product gas from the reactor was led to a gas-liquid separator and a dehumidifier where the moisture in the product gas was thoroughly removed, and then led to a GC-TCD (GC 6820, Agilent Technologies) for analysis.

After the reduction step, N$_2$ of 500 mL/min was introduced to the reactor for 0.5 h to replace the reducing gas in the reactor. Thereafter, air of 225 mL/min was fed to the reactor. The product gas was analyzed by GC-TCD.

For the reduction step, the accumulated reduction utilization ratio of OC from the beginning of experiment to a time point of m min was expressed as Eq. (1):

$$C_{m,re} = \frac{\int_0^m (V_{H_2,in,t} - V_{H_2,out,t} - 4V_{CH_4,out,t})dt}{22.4 \times M_{H_{2theo}}} \tag{1}$$

where, $V_{H_2,in,t}$ (mL/min) and $V_{H_2,out,t}$ (mL/min) are the flowrates of H$_2$ in and out of the reactor, respectively. $V_{CH_2,out,t}$ (mL/min) is the flowrate of CH$_4$ out of the reactor. $M_{H_{2theo}}$ (mmol) is the theoretically required amount of H$_2$ for OC being completely reduced.

For the oxidation step, the accumulated oxidation utilization ratio of OC from the beginning of experiment to a time point of m min was expressed as Eq. (2):

$$C_{m,ox} = \frac{\int_0^m (V_{O_2,in,t} - V_{O_2,out,t})dt}{22.4 \times M_{O_2 theo}} \tag{2}$$

where, $V_{O_2,in,t}$ (mL/min) and $V_{O_2,out,t}$ (mL/min) are the flowrates of O$_2$ in and out of the reactor, respectively. $M_{O_{2theo}}$ (mmol) is the theoretically required amount of O$_2$ for OC being oxidised completely.

The experiment on cycle performance began with the times acquired for complete reduction and oxidation, which was input to PLC. In the reduction step, electromagnetic valve 6 was open and electromagnetic valve 7 was close. When the reduction step was over, electromagnetic valve 6 was switched to the close position and electromagnetic valve 7 was switched to the open position, and then the oxidation step began, and vice versa. Once the oxidation step was over, the cycle number was counted up with 1. The performances of OC were measured for about every 10 cycles.

2.3. Characterization of Cu/SiO$_2$

Composition and morphology of the fresh and the degraded OC were characterized with X-ray diffraction (XRD) and Scanning electron microanalysis (SEM). XRD analysis was carried out using a