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Short communication

Liquid sintering behavior of Cu-based oxygen carriers for chemical looping process

Young Ku [a,*], Shr-Han Shiu [a], Yu-Cheng Liu [a], Hsuan-Chih Wu [a], Yu-Lin Kuo [b], Hao-Yeh Lee [a]

[a] Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan
[b] Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

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ABSTRACT

Chemical looping and chemical-looping with oxygen uncoupling processes using CuO oxygen carriers are demonstrated to be novel and efficient with inherent separation of CO_2. However, liquid-sintering occurred during the application of CuO is confirmed to significantly reduce its reactivity. Hence, ZrO_2 was employed as support for CuO in this study to diminish agglomeration of CuO particulates during chemical looping operations. Experimental results demonstrated that CuO/ZrO_2 oxygen carriers contain 40 to 60% ZrO_2 exhibited adequate mechanical strength and reactivity for syngas combustion. The supplement of 1% starch as pore-forming agent to CuO/ZrO_2 oxygen carriers could not only maintain the mechanical strength, but also improve the oxygen carrier conversion for CLOU process.

1. Introduction

In order to combat global warming and mitigate the CO_2 emissions, various carbon capture, storage and utilization technologies are recently developed. Among, chemical looping process (CLP) is considered as an attractive and promising alternative for fuel combustion because nearly pure CO_2 can be obtained and ready for further management. However, solid fuels were required to be gasified prior to the combustion with various solid oxygen carriers for CLP operations, therefore, chemical looping with oxygen uncoupling process (CLOU) is developed for the combustion of solid fuels [1,2]. During the operation of CLOU process, gaseous oxygen was initially released from the oxygen carriers, and was then combusted directly with the solid fuels. Thus, the amount of oxygen carriers required for combustion might be vastly reduced and the combustion efficiency of solid fuels is markedly enhanced [3,4]. It is reported that the combustion rate of solid fuels for CLOU operations was approximately 10 to 50 times higher than those for CLP operations [1,5].

Numerous oxygen carriers, such as Mn_2O_3, Co_3O_4 and CuO can be selected as oxygen carriers for CLOU operations through thermodynamic calculations and preliminary experiments [2,6,7]. Among the these metal oxides, CuO oxygen carriers exhibits the highest oxygen capacity (0.1 g O_2/g for CuO compared to 0.03 g O_2/g and 0.06 g O_2/g for Mn_2O_3 and Co_3O_4, respectively) [1,8]. CuO oxygen carriers are reported to be easily reduced to metallic Cu and to exhibit high reaction rates and excellent chemical stability [1,9]. However, reactivity and mechanical properties of these CuO oxygen carriers were seriously degraded after multi-cycle operations because of the serious agglomeration occurred during CLP operations [2,10,11], possibly due to the relatively low melting points of copper-containing compounds. Thus, several support materials, such as SiO_2, Al_2O_3, $MgAl_2O_4$ and ZrO_2 were utilized to enhance the physical and mechanical stability of CuO oxygen carriers. Corbella et al. indicated that copper oxide was well-dispersed using mesoporous silica as support, and high selectivity to CO_2 formation was achieved for chemical looping combustion of CH_4, CO and H_2 with CuO/SiO_2 oxygen carriers containing 10 wt% CuO calcined at 800 °C [12]. Chuang et al. found that the Al_2O_3 modified CuO oxygen carriers prepared through coprecipitation demonstrated higher redox stability [13]. Arjmand et al. stated CuO supported on Al_2O_3 was appropriate for CLC and CLOU operations, and indicated $CuAlO_2$ was formed during incomplete reduction [2]. Wang et al. reported CuO oxygen carriers prepared by mechanical mixing using SiO_2, TiO_2 and ZrO_2 were suitable for chemical looping applications [14]. Wang et al. revealed that both reduction and oxidation rates of CuO/ZrO_2 were high for experiments carrier out at temperature higher than 860 °C and 500 °C, respectively; and no agglomeration was observed for operations with CuO/ZrO_2 oxygen carriers [15]. Imtiaz et al. indicated that the amount of oxygen release released from Al_2O_3-supported CuO was less than its theoretical value because of the agglomeration of the nano-sized Al_2O_3 grains [16]. Adánez-Rubio et al. reported that the application of Cu–Mn mixed oxide for CLOU process demonstrated high oxygen release rate, high

* Corresponding author.
E-mail address: ku508@mail.ntust.edu.tw (Y. Ku).

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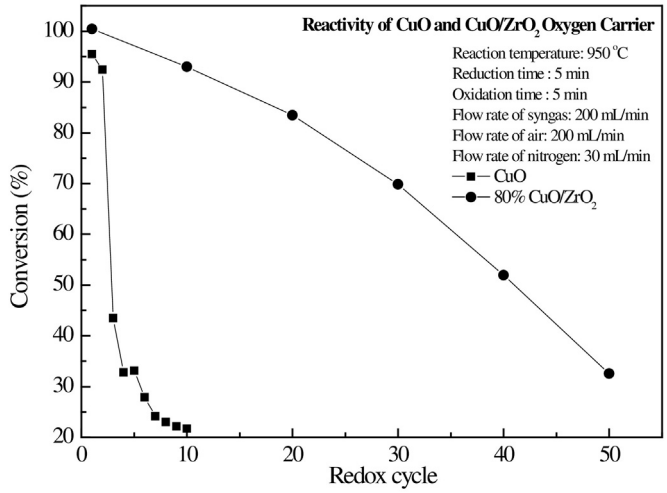

Fig. 1. Effect of redox cycle on syngas conversion for CLP operations using CuO and CuO/ZrO_2 oxygen carriers containing 20% ZrO_2.

oxygen carrier conversion and no agglomeration [17]. However, the detailed liquid sintering behavior of CuO during the chemical looping operation was seldom discussed and still remains unclear.

In this study, prepared zirconium-supported CuO oxygen carriers (CuO/ZrO_2) with various ZrO_2 fractions and sintered at different temperatures were investigated through consecutive redox-cycle operations of thermogravimetric analyzer (TGA) to investigate the reactivity decrease for CuO/ZrO_2. The oxygen carrier conversions of prepared CuO/ZrO_2 with syngas (CO/H_2) for CLP operation, and with nitrogen for CLOU operation were also determined in TGA. The mechanical strength of CuO/ZrO_2 particles containing different amounts of starch (0, 1, 5 and 10%) were determined by texture analyzer; and the reactivity of these CuO/ZrO_2 particles were evaluated by TGA with continuous 5 redox cycles.

2. Experimental

The oxygen carriers used in this study were prepared with predetermined amounts of reagent-grade CuO (Aldrich, 99.99%), ZrO_2 (Sigma-Aldrich, 99%) and starch (Acros). Zirconium-supported CuO oxygen carriers (CuO/ZrO_2) with various ZrO_2 fractions (20, 40, 50 or 60 wt%) were prepared by mixing pre-weighed amounts of CuO and ZrO_2 powders. These agents were loaded into a planetary ball mill to be operated at 380 rpm for 2 h. The well-mixed particles were then sintered in a muffle oven at constant temperature preset between 1000 and 1300 °C for 2 h. The composition ratio of CuO/ZrO_2 had been checked by the TGA analysis based on the oxygen balance calculation.

For CLP experiments conducted in this study, 50 to 125 mg CuO/ZrO_2 oxygen carriers were loaded in an alumina crucible for thermogravimetric (TGA) analysis using a Netzsch STA 449F3 analyzer. The temperature of TGA chamber was elevated from room temperature to 950 °C with a ramping rate of 20 °C/min in air atmosphere. 200 mL/min gas stream composed of 20% syngas (10% H_2 and 10% CO balanced in N_2) was then introduced into the TGA chamber for the reduction of CuO/ZrO_2 oxygen carriers. After the reduction phase, 200 mL/min N_2 was introduced for sweeping reducing gas remained in the TGA chamber. Subsequently, 200 mL/min air was introduced to oxidize the reduced oxygen carriers. For CLOU experiments, similar procedures were conducted to the CLP experiments, except that 200 mL/min N_2 was introduced, to substitute syngas, into TGA chamber during the reduction phase of CuO/ZrO_2 oxygen carriers. The redox conversion of oxygen carriers was calculated, by the following equation:

$$X_{oc} = \frac{m(t) - m_{red}}{m_{oxi} - m_{red}} \quad (1)$$

where X_{oc} is the redox conversion; m_{oxi} is the weight of fully oxidized oxygen carrier; m_{red} is the weight of fully reduced oxygen carrier; $m(t)$ is the weight of oxygen carrier at a specific operation time, t.

Surface morphology and average particle size of fresh and used oxygen carriers were analyzed by a Field-emission Scanning Electron Microscope (FE-SEM, JOEL JSM-6500F). Surface area, pore volume and pore size of oxygen carriers were determined by a Brunauer Emmett

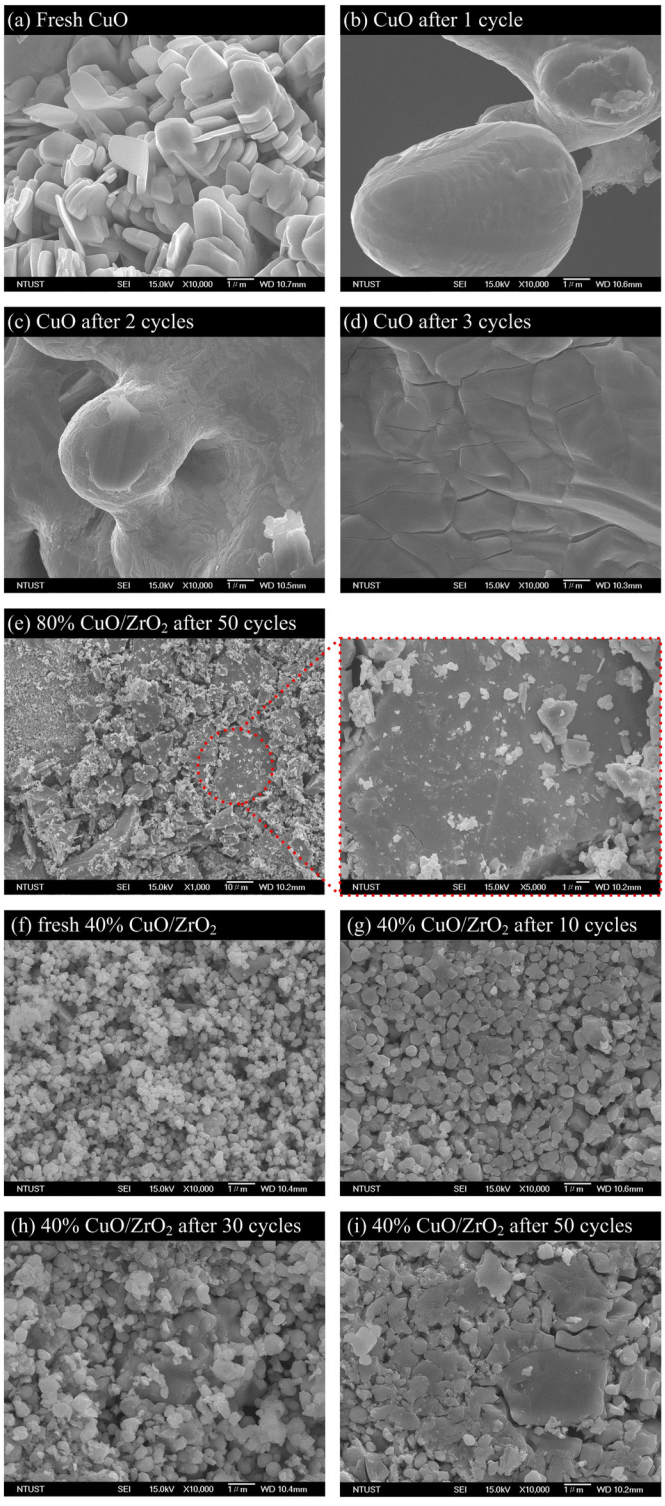

Fig. 2. SEM images of (a) fresh CuO, (b) CuO after 1 cycle, (c) CuO after 2 cycles, (d) CuO after 3 cycles, (e) 80% CuO/ZrO_2 after 50 cycles, (f) fresh CuO/ZrO_2, (g) 40% CuO/ZrO_2 after 10 cycles, (h) 40% CuO/ZrO_2 after 30 cycles and (i) 40% CuO/ZrO_2 after 50 cycles for CLP operations.