FE2O3-CUO/AL2O3 OXYGEN CARRIERS APPLIED TO FIXED BED REACTOR FOR CHEMICAL LOOPING PROCESS

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Abstract - In this study Fe_2O_3-CuO/Al_2O_3 oxygen carriers were be focused, various calcined temperatures were employed to fabricate the oxygen carriers. Fe_2O_3-CuO/Al_2O_3 oxygen carriers, which calcined at 1200 °C, possess the optimal performance for reactivity test, recyclability test and mechanical test. FCA3112 oxygen carriers were used for chemical looping combustion in fixed bed reactor. In order to determine the reduction time, long term reduction at 900 °C was conducted. Subsequently, the combustion efficiency was evaluated at 850-925 °C. Results show the conversion of FCA3112 oxygen carriers increased when the reaction temperature is increased. On the other hand, the optimal reaction temperature is at 925 °C for FCA3112 oxygen carriers.

Keywords - Chemical looping process, Fixed bed reactor, Metal Oxide, Oxygen carriers.

I. INTRODUCTION

Chemical Looping Process is a novel technology which uses metal oxide to provide the oxygen for combustion instead of air. The metal oxide, which is called the oxygen carriers, provides lattice oxygen for the fuel combustion in Fuel Reactor (FR). Subsequently, they are moved to Air Reactor (AR) for oxidation.

In the CLP, Oxygen carriers are an important factor for chemical looping process. Iron based oxygen carriers have been got lots of attention due to good performance and low cost. Moreover, copper based is also a good candidate due to high oxygen capacity and high reduction rate. Recently, numerous research focus on multiple active phases oxygen carriers, not only they possess different characteristics but also create mixed metal oxide.

II. PREPARATION OF OXYGEN CARRIERS

First, the hematite, copper oxide, and alumina were mixed with starch and stirred at room temperature. The well-mixed iron-based slurry was dried at 130 °C for 10 h to form particles. After the moisture was removed, the oxygen carriers were pulverized and sieved to obtain the desired particle size of 1.2-1.4 mm (sieving preparation) and simultaneously were generated numerous powders. Subsequently, iron-based oxygen carriers were calcined at 1000-1200 °C for 2 h at air atmosphere in a muffle furnace, and then obtained the oxygen carriers which used in this study.

III. RESULTS AND DISCUSSIONS

A. Characterization analysis of Fe_2O_3-CuO/Al_2O_3 oxygen carriers

Fe_2O_3-CuO/Al_2O_3 oxygen carriers are composed by 60 wt.% of Fe_2O_3, 20 wt.% of CuO, and 20 wt.% of Al_2O_3 and contained no starch, the last one number represent the calcined temperature from 1000-1200 °C, Fe_2O_3-CuO/Al_2O_3 oxygen carriers will be named FCA3110, FCA3111, and FCA3112 in this study. Table I shows the main characteristics of FCA3110, FCA3111, and FCA3112 oxygen carriers in this study. The XRD patterns of fresh oxygen carriers and that after 20 redox cycles under H_2 and CO atmosphere respectively, Fe_2O_3-CuO/Al_2O_3 oxygen carriers prepared by pulverization process and calcined at various temperatures, as shown in Fig. 1 and Fig. 2.

The XRD pattern of these three fresh oxygen carriers have some overlapping situations. Therefore, Fe_2O_3, CuO, and $CuFe_2O_4$ spinel can't be determined easily. Finally, the peaks of these main phases can be evaluated through some references and Fe_2O_3-CuO phase diagram. By the 20th redox cycle, two main phases can be regenerated successfully among FCA3110, FCA3111, and FCA3112. Both of these oxygen carriers show a good redox capacity not only under H_2 but also under CO atmosphere.

B. Reactivity analysis of Fe_2O_3-CuO/Al_2O_3 oxygen carriers

This part compares the recyclability and reactivity of Fe_2O_3-CuO/Al_2O_3 oxygen carriers calcined at various temperatures and then discusses which kind of oxygen carriers are more suitable in CLP.

In the reduction stage, the reducing gas (hydrogen or carbon monoxide) is sent into TGA to react with the oxygen carriers for 10 min respectively. Subsequently air, as the oxidizing gas, is pumped in for 10 min in order to fully oxidize the oxygen carriers. During these two stages, nitrogen used to purge for the system 5 min to prevent gas mixing. Fig. 3 and Fig. 4 reveal the recyclability of Fe_2O_3-CuO/Al_2O_3 oxygen carriers under hydrogen and carbon monoxide atmosphere at 900 °C in TGA respectively.

Results show all of Fe_2O_3-CuO/Al_2O_3 oxygen carriers at various calcined temperature, which have a stable recyclability after 20 redox cycles under either reducing gas.

Table I Main characteristic of the oxygen carriers.

Active oxide	Fe_2O_3		
Inert support	Al_2O_3		
Modified oxide	CuO		
Fabrication Technique	Pulverization		
Particle size (mm)	1.2-1.4		
Calcined temperature (°C)	1000	1100	1200
Crush strength (N)	4.38	11.32	20.50
ρ_B(kg/m^3)	1068.1	1184.4	1506.4

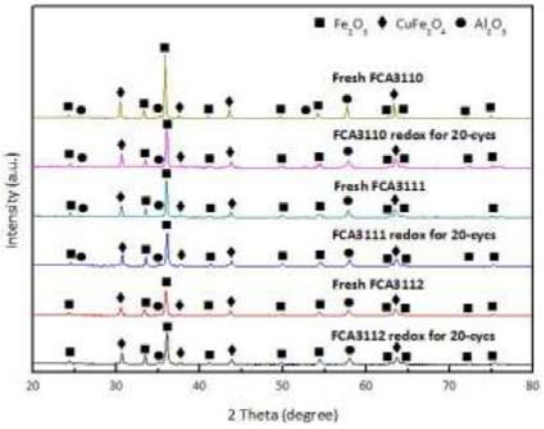


Fig. 1. The XRD patterns of fresh and after 20 redox cycles under H_2 atmosphere Fe_2O_3-CuO/Al_2O_3 oxygen carriers calcined at 1000 °C-1300 °C.

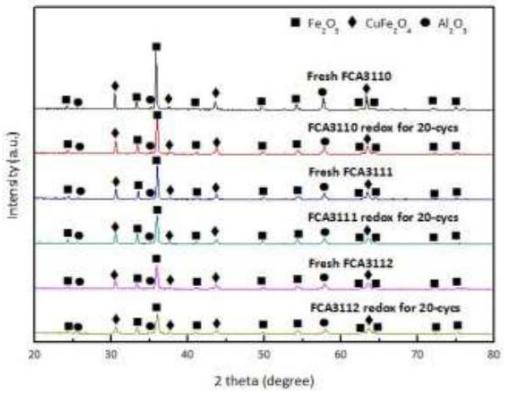


Fig. 2. The XRD patterns of fresh and after 20 redox cycles under CO atmosphere Fe_2O_3-CuO/Al_2O_3 oxygen carriers calcined at 1000 °C-1300 °C.

On the other hand, all of them have a larger weight loss under hydrogen atmosphere than under carbon monoxide, this may be because the hydrogen is more active with Fe_2O_3-CuO/Al_2O_3 oxygen carriers than carbon monoxide.

Furthermore, FCA3110 oxygen carriers have the most weight loss than others under two reducing gas. During the purge stage, Fe_2O_3-CuO/Al_2O_3 oxygen carriers have a nearly 1 % weight loss, the reason why is gas phase oxygen releasing of CuO at high temperature.

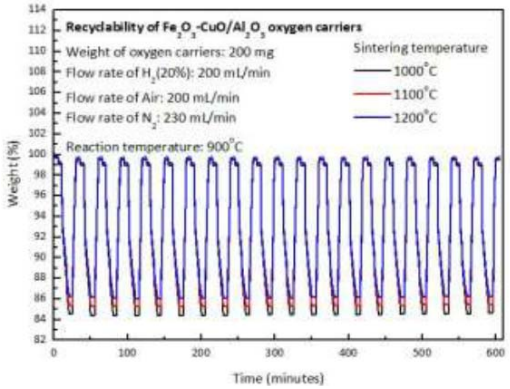


Fig. 3. Recyclability of Fe_2O_3-CuO/Al_2O_3 oxygen carriers under H_2 atmosphere at 900 °C in TGA.

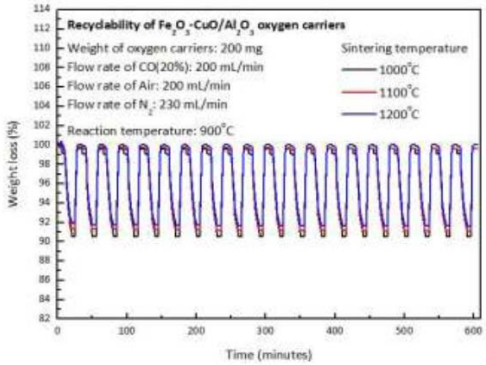


Fig. 4. Recyclability of Fe_2O_3-CuO/Al_2O_3 oxygen carriers under CO atmosphere at 900 °C in TGA.

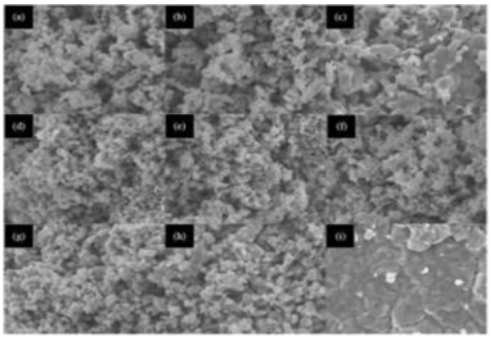


Fig. 5. SEM images of (a)-(c) Fresh FCA3110, FCA3111 and, FCA3112 oxygen carriers 5,000x, respectively (d)-(f) FCA3110, FCA3111 and, FCA3112 oxygen carriers reduced by H_2 5,000x, respectively (g)-(i) FCA3110, FCA3111, and FCA3112 oxygen carriers reduced by CO 5,000x, respectively.

Fig. 5 shows SEM images of Fresh FCA3110, FCA3111 and, FCA3112 oxygen carriers under different reducing gas for 20 redox cycles.

Results indicate the Fe_2O_3-CuO/Al_2O_3 oxygen carriers have good performance and no agglomeration, which can be observed under hydrogen atmosphere at various calcined temperature. On the other hand, Fe_2O_3-CuO/Al_2O_3 oxygen carriers have good performance under carbon monoxide atmosphere, except for FCA3112 exhibits severe agglomeration.

C. Long term reduction of FCA3112 oxygen carriers in fixed bed

The component of reducing gas is 18.3 % hydrogen, 9 % of carbon monoxide, and 9 % of carbon dioxide,

and the total gas flow rate is set at 1.5 L/min to prevent the oxygen carriers fluidized. Moreover, FCA3112 is heated by air from room temperature to 900 °C and keep for 20 min to make sure the system has been reached stable status. Subsequently, the reduction stage is starting for 90 min to observe the behavior of reduction. Before the oxidation stage starts, nitrogen is pumped in for 20 min. Finally, air as the oxidation agent is sent for 1 h to complete full oxidation of the oxygen carriers. .

In Fig. 6, the results report the consumption of hydrogen is the same with inlet molar flow rate in the first 3.5 min, which means all of hydrogen is combusted to steam. On the other hand, the consumption of carbon monoxide increased gradually in the first 7 min, this may be the reactivity of carbon monoxide is worse than hydrogen, and then slightly decreased. Finally, the fuel consumption reaches equilibrium after the 20 min of reduction.

Fig. 7 demonstrates the conversion of FCA3112 oxygen carriers for long term reduction at 900 °C in fixed bed. The conversion of FCA3112 increases smoothly at whole reaction time, this result correlates with Fig. 6. The conversion of FCA3112 oxygen carriers can reach nearly 80 % after 90 min of reduction.

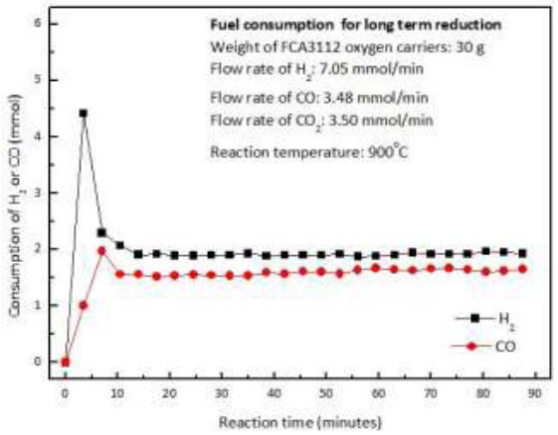


Fig. 6. Fuel consumption for long term reduction at 900 °C in fixed bed.

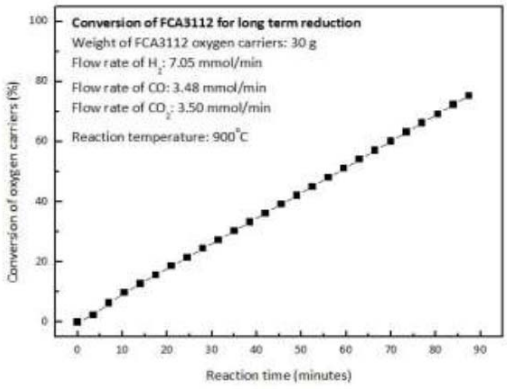


Fig. 7. Conversion of FCA3112 oxygen carriers for long term reduction at 900 °C in fixed bed.

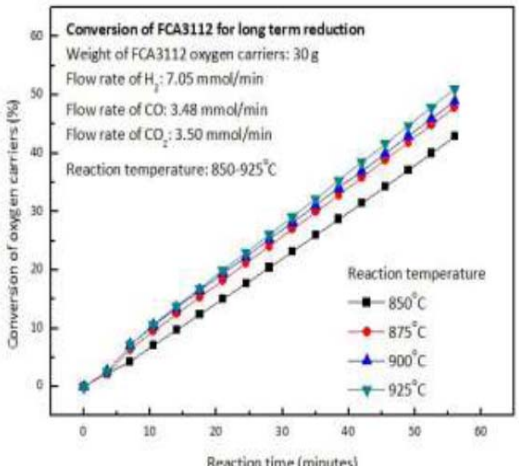


Fig. 8. Conversion of FCA3112 oxygen carriers at various reaction temperatures in fixed bed.

In Fig. 8, there aren't a lot of different for the conversion of FCA3112 when the reaction temperature is over 875 °C.
Results show the conversion of the oxygen carriers increased when the reaction temperature is increased. The optimal reaction temperature for reduction of FCA3112 is at 925 °C.

CONCLUSIONS

Fe_2O_3-CuO/Al_2O_3 oxygen carriers which calcined at various temperatures were prepared in this study. The characterization and reactivity have been analyzed in the result. Moreover, the long term reduction and effect of reaction temperature for FCA3112 oxygen carriers were also evaluated. The concluding remarks are summarized as follows:

1. The conversion and recyclability of Fe_2O_3-CuO/Al_2O_3 oxygen carriers calcined at various temperatures keep high and stable at two different reducing gas.
2. Compared two different reducing gas, Fe_2O_3-CuO/Al_2O_3 oxygen carriers under H_2 atmosphere has higher conversion.
3. XRD pattern shows Fe_2O_3-CuO/Al_2O_3 oxygen carriers have good redox status at various calcined temperature. SEM indicates there is no agglomeration can be for Fe_2O_3-CuO/Al_2O_3 oxygen carriers under H_2 atmosphere calcined at various temperatures. On the other hands, only FCA3112 has agglomeration occurred under CO atmosphere.
4. Long term reduction for FCA3112 under syngas atmosphere is evaluated by the fixed bed reactor, nearly 80 % of conversion could achieve after 90 min.
5. Effect of reaction temperature is tested at 850-925 °C, the conversion of FCA3112 increased when the reaction temperature is increased. The optimal reaction temperature for reduction is at 925 °C.

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