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Continuous O_2-CO_2 production using a Co-based oxygen carrier in two parallel fixed-bed reactors

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Abstract−Oxygen-enriched carbon dioxide stream with oxygen concentration higher than 20 vol% was produced continuously by using a Co-based oxygen carrier packed in two parallel fixed-bed reactors operated in a cyclic manner. Oxygen was absorbed by the oxygen carrier with air being fed. An oxygen-enriched carbon dioxide stream was obtained when the fixed-bed was regenerated with carbon dioxide as a purge gas. Multiple absorption and desorption cycles indicated that the Co-based oxygen carrier had high cyclic stability. XRD analysis determined the absorbed and desorbed products were Co_3O_4 and CoO, respectively. The TGA results indicated that Co-based oxygen carrier did not react with NO or SO_2 during the desorption stage. This Co-based oxygen carrier offers potential for applications in the O_2-CO_2 production for the oxy-fuel coal combustion process.

Key words: Oxy-fuel Combustion, Oxygen Production/Separation, Co-based Oxygen Carrier

INTRODUCTION

According to the Climate Change 2007 Synthesis Reports of the Intergovernmental Panel On Climate Change (IPCC), CO_2 emission from the use of fossil fuel contributes 56.6% of the total anthropogenic GHGs, which will cause possible disastrous effects on climate change [1]. Oxy-fuel combustion is among those promising options for capturing CO_2 from the use of fossil fuel [2]. Despite its many advantages compared with traditional air combustion, such as smaller quantities of NOx and SO_2 [3], significantly high energy consumption and investment cost of O_2 production are the main challenges for this technology [4,5]. A novel high temperature sorption-based process referred to as ceramic autothermal recovery (CAR) for O_2 production was proposed by BOC [6] and Lin et al. [7], the total power consumption of the CAR plant was about 74% of that of the cryogenic air separation plant, and capital cost could be reduced by more than 50% [6].

The CAR process is based on storage and release of O_2 in two (or multiple) fixed-bed reactors containing perovskite-type materials operated at high temperatures. The process operation is made continuous by operating the two beds in a cyclic process: air is passed through one bed to allow absorption and storage of O_2; the stored O_2 is then released for use in the boiler by partial pressure reduction using a sweep gas such as hot recycled flue gas, steam or an admixture of the two. The CAR process realizes autothermal recovery by using the exothermic oxygen absorption to heat the endothermic oxygen release process [6]. Leions [8] also used petroleum coke to provide extra heat during the oxygen release process. A major challenge of the CAR process using perovskite material is that perovskite material undergoes a reversible reaction which can be expressed by the following formulas [9,10]:

$$La_{0.1}Sr_{0.9}Co_{0.5}Fe_{0.5}O_{2.6}+0.9CO_2 \Leftrightarrow 0.9SrCO_3+0.05La_2O_3+0.5CoO+0.25Fe_2O_3+0.15O_2 \quad (1)$$

$$Sr_{0.5}Ca_{0.5}Co_{0.5}Fe_{0.5}O_{2.47}+CO_2 \Leftrightarrow 0.5SrCO_3+0.5CaCO_3+0.5CoO+0.25Fe_2O_3+0.11O_2 \quad (2)$$

This reversible process makes perovskite material react with CO_2 to form carbonate when using CO_2 to release O_2. In the next step, O_2 storage step, the carbonate formed will decompose and gas product CO_2 will be released into air, diluted by N_2. This will result into failing to capture CO_2 from flue gas [11]. So oxygen carrier with high reactivity, high reaction rate, high stability and not reacting with CO_2 is critical for CAR O_2 production process. It is found that cobalt oxide can be used as oxygen carrier and has all these good characters mentioned above. The storage and release of O_2 are based on the following reversible reaction:

$$6CoO+O_2 \Leftrightarrow 2Co_3O_4 \quad (3)$$

In our previous study [12], the O_2 absorption/desorption processes of Co-based oxygen carrier occurred in a single reactor operated alternately to test the effects of some main factors, such as reaction temperature and gas flow rate. For commercial application, both absorption and desorption need to be carried out continuously to produce a continuous oxygen-enriched carbon dioxide. In this study, we investigated the continuous production of oxygen-enriched carbon dioxide with two fixed-bed reactors in two steps, O_2 storage and followed by O_2 release. The two steps were done simultaneously and continuously in a cyclic manner by switching air and CO_2 feeds between the two reactors. The effects of NO and SO_2 with a concentration near real flue gas were also studied in TGA experiments.

EXPERIMENTAL STEP-UP AND PROCEDURE

1. Dual Fixed-bed Reactors System

Continuous O_2-CO_2 production was performed in two parallel

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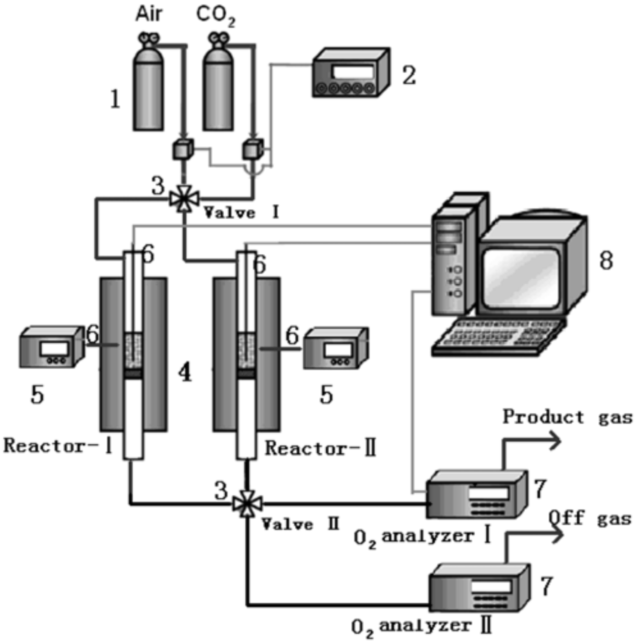

Fig. 1. Dual fixed-bed reactors setup.

1. Gas resource
2. Mass flow control unit
3. Four-way valve
4. Fixed-bed reactor
5. Temperature control unit
6. Thermocouple
7. O$_2$ analyzer
8. Data acquisition

fixed-bed reactors that were heated by electric furnaces; one of the reactors was used as the absorption reactor, while the other was used as the desorption reactor. Fig. 1 shows the experimental setup of the fixed-bed reactors system. Two four-way valves were connected to the inlets and the outlets of the two reactors in order to switch the two different gaseous feeds, the outlet product gas and off gas. The gaseous feeds entered near the top of reactors and were preheated as they flowed downward into the preheat section. Then, the preheated gases flowed through the Co-based oxygen carrier and exited from the bottom of the reactors. The outlet gases were analyzed using O$_2$ analyzers and the reaction temperatures in both reactors were measured and controlled using thermocouples. The Co-based oxygen carrier was Co_3O_4/Al_2CoO_4 (70/30 wt%), crushed into powder with particle sizes in the range of 200-450 μm. The oxygen carrier packing length was 100-150 mm in the quartz tube with a diameter of 30 mm.

At first, CO$_2$ was fed into reactor I to perform desorption and air was fed into reactor II to perform absorption. When the O$_2$ concentration in the outlet of desorption reactor decreased to about 20%, the two four-way valves were switched and the temperatures of the reactors were also changed, as indicated in Table 1. Operating in this cyclic manner, a product gas with high O$_2$ concentration was continuously obtained from the right outlet of the valve I, which was monitored by O$_2$ analyzer I and recorded by computer. O$_2$ analyzer II was used to monitor the O$_2$ concentration in the off gas and to judge whether absorption processes were finished, so the data were not necessarily recorded. Air flow rate was relatively large so complete absorption was achieved in all cycles during the test.

2. Effects of NO and SO$_2$ on Co-based Oxygen Carrier During TGA

A DuPont 951 TGA (TA Instrument 1200) was used to study the effects of NO and SO$_2$ on the Co-based oxygen carrier. A small amount of the Co-based oxygen carrier (about <15 mg) was placed in a quartz sample holder and brought to 900 °C under N$_2$ flow for desorption. After complete desorption, the temperature decreased below 200 °C. When approaching this temperature, the valve was switched to allow the NO (2,790 ppm diluted by Ar) or SO$_2$ (2,570 ppm diluted by N$_2$) to flow over the oxygen carrier, and the sample was heated at a constant rate of 10 °C/min to about 920 °C. Time, mass and temperature were recorded by the computer.

3. Preparation of the Co_3O_4/Al_2CoO_4 Oxygen Carrier Particle

The Co_3O_4/Al_2CoO_4 sample was from two primary materials, activated alumina (Al_2O_3) as the support and $Co(NO_3)_2\cdot 6H_2O$ as the effective component. The detailed preparation procedures of the Co_3O_4/Al_2CoO_4 sample are as follows. (1) Activated alumina with particle size 200-450 μm was selected and added into distilled water. (2) Cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$) was then also added into the mixture of distilled water and activated alumina. (3) This solution was stirred for 1 h at 348 K and was dried at 353 K for another 18 h before it was calcined at 773 K for 3 h in air. By this method, water, and nitric acid in the solution could be evaporated off at different stages. Spherical particles were obtained. (4) These particles were calcined in air at 1,173 K for 1.5 h. (5) Steps (2)-(4) were repeated for 10-15 times until the mass ratio of Co_3O_4 to Al_2CoO_4 was about 7/3.

It was found from the results of XRD analysis that the synthesized Co-based oxygen carrier includes only Co_3O_4 and Al_2CoO_4, and it was assumed that all Al_2O_3 reacts completely with Co_3O_4 to form Al_2CoO_4. Thus, the mass ratio of Co_3O_4 to Al_2CoO_4 in the Co-based oxygen carrier could be calculated according to the original mass of Al_2O_3 and $Co(NO_3)_2\cdot 6H_2O$.

RESULTS AND DISCUSSIONS

1. Dual Fixed-bed Performance

The choice of reaction temperature was based on previous TGA experimental results [12], which indicated that the O$_2$ equilibrium pressures for the Co_3O_4 oxygen carrier as a function of temperature (600 °C<T<950 °C) may be estimated with:

Table 1. Experimental conditions

Parameters		Temperature (°C)	Air flow rate (mL/min)	CO$_2$ flow rate (mL/min)	Solid mass (g)
Reactor I	Absor. process	600-850	1400	0	About 250
	Desor. process	935	0	400	
Reactor II	Absor. process	600-850	1000	0	About 150
	Desor. process	925	0	400	

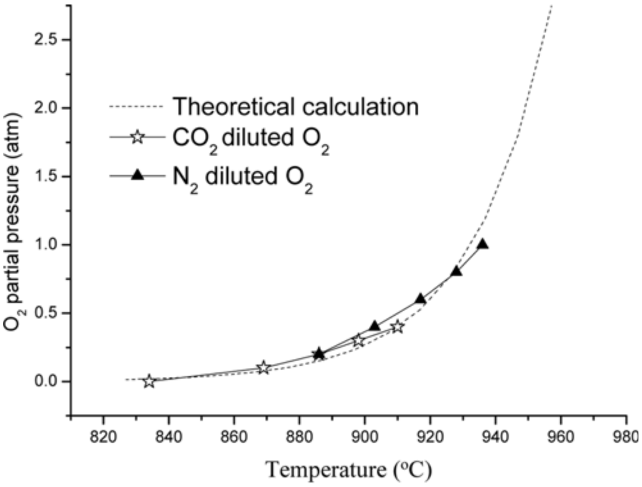

Fig. 2. O_2 equilibrium pressure of Co_3O_4-CoO.

$$P_{O_2,e}=101325\times\exp\left[-42.913\times\left(\frac{1000}{T}\right)^3+193.32\times\left(\frac{1000}{T}\right)^2-291.78\times\left(\frac{1000}{T}\right)+133.49\right](\mathrm{Pa}) \quad (4)$$

Thermodynamic calculations were compared with experimental results in Fig. 2. From Fig. 2 it can be seen that the desorption temperature for Co_3O_4 decomposition in the CAR system is critical and governed by the thermodynamics of the desorption system. At 101,325 Pa, temperature ranging from 800 °C to 900 °C is required during desorption to acquire 0 to 30% O_2. Since oxygen absorption on the Co-based material is exothermic and oxygen release is endothermic, when the heat for oxygen carrier desorption is provided by the released heat of absorption step (which may be operated under higher pressure and higher temperature), the absorption/desorption cycle of O_2-CO_2 production process can be operated auto-thermally, i.e., once initiated the process operates almost auto-thermally with little or no heat input.

Natural gas or petroleum coke can also be added during desorption to react with some of the released O_2 and provide extra heat [8]. The reason for choosing natural gas and petroleum coke is that almost no ash is produced in the combustion process.

Experimental results for the continuous production of oxygen-enriched carbon dioxide using a Co-based oxygen carrier in two parallel reactors operated in a cyclic manner with a feed switchover time of 25-40 min are shown in Figs. 3 and 4. The results indicate that a steady O_2-CO_2 mixed stream with O_2 concentration higher than 20% can be obtained in the process. For both reactors, each cycle consisted of an absorption and a desorption process, and the two reactors were operated in a cyclic manner, so during one cycle there were two desorption processes curves in Fig. 3, one for Reactor I and the other for Reactor II. The observed fast increase in O_2 concentration at the beginning of every desorption process is due to the mixed and replacement process of new product gas with the

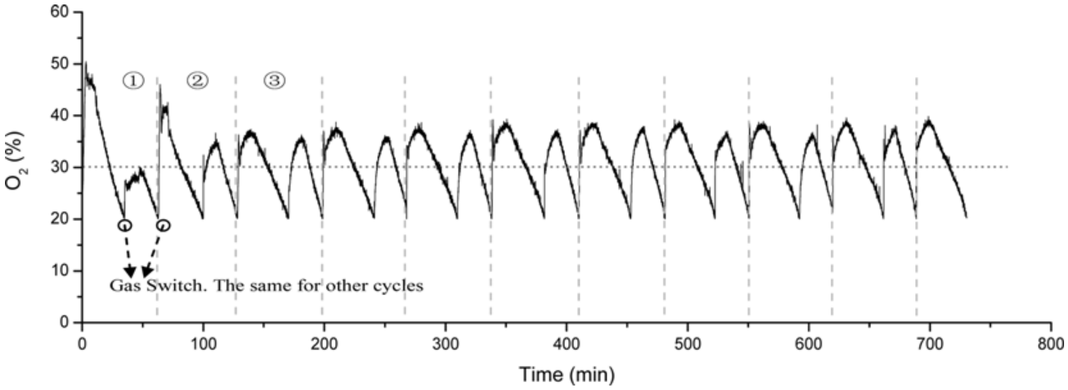

Fig. 3. Oxygen concentration profiles.

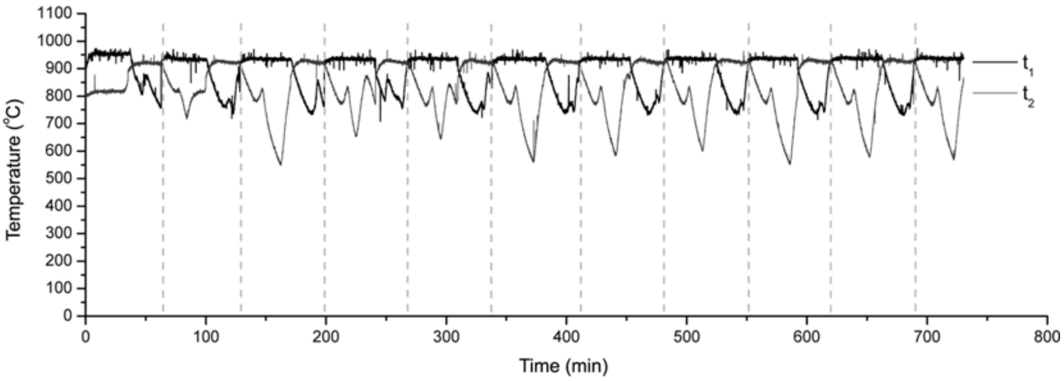

Fig. 4. Temperature profiles.

original product gas, immediately after the switchover of the valve II. O_2 concentration of the new product gas quickly reaches its maximum; then with the increasing of desorption time, the fraction of Co_3O_4 uncalcined in the reactor decreases and the O_2 concentration also decreases. Desorption temperature is critical to O_2 concentration, the maximum O_2 concentration is obtained at higher desorption temperature. At the beginning of the experiment, proper reaction temperature was not determined. The desorption temperatures are about 952, 920, and 940 °C, respectively, for the first three desorption processes, and the maximum O_2 concentrations differ greatly from the rest of the desorption processes. The masses of oxygen carrier also have significant effects by comparing reactors I and II; the desorption processes for more oxygen carrier last longer under the same CO_2 flow rate, which indicates more O_2 is released. After desorption, the oxygen carrier must undergo absorption in the air for O_2 storage. If the absorption is not completely achieved, there will be some waste of O_2 storage capacity. Therefore, the air flow rates are relatively large compared to stoichiometric amount during the absorption process to achieve complete absorption before switchover. The absorption reaction is exothermic and favored at lower temperature. Only if the equilibrium decomposition pressure of Co_3O_4 is lower than the O_2 partial pressure in the air can the absorption of O_2 proceed thermodynamically. It is calculated that at least 80% utilization ratio was achieved in every cycle. The O_2 storage capacity did not decrease with increasing the cycle number. Furthermore, it is evident that the cyclic reactivity and stability of the Co-based oxygen carrier are high. Nevertheless, the results of Fig. 3 clearly show that oxygen-enriched carbon dioxide with O_2 concentration high enough for the oxy-fuel combustion can be attained continuously by carrying out absorption and desorption (as expressed by reversible reaction 3) simultaneously in two fixed-bed reactors operated in a cyclic manner.

In our previous study [12], XRD analysis was performed to understand the reaction mechanism during the oxygen absorption and desorption cycles on the Co-based oxygen carrier. For better understanding, the Co-based Oxygen carrier used was prepared from $Co(NO_3)_2 \cdot 6H_2O$ with no Al_2O_3 added. Samples from absorbed and desorbed stages were studied by X-ray diffraction (XRD), as shown in Fig. 5. Only Co_3O_4 was detected in the absorbed sample. It was observed that only CoO exists in the desorbed sample. The results indicate that CoO reacts with O_2 in the absorption step to form Co_3O_4, while Co_3O_4 decomposes to CoO and O_2.

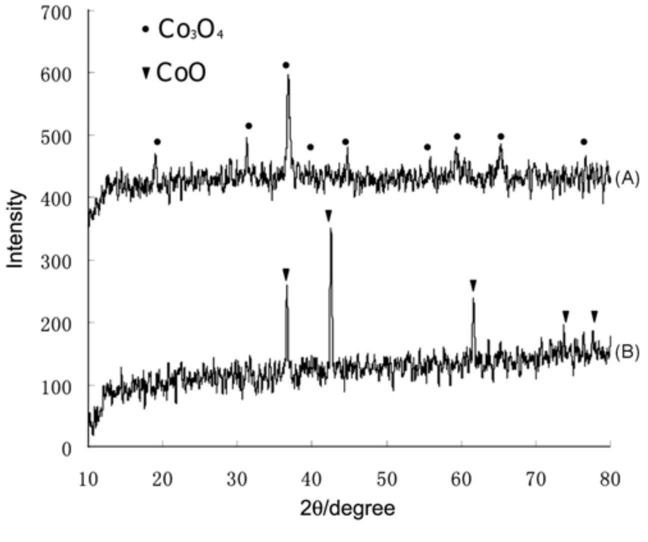

Fig. 5. XRD results of the Co-based oxygen carrier after oxygen absorption stage (A) and after oxygen desorption (B).

2. Effect of NO on Oxygen Carrier

TGA experimental results show that Co-based oxygen carrier does not react with NO (2,790 ppm diluted by Ar) in the temperature range of 200-920 °C, as the weight of oxygen carrier does not change during the constant rate heating process. It indicates that the existence of NO in the flue gas will not deactivate Co-base oxygen carrier when real flue gas is used as purge gas during the oxygen desorption process, at a temperature near 920 °C. This result is also obvious for the Co-based oxygen carrier was obtained by heating Cobalt nitrate at about 500 °C and 900 °C.

3. Effect of SO_2 on Oxygen Carrier

The weight change and temperature with time of TGA experiments can be seen in Fig. 6. It indicates that Co-based oxygen carrier does react with SO_2 (2,570 ppm diluted by N_2) and the weight of oxygen carrier increases in the temperature range of 200-660 °C. However, the weight decreases as the temperature becomes higher.

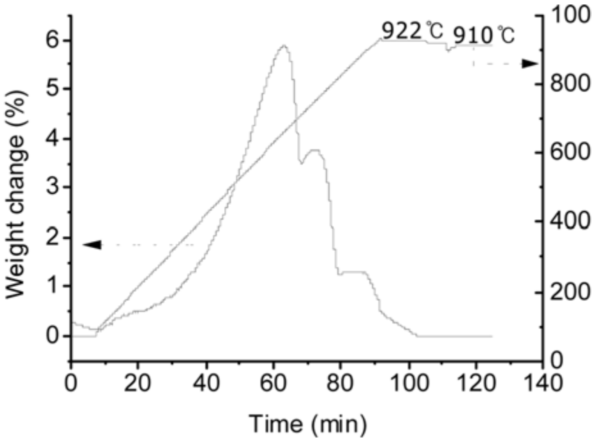

Fig. 6. The TGA plots of SO_2 effect on oxygen-carrier.

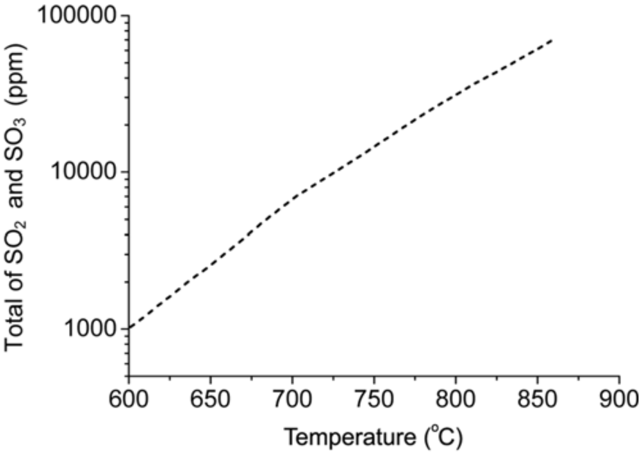

Fig. 7. SO_2 and SO_3 equilibrium concentration with CoO.

Finally, it decreases to the original level at isothermal stage of 922 °C. It is also found that the Co-based oxygen carrier does not react with SO_2 at isothermal stage of 910 °C. So the existence of SO_2 in the flue gas will not deactivate the Co-based oxygen carrier when real flue gas is used as purge gas during the oxygen desorption process, at a temperature near 920 °C. The SO_2 and SO_3 equilibrium concentration with CoO at different temperatures can be calculated from the relative thermochemical data. A reaction can only proceed if the Gibbs free energy change is less than zero. At the SO_2 and SO_3 equilibrium concentration, when the forward reaction and reverse reaction are balanced, the Gibbs free energy change is zero. The values of the Gibbs free energy of the reactants and products at various temperatures may be obtained from the literature [13], and then the SO_2 and SO_3 equilibrium concentration can be calculated, as shown in Fig. 7. It is found that cobalt sulfite and sulfate could be formed at significant concentration of SO_2 and SO_3. However, it is not likely that conditions with such high concentrations of sulfur oxides will be encountered in the flue gas during normal operation.

CONCLUSIONS

It is feasible to produce a continuous stream of oxygen-enriched carbon dioxide with oxygen concentration higher than 20% by using a Co-based oxygen carrier packed in two parallel fixed-bed reactors operated in a cyclic manner. Neither NO nor SO_2 in the real flue gas will react with the Co-based oxygen carrier when real flue gas is used as purge gas during the oxygen desorption process. This Co-based oxygen carrier offers potential for O_2-CO_2 production using real flue gas as a purge gas, for oxy-fuel coal combustion.

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