

Improved performance of barium cobalt-based perovskites materials: Influence of B-site substitution and metal oxide supported perovskite on oxygen desorption property and reactivity

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Oxy-fuel combustion is one of the proposed technologies which have the potential to achieve a zero CO₂ emission. To enhance the oxygen production performance of the oxygen carrier, different LaBO_{3-δ} (B=Co, Ni, Fe, Cr) and metal oxide (CeO₂, Al₂O₃, ZrO₂) supported BaCoO_{3-δ} perovskites have been successfully synthesized by the EDTA sol-gel method and further applied for producing oxygen. The oxygen desorption/production performance of synthesized perovskites were studied in a fixed-bed reactor system. Furthermore, the effects of H₂O and air as regeneration gas of metal oxide supported BaCoO_{3-δ} perovskite oxygen carrier were investigated in detail. Results shows that the oxygen desorption amount of different B-site substituted LaBO_{3-δ} (B=Co, Ni, Fe, Cr) perovskites decrease in the order of LaNiO_{3-δ} > LaCoO_{3-δ} > LaCrO_{3-δ} > LaFeO_{3-δ}. While compared with pure BaCoO_{3-δ} and different metal oxide supported BaCoO_{3-δ}, CeO₂ supported BaCoO_{3-δ} features higher production amount of oxygen. Multiple cycles demonstrated that BaCoO_{3-δ}/CeO₂ displays higher stability and regeneration capacity, which is the key factor to provide stable O₂/CO₂ gas stream for oxyfuel combustion application. In short, the novel BaCoO_{3-δ}/CeO₂ oxygen carrier developed in this work exhibits high oxygen desorption capacity and stability. In addition, it provides a promising potential for oxygen production in industrial application.

Keywords: CO₂ capture; Oxygen carrier; Supported-perovskite; Oxygen production.

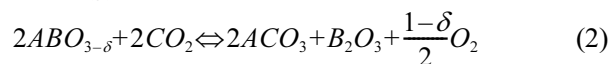
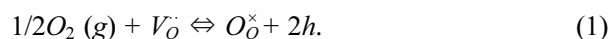
Introduction

The combustion of fossil fuels contributes to the emission of carbon dioxide into the atmosphere, leading to global warming [1, 2]. Oxyfuel combustion technology is a very effective technology path to reduce carbon dioxide emissions [3-5]. This type of combustion requires a high concentration of oxygen. The current cryogenic process is the only commercially available way to provide large-scale pure oxygen, but the large investment in oxygen production and high energy consumption is its major economic challenge and drawback. For oxyfuel combustion, only an O₂/CO₂ mixture gas with an oxygen concentration of 30% ~40% is required for the fuel combustion but not the pure oxygen.

Perovskite-like oxides-ABO₃ (where A and B are usually rare earth and transition metal cations, respectively) can be tailored to create a wide family of catalysts by varying either the A-site or the B-site metal ion. Perovskite-type oxides have been investigated intensively as functional materials because of their potential technology in the applications such as fuel cells, a component of capacitors,

microwave technology, electrodes, and immobilization of nuclear wastes, as well as being catalysts for oxidation and hydrogenation [6-12].

A new application of producing pure O₂ or O₂/CO₂ gas streams by using perovskite-type oxygen carriers for oxyfuel combustion is proposed by Lin *et al.* [13]. The reversible adsorption/desorption processes based on the perovskite-type oxygen carrier is described as below:



Where $V_{\dot{O}}$ is the oxygen vacancy, $O_{\dot{O}}^{\times}$ and h^{\cdot} denote lattice oxygen and electronic-hole, respectively.

A relatively low oxygen desorption amount may be a major drawback of this technique. This problem may pose a challenge to the high efficiency of the oxygen product volume in practical applications. Therefore, the development of perovskite-type oxygen carrier materials with excellent oxygen desorption performance and cyclic performance is necessary.

A common approach to improve the properties of perovskite-type oxygen carrier is using A/B site substitution in the metal oxides. Our previous study demonstrated that barium cobalt-based (Ba-Co-O) perovskites oxygen carriers present higher oxygen desorption capability

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and oxygen releasing rate [3, 4]. As La-based perovskites are the most common perovskites, $\text{LaBO}_{3-\delta}$ (B=Co, Ni, Fe, Cr) and $\text{BaCoO}_{3-\delta}$ are selected as candidate oxygen carrier in this study [14, 15]. CeO_2 -based materials are of intensive interest because of their outstanding oxygen storage capacity, and CeO_2 can supply active oxygen species to perovskite [16, 17]. To support BaCoO_3 , zirconia (ZrO_2) is particularly adopted because ZrO_2 remains highly stable under oxidizing and reducing atmospheres, making ZrO_2 as a promising support [18, 19]. Moreover, Al_2O_3 is another typical support, and the use of a load material having high thermal conductivity can reduce the sintering of the oxygen carriers. The additives can improve reaction performance and stability for perovskites materials in the oxygen-permeable membrane application [20, 21]. However, there is rare research about using supports to improve the reaction performance of perovskites. The effect of the supports on the reaction and the oxygen desorption capability are still unclear, and the durability of the supported perovskites has not yet been developed.

The current work aimed to study the effects of B-site (B=Co, Ni, Fe, Cr) substitution on oxygen desorption performance for La-based perovskites and the effect of supports on oxygen production/cyclic performance of metal oxide supported $\text{BaCoO}_{3-\delta}$. All the perovskite-type oxides were synthesized by EDTA sol-gel combustion method. The reactivity and performance of different pure and supported perovskites were investigated in a fixed-bed reactor system.

Materials and Methods

Oxygen carrier preparation

The pure $\text{LaBO}_{3-\delta}$ (B=Co, Ni, Fe, Cr) and $\text{BaCoO}_{3-\delta}$ perovskite samples were synthesized by EDTA sol-gel

method as shown in our previous study [5]. And metal oxide supported perovskite oxygen carriers in this study were prepared also by a sol-gel synthesis method. The detail preparation process for $\text{BaCoO}_{3-\delta}/\text{ZrO}_2$ for example is as follows: Metal nitrates $\text{Ba}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used as the raw materials and all of analytical purities. A design amount of metal nitrates and citric acid were dissolved in the NH_3 -EDTA solution. The mole ratios of EDTA: citric acid: total metal ions were controlled as 1:1.5:1. A desired amount of ZrO_2 was added in the string precursor solution. The solution was then gently heated and stirred at 70°C for 5 h and further dried at 105°C for 10 h, respectively. Then the dry residual was calcined at 850°C for 8 h. Finally, the resultant black powders were characterized and tested.

Experimental procedure

Oxygen adsorption/desorption experiments were performed in a fixed-bed reactor system as shown in Fig. 1. It consisted of a gas feeding system (including N_2 , air, CO_2 and a steam generator), an electric furnace with a quartz reactor, a gas analyzer and a computerized data-acquisition system.

About 5.0 g of synthesized perovskite powder is filled in the middle of the quartz reactor. Air/ H_2O and CO_2 are used as the feed gas for the adsorption step and the purge gas for the desorption step, respectively.

Output calculation

The total oxygen desorption amount calculation is performed by an integration scheme based on the obtained oxygen concentration distribution. And the following formula can be used:

$$V_{O_2} = \frac{\sum C_{O_2} \times F_{out}}{m} \quad (3)$$

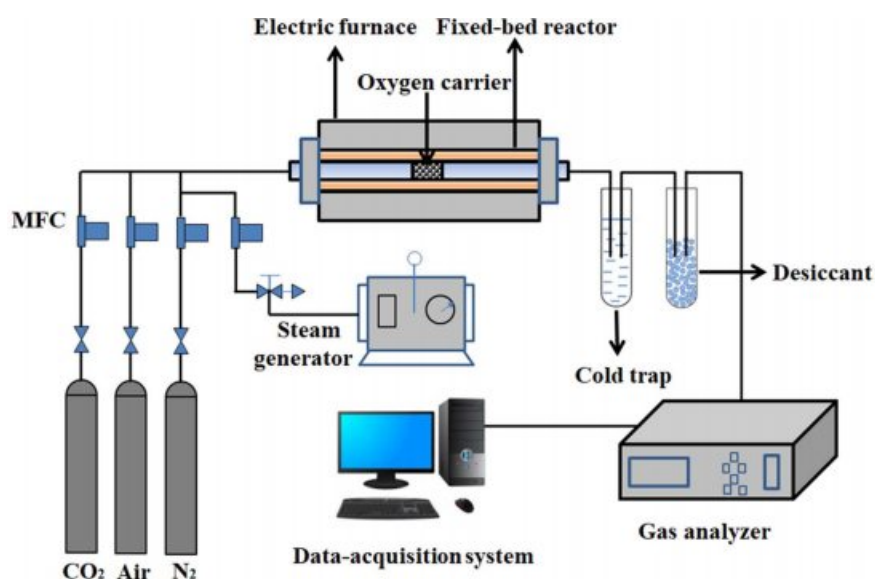


Fig. 1. Schematic diagram of fixed bed reactor system.

where ΣC_{O_2} is the integration of the entire oxygen concentration during the desorption, F_{out} (L/s) is the flow rate of desorption effluent, m (g) is the mass of perovskite powders, V_{O_2} (mL/g·sample) is the oxygen desorption amount for 1 g of the perovskite sample.

Results and Discussion

Effects of B-site substitution on oxygen desorption performance for la-based perovskites

The effects of different B-site substitution by different transition metal ions on the oxygen production performance of $LaBO_{3-\delta}$ were investigated. Fig. 2 demonstrates the comparison of the oxygen desorption performance for $LaBO_{3-\delta}$ (B = Co, Ni, Fe, Cr). It is obvious that B-site total substitution has significant effect on the oxygen desorption performance of $LaBO_{3-\delta}$. It shows that the oxygen desorption amount of B-site total substitution for $LaBO_{3-\delta}$ is in the following order: $LaNiO_{3-\delta} > LaCoO_{3-\delta} > LaCrO_{3-\delta} > LaFeO_{3-\delta}$. It indicates that $LaNiO_{3-\delta}$ has the optimum oxygen desorption performance among the above B-site-substituted $LaBO_{3-\delta}$ perovskite. The oxygen desorption amount for $LaNiO_{3-\delta}$ is about 13 ml O_2 /g×perovskite.

Effect of metal oxide supported perovskite oxygen carriers on oxygen desorption performance

The performance of metal oxide supported $BaCoO_{3-\delta}$ oxygen carriers was studied in the fixed-bed reaction. The absorption and desorption temperature are 800 °C and 850 °C respectively.

Its performance was compared with the pure $BaCoO_{3-\delta}$ oxygen carriers. Comparison of oxygen desorption curves and oxygen desorption amount of pure $BaCoO_{3-\delta}$, $BaCoO_{3-\delta}/CeO_2$ (BCC), $BaCoO_{3-\delta}/Al_2O_3$ (BCA) and $BaCoO_{3-\delta}/ZrO_2$ (BCZ) are shown in Fig. 3 and Fig. 4. Results showed that the order of oxygen production amount was as follows: BCC > BC > BCZ > BCA. That is to say, BCC perovskite has the improved oxygen

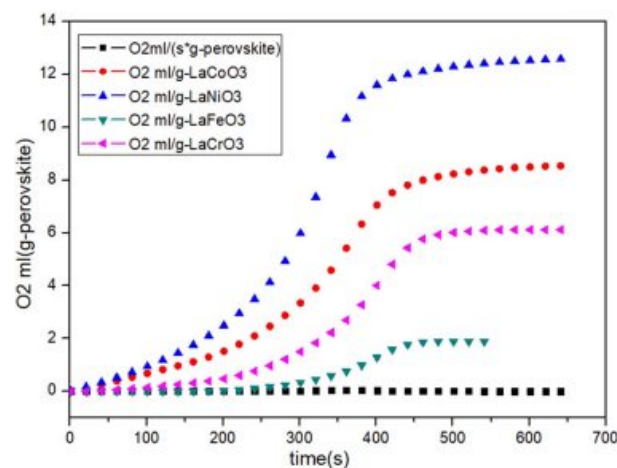


Fig. 2. Oxygen desorption curves for $LaBO_{3-\delta}$ (B=Sr, Ba, Mg, Ca).

desorption performance. On the other hand, the Al_2O_3 and ZrO_2 reduced the oxygen desorption property of $BaCoO_{3-\delta}$ oxygen carrier. The results showed that CeO_2 -supported perovskite has better oxygen production performance in the desorption process. As an oxygen storage material, CeO_2 exhibits high oxygen mobility and oxygen capacity at high temperatures. The lattice oxygen in CeO_2 can be supplied to perovskites in the high temperature process [22-24]. Therefore, CeO_2 is an excellent support material for oxygen carriers, which can enhance the performance of $BaCoO_{3-\delta}$ nanoparticles.

Effects of H₂O regeneration gas on oxygen desorption performance and cyclic performance

Main feature of this type of perovskites is that they can adsorb O_2 from air at high temperature to restore its perovskite structure. In order to study the self-recovery ability of perovskite carriers, water vapor and air are chosen to compare their recycling regeneration capacity. Fig. 5, Fig. 6, Fig. 7 and Fig. 8 show the cyclic performance of pure $BaCoO_{3-\delta}$ and supported

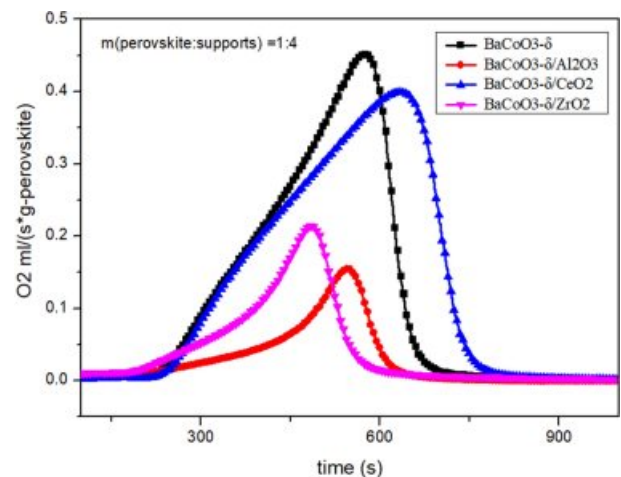


Fig. 3. Comparison of oxygen desorption curves for pure and supported $BaCoO_{3-\delta}$.

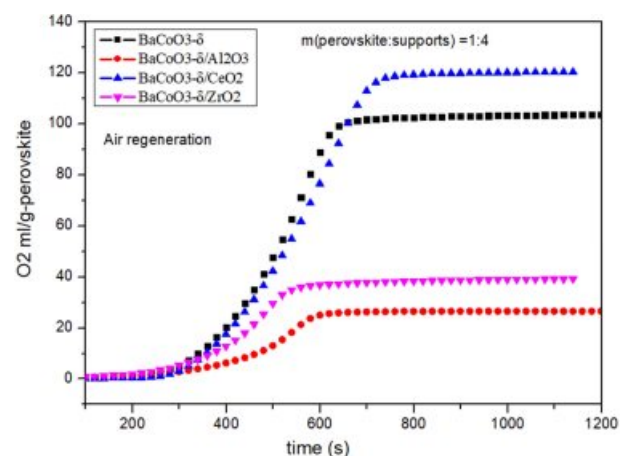


Fig. 4. Comparison of oxygen desorption amount of pure and supported $BaCoO_{3-\delta}$.

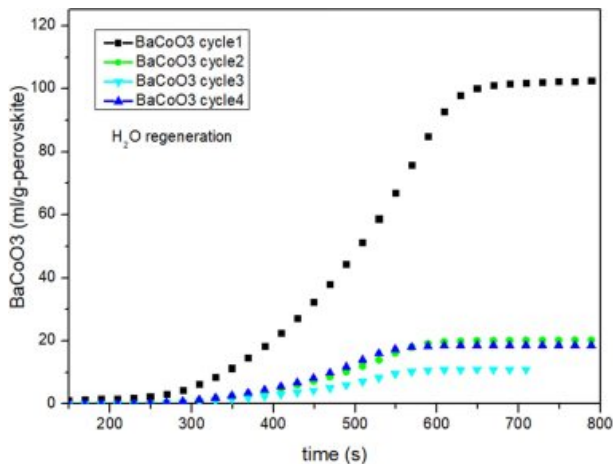


Fig. 5. Cyclic performance of pure BaCoO_{3-δ} (H₂O as regeneration adsorbent).

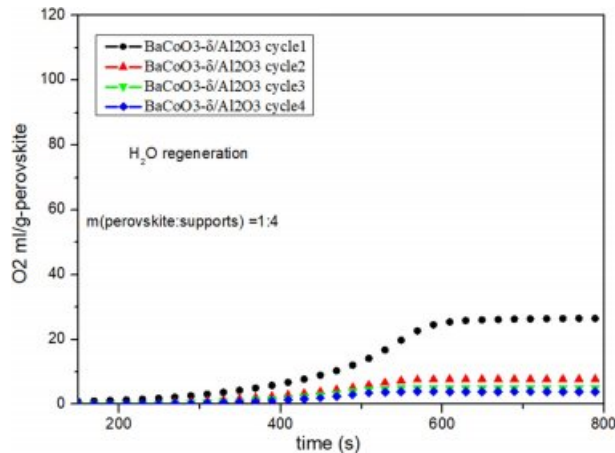


Fig. 8. Cyclic performance of BaCoO_{3-δ}/Al₂O₃ (H₂O as regeneration adsorbent).

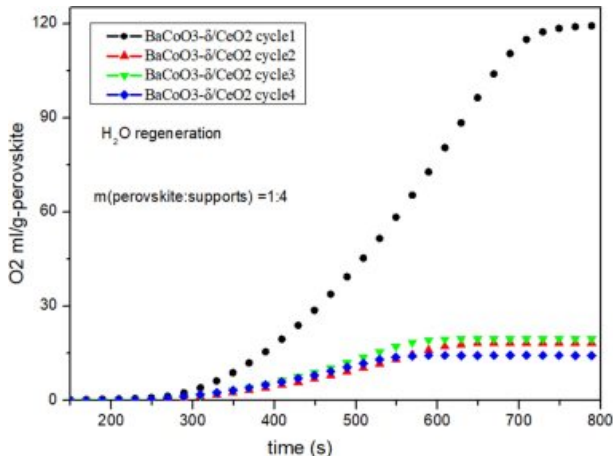


Fig. 6. Cyclic performance of BaCoO_{3-δ}/CeO₂ (H₂O as regeneration adsorbent).

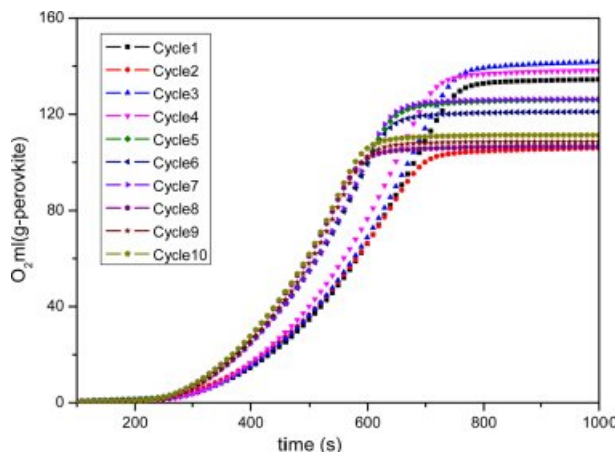


Fig. 9. Long-term testing of BaCoO_{3-δ}/CeO₂ oxygen carrier.

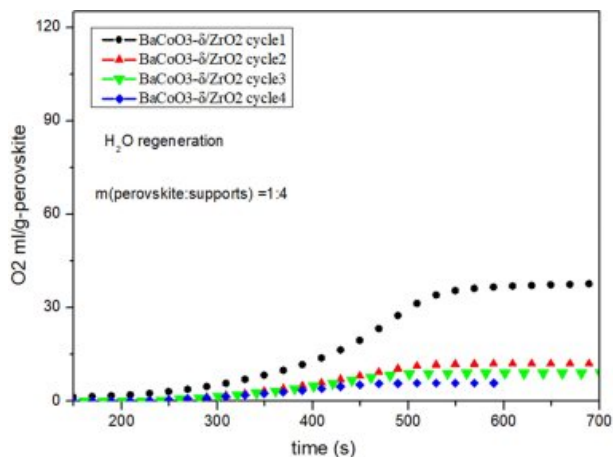


Fig. 7. Cyclic performance of BaCoO_{3-δ}/ZrO₂ (H₂O as regeneration adsorbent).

BaCoO_{3-δ} oxygen carrier under the H₂O instead of Air as regeneration gas conditions. Results show that all the perovskite oxygen carriers have good oxygen desorption

performance in the first cycle. However there is a significant drop during cycle 2 to cycle 4 for all the samples. It is indicated that H₂O as regeneration adsorbent does not appropriate for perovskite recovery.

Cyclic performance

Stability is a key parameter for the performance of oxygen carriers, providing a stable O₂/CO₂ recycle gas for oxyfuel combustion applications. This work evaluated the stability of the proposed BaCoO_{3-δ}/CeO₂ perovskite oxygen carrier and applied it for 10-cycles long-term testing. Fig. 9 and Fig. 10 shows the cyclic capacity of BaCoO_{3-δ}/CeO₂ perovskite oxygen carrier. It indicates that the oxygen desorption performance does not show an obvious decrease during the 1-7 cycles. After cycle 7, there is a litter decrease of the oxygen desorption amount for BaCoO_{3-δ}/CeO₂. The oxygen desorption amount of BaCoO_{3-δ}/CeO₂ could still achieve 110 ml/g sample after 10 cycles. Therefore, the novel perovskite-type oxygen carrier BaCoO_{3-δ}/CeO₂ has excellent regeneration capacity in cyclic use, which is very important for practical application.

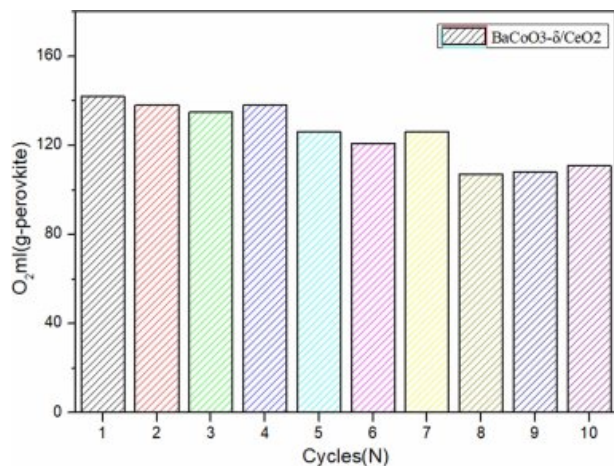


Fig. 10. Comparison of cyclic oxygen desorption amount of BaCoO_{3-δ}/CeO₂ oxygen carrier.

Conclusions

In this study, different LaBO_{3-δ} (B=Co, Ni, Fe, Cr) and metal oxide (CeO₂, Al₂O₃, ZrO₂) supported BaCoO_{3-δ} perovskites have been successfully prepared by the EDTA sol-gel method and applied for oxygen production. Results show that B-site total substitution has significant effect on oxygen desorption properties of LaBO_{3-δ}. LaNiO_{3-δ} has the optimum oxygen desorption performance among the B-site-substituted LaBO_{3-δ} perovskite. Effects of H₂O regeneration gas on oxygen desorption performance and cyclic performance indicated that H₂O as regeneration adsorbent comparing to air does not appropriate for perovskite recovery. CeO₂ supported perovskite featured better oxygen production performance. Furthermore, BaCoO_{3-δ}/CeO₂ exhibits an excellent regeneration capacity in cyclic use which is very important for practical application.

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