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# Different oxidation routes for lattice oxygen recovery of double-perovskite type oxides LaSrFeCoO<sub>6</sub> as oxygen carriers for chemical looping steam methane reforming

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## ABSTRACT

Double-perovskite type oxide LaSrFeCoO<sub>6</sub>(LSFCO) was used as oxygen carrier for chemical looping steam methane reforming (CL-SMR) due to its unique structure and reactivity. Two different oxidation routes, steam-oxidation and steam-air-stepwise-oxidation, were applied to investigate the recovery behaviors of the lattice oxygen in the oxygen carrier. The characterizations of the oxide were determined by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) and scanning electron microscopy (SEM). The fresh sample LSFCO exhibits a monocrystalline perovskite structure with cubic symmetry and high crystallinity, except for a little impurity phase due to the antisite defect of Fe/Co disorder. The deconvolution distribution of XPS patterns indicated that Co, and Fe are predominantly in an oxidized state (Fe<sup>3+</sup> and Fe<sup>2+</sup>) and (Co<sup>2+</sup> and Co<sup>3+</sup>), while O 1s exists at three species of lattice oxygen, chemisorbed oxygen and physical adsorbed oxygen. The double perovskite structure and chemical composition recover to the original state after the steam and air oxidation, while the Co ion cannot incorporate into the double perovskite structure and thus form the CoO just via individual steam oxidation. In comparison to the two different oxidation routes, the sample obtained by steam-oxidation exhibits even higher CH<sub>4</sub> conversion, CO and H<sub>2</sub> selectivity and stronger hydrogen generation capacity.

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## 1. Introduction

As a subclass of perovskite-type oxides ABO<sub>3</sub>, the double perovskite-type oxide AA'BB'O<sub>6</sub> have attracted more and more attentions as magnetic materials [1], superconducting materials [2], and catalytic materials [3–5], due to its unique structure and multiple properties. In the double perovskite-type A'A''B''O<sub>6</sub> structure, B'–O<sub>6</sub> and B''–O<sub>6</sub> octahedras are arranged alternately by the way of corner-sharing with A cations occupy the voids between the octahedral [6]. The sequence of B'–O–B'' chain is formed by B'

and B'' cations in an ideal double perovskite-type structure. While an order-reduced or disordered state is associated with a random distribution of B'–O–B', B'–O–B'' or B''–O–B'' chains [7]. It is generally believed that the catalytic activity of double perovskite-type oxide is mainly decided by the B-site cations, while the A-site cations play a role in the controlling of valence state of B-site metals and stabilizing the structure, simultaneously causing the lattice defects [8]. Therefore the most interesting phenomenon in double perovskite-type oxide is the interaction and synergistic effects between the B' and B'' cations. The catalytic activities of double perovskite-type oxides can be effectively improved through the synergy and coordination of the metals in the special structure and the different configurations and exchange interactions between A'/A'' and B'/B'' metals provide an extensive modeling space for researchers.

At present, chemical looping steam methane reforming (CL-SMR, as shown in Fig. 1) technology is mainly concentrated on the

*Abbreviations:* LSFCO, LaSrFeCoO<sub>6</sub>; CL-SMR, chemical looping steam methane reforming; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy; H<sub>2</sub>-TPR, hydrogen temperature-programmed reduction; SEM, scanning electron microscopy; LSFCO-S, reacted sample after CH<sub>4</sub>-H<sub>2</sub>O cycle; LSFCO-A, reacted sample after CH<sub>4</sub>-H<sub>2</sub>O-air cycle.

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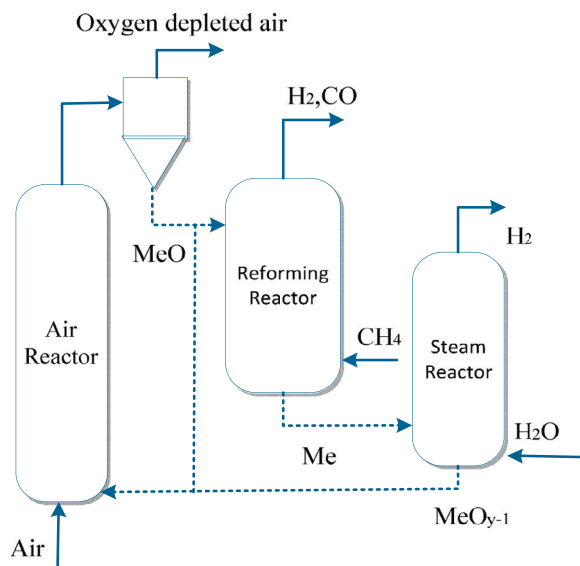


Fig. 1. CL-SMR for syngas and hydrogen production.

finding of excellent oxygen carriers with high methane conversion, high syngas selectivity, high sintering resistance and good activity for water splitting to produce hydrogen. In the CL-SMR process, methane is partially oxidized to syngas by the lattice oxygen of the oxygen carrier in the reformer reactor ( $M_xO_y + CH_4 \rightarrow M_xO_{y-\delta_1-\delta_2} + (2H_2 + CO)$ ), and the reduced oxygen carrier is oxidized by steam to recover oxygen and simultaneously to produce hydrogen in the steam reactor ( $M_xO_{y-\delta_1-\delta_2} + H_2O \rightarrow M_xO_{y-\delta_1} + H_2$ ). Usually, an air oxidation stage is needed if the oxygen carrier cannot completely recover oxygen by steam oxidation ( $M_xO_{y-\delta_1} + O_2 \rightarrow M_xO_y$ ) [9–11]. Through this process, not only syngas was obtained, the environmental friendly energy carrier hydrogen also can be produced via two steps, without requiring additional gas treatments such as reforming or shifting and separation processes. In previous researches, various metals [12,13], complex metals [14,15], perovskite oxides [16–18] or double perovskite-type oxides [5] had been used as catalysts for methane conversion. Results showed that perovskite-type oxides exhibited excellent performance with high catalytic activity and stability. Various substitutions or doping of perovskite-type oxides are exploited to satisfy the requests for various needs. As mentioned above, double perovskite-type oxide is different from the single perovskite-type oxide with special  $B'-O-B''$  or  $B''-O-B'$  chains. As far as we know, there is no report dealing with the catalytic performance of double perovskite-type oxide for chemical looping steam methane reforming, especially from the points of both chemical reforming of methane and water splitting. Also the cyclic reactivity of double perovskite-type oxide for oxygen delivery has no research.

Generally, there are two kinds of oxygen species in the double perovskite-type oxide. One is the adsorbed oxygen that related to the defect oxides, or surface molecular oxygen with low coordination, which is beneficial to the complete oxidation of  $CH_4$  to produce  $CO_2$  and  $H_2O$ . Another is the lattice oxygen that is conducive to the partial oxidation of  $CH_4$  for the generation of syngas. As an oxidizing agent, steam with lower activity just can guarantee the partial or total recovery of lattice oxygen. Therefore, steam and air have been used successively to guarantee the recovery of lattice oxygen and adsorbed oxygen in the CL-SMR process. Galinsky [19] used perovskite  $CaMn_{1-x}B_xO_{3-\delta}$  as oxygen carriers for chemical looping with oxygen uncoupling. After the reduction step, air

is used to regenerate the oxygen carrier while producing heat for power generation. Neal [20] reported that the perovskite support such as  $La_{0.8}Sr_{0.2}FeO_3$  (LSF) can enhance the activity of iron oxide for methane conversion by nearly two orders of magnitude. After the partial oxidation of methane using the lattice oxygen in the  $MeO_x@LSF$ , the lattice oxygen depleted from the redox catalyst is subsequently regenerated with air in the catalyst regenerator. According to Zhu who used Ce–Fe oxides as oxygen carrier [21], the lattice oxygen of Ce–Fe oxides can be recovered by steam oxidation to the original states; while the high-activity adsorbed oxygen and parts of metal ions are unable to be recovered. The elimination of adsorbed oxygen has a positive effect in the CL-SMR for the generation of target product of syngas. Their results showed that the decrease of  $CH_4$  conversion and increase of CO and  $H_2$  selectivity were just because of the removal of adsorbed oxygen. And the hydrogen generation capacity in the steam oxidation stage had no obvious decline. But the degree of the recovery of lattice oxygen is not discussed.

In the present work, double perovskite-type metal oxide  $LaSrFeCoO_6$  (LSFCO) made by micro-emulsion method was used as oxygen carrier for the CL-SMR process. The reactivities of  $LaSrFeCoO_6$  were investigated in a fixed-bed reactor and the different oxidation routes of steam-oxidation and steam-air stepwise-oxidation were performed to discuss the lattice oxygen recovery process. The fresh and reacted oxides were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM),  $H_2$  temperature-programmed reduction ( $H_2$ -TPR) techniques, and X-ray photoelectron spectroscopy (XPS), attempting to correlate the activity, structure and surface properties.

## 2. Experimental

### 2.1. Synthesis of the double perovskite-type oxide $LaSrFeCoO_6$

Micro-emulsion method was used to prepare the double perovskite-type oxide LSFCO. The required amounts of  $La(NO_3)_3 \cdot 6H_2O$ ,  $N_2O_6Sr$ ,  $CoN_2O_6 \cdot 6H_2O$  and  $Fe(NO_3)_3 \cdot 9H_2O$  were weighed at a desired stoichiometric ratio and dissolved in deionized water. Then the surfactant Tritonx-100, cosurfactant n-butyl alcohol and oil phase cyclohexane were added to make a mixture of solution A. Meanwhile, the same ratio of surfactant Tritonx-100, cosurfactant n-butyl alcohol and oil phase cyclohexane were added into  $(NH_4)_2CO_3-NH_4OH$  to make a mixture of solution B. After that, the solution B was slowly dripped into solution A to form sediment under a water bath at  $50^\circ C$ . The sediment was allowed to settle for 2 h and filtered by the suction funnel. Then two times of ethanol and deionized water were used to wash the sediment. After that, the sediment was dried overnight in a convection oven at  $110^\circ C$ . Finally, the as-prepared precursor was thermally decomposed at  $500^\circ C$  for 2 h and calcined at  $1000^\circ C$  for 6 h. The resulting product was grounded to obtain the fresh double perovskite-type oxides of LSFCO.

### 2.2. Characterization

The surface morphology and characteristics of the samples were performed by scanning electron microscopy with energy dispersive X-ray (SEM/EDX) on a Hitachi S4800 instruments. The crystal phases of the oxides were identified by XRD in a Japan Science D/max-R diffractometer with  $Cu K\alpha$  radiation ( $\lambda = 0.15406$  nm), operating voltage of 40 kV and current of 40 mA, and the diffraction angle ( $2\theta$ ) was scanned from  $10^\circ$  to  $80^\circ$ . The hydrogen-temperature programmed reduction ( $H_2$ -TPR) experiments were conducted in 5.0 vol%  $H_2$  balanced with helium at a flow rate of 60 mL/min from room temperature to  $800^\circ C$  with a heating rate of  $10^\circ C/min$ . X-ray photoelectron spectroscopy (XPS) was used to probe the near-

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