

# Synergistic improvements in stability and performance of the double perovskite-type oxides $\text{La}_{2-x}\text{Sr}_x\text{FeCoO}_6$ for chemical looping steam methane reforming



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## HIGHLIGHTS

- Double perovskites exhibit high reactivity and stability for CL-SMR.
- Substitution of A site metal obviously affects the valence states of B/B' sites.
- The metal cations and the oxygen vacancies coordinately control the reactivity.
- $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeCoO}_6$  shows the best capacity for oxygen transport and steam splitting.

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## ABSTRACT

Chemical looping steam methane reforming (CL-SMR) is a potential route to efficiently co-produce syngas and hydrogen. Development of oxygen carrier with high activity, good recyclability, strong resistance to carbon deposition and excellence capacity for steam splitting is highly desired for this process. The article investigated a novel and unique structure of double perovskite-type oxides  $\text{La}_{1-x}\text{Sr}_x\text{FeCoO}_6$  ( $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$ ) as oxygen carrier. XRD, XPS and  $\text{H}_2$ -TPR technologies were adopted to characterize the physical and chemical properties of them. Meanwhile, isothermal reactions and cyclic redox reactions were carried out in a fixed-bed reactor to determine the influences of Sr-substitution on the reactivity of  $\text{La}_{1-x}\text{Sr}_x\text{FeCoO}_6$ . XRD results confirmed the formation of double perovskite crystal structure for all the samples, while substitution of Sr induced a certain degree of Fe/Co disorder generating oxygen vacancies and/or higher oxidation states of metal cations. Synergistic interactions between surface metal ions, such as  $\text{Fe}^{4+}/\text{Fe}^{5+}$  with  $\text{Co}^{3+}$  which were detected by XPS, strongly enhance the reducibility of oxygen carriers. Three zones including total oxidation of methane by surface oxygen, partial oxidation of methane by lattice oxygen and carbon deposition were divided. Among the six samples with different substitution of Sr,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeCoO}_6$  exhibited the best oxygen transport ability, thermal stability, as well as capacity for hydrogen generation. A stable  $\text{CH}_4$  conversion at  $\sim 90\%$  with desired  $\text{H}_2/\text{CO}$  ratio at 2.0–2.5 in the methane reduction stage, and an average hydrogen yield at  $\sim 5.9$  mmol/g oxygen carrier with  $\sim 93.8\%$  of hydrogen concentration in the steam oxidation stage were obtained during twenty successive redox reactions, which made them very attractive for the purpose of chemical looping partial oxidation of carbon fuel in real applications.

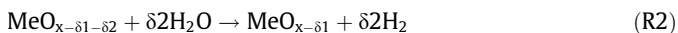
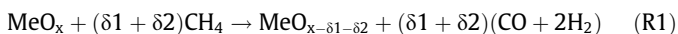
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## 1. Introduction

Chemical looping steam methane reforming (CL-SMR) is viewed as one of the most important and promising technologies for syngas and hydrogen co-production, the schematic diagram of that is shown in Fig. 1. Usually, three steps are included in this technology via using a metal oxide ( $\text{MeO}_x$ ) as oxygen carrier to provide the required oxygen and energy, which can be described as follows: (I) An oxygen carrier ( $\text{MeO}_x$ ) is partially reduced by methane to produce syngas in the fuel reactor (R1). (II) Then the reduced oxygen carrier ( $\text{MeO}_{x-\delta_1-\delta_2}$ ) recovers most of lattice oxygen by steam oxidation to an intermediate state ( $\text{MeO}_{x-\delta_1}$ ) and simultaneously produces  $\text{H}_2$  (R2). (III) Finally, the intermediate state oxygen carrier ( $\text{MeO}_{x-\delta_1}$ ) is oxidized to its initial state ( $\text{MeO}_x$ ) via air oxidation (R3) [1]. Compared to the traditional steam methane reforming (SMR), CL-SMR process produces syngas with a  $\text{H}_2/\text{CO}$  molar ratio of 2.0 which can be used directly for the subsequent chemical utilizations such as Fischer-Tropsch synthesis without the downstream refinement. Besides, another superiority of CL-SMR technology is that the pure hydrogen can be obtained exiting the steam reactor, avoiding the additional gas treatments such as reforming and separation processes [2]. Meanwhile, the oxygen carrier acts as an oxygen delivery, heat carrier and catalyst in the chemical looping cycling process [3], eliminating the risk of explosion owing to the premixing of  $\text{CH}_4$  with air. Therefore, a high quality of syngas and hydrogen can be produced simultaneously through two steps:



One of the most significant challenges in CL-SMR process is the identification of suitable and effective oxygen carrier with high methane conversion, high syngas selectivity, effectively sintering resistance and good activity for steam splitting. Meanwhile, it also should be able to undergo multicycle redox reactions at high operating temperatures. Previously, there were a large number of

works on the performances of oxygen carriers for chemical looping process, including Fe [4,5], Cu [6,7], Ni [8–10], Mn [11], Ce [12–14] based oxides and various mixed oxides [15–18]. However, such oxides exhibited many challenges limiting their commercial applications, such as high cost and high agglomeration for Cu, high toxic nature for Ni, difficulty of regeneration and low reactivity for Mn and low selectivity for Fe. Other than these oxides, perovskite-type oxides with general formula of  $\text{ABO}_3$  are receiving more and more attentions and shown to be effective as oxygen carriers for chemical-looping process with good redox properties [19–23]. It is known as a good catalyst with high activity, high thermal stability and good mechanical property, where A-site is usually an alkaline earth metal and B-site is a transition metal ion. It can serve not only as lattice oxygen carrier but also as catalyst for  $\text{CH}_4$  activation [24]. Zheng et al. [25] prepared  $\text{LaFeO}_3$  supported  $\text{CeO}_2$  for chemical-looping reforming of methane. They found that the oxygen mobility and reactivity for methane oxidation of 10% $\text{CeO}_2/\text{LaFeO}_3$  are strongly improved by the abundant oxygen vacancies on the mixed oxides which are induced by the coexistence of  $\text{Ce}^{3+}$  and  $\text{Fe}^{2+}$  ions. But the removal of the most reactive oxygen mainly occurred at low temperatures for Ce-based oxygen carrier. Arya et al. [26] synthesized Fe-Mn and Fe-Co oxides, perovskites  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$  as oxygen carriers for chemical looping with oxygen uncoupling. They found that La containing perovskite supports could enhance the properties of oxygen donation in Mn-Fe and Co-Fe oxides. Galinsky [27] used  $\text{CaMn}_{1-x}\text{B}_x\text{O}_{3-\delta}$  ( $\text{B} = \text{Al}, \text{V}, \text{Fe}, \text{Co}$  and  $\text{Ni}$ ) as oxygen carriers for chemical looping process and investigated the effects of various B-site dopants for  $\text{CaMnO}_3$  based oxygen carrier.  $\text{CaMn}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$  exhibited notable redox activity and superior activity. But due to the unstable properties of Mn ion, the substitution of Mn in perovskite-type oxide is always challenging. In our previous research [2], perovskites  $\text{LaFe}_{1-x}\text{Co}_x\text{O}_3$  were used as oxygen carriers for methane partial oxidation. Suitable substitution value of Co ion in B-site could increase the amount of adsorbed oxygen and decrease the  $\text{CH}_4$  decomposition in the reaction of partial oxidation of methane. All these results showed that the B site metal in perovskite type oxide is the dominating active site and plays the most important role during catalysis. But more recently, more and more researches have been focusing on the substitution of A-site metals in perovskite-type oxides. Results showed that metal in A-site could affect the oxygen vacancies and valence states of B-site elements, consequently improving the reactivity although it's non-catalytic. Among these researches, substituted perovskites derived from  $\text{LaFeO}_3$ , e.g. partial substitution of  $\text{La}^{3+}$  by  $\text{Sr}^{2+}$  have been extensively studied. Taylor [28] used  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  as oxygen storage materials (OSMs) for chemical-looping natural gas combustion and methane reforming. Results showed that  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  were promising as OSMs for methane reforming reactions due to their high selectivity and good stability. Li and his co-workers [29–31] investigated  $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$  (LSF) and LSF supported core-shell  $\text{Fe}_2\text{O}_3@\text{LSF}$  for methane partial oxidation. They found that the high activity of oxides is largely attributed to the enhanced  $\text{O}^{2-}$  and the electron transports facilitated by the LSF support. He et al. [32] found that substitution of Sr for La in perovskite with a proper degree of 0.3–0.5 would inhibit methane decomposition and enhance the reactivity of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  in the methane partial reduction process. Galinsky [33] investigated the effects of A-site dopants of Sr and Ba on  $\text{CaMnO}_3$  based oxygen for chemical looping oxygen uncoupling. Sr doped oxide  $\text{Ca}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$  exhibited excellent stability in 100 isothermal redox cycles. But up to now, carbon deposition during the methane reduction reaction at high temperature is still an insurmountable problem in methane reduction, which may lead to the challenges such as oxygen carrier deactivation, low selectivity of syngas, and low purity of hydrogen.

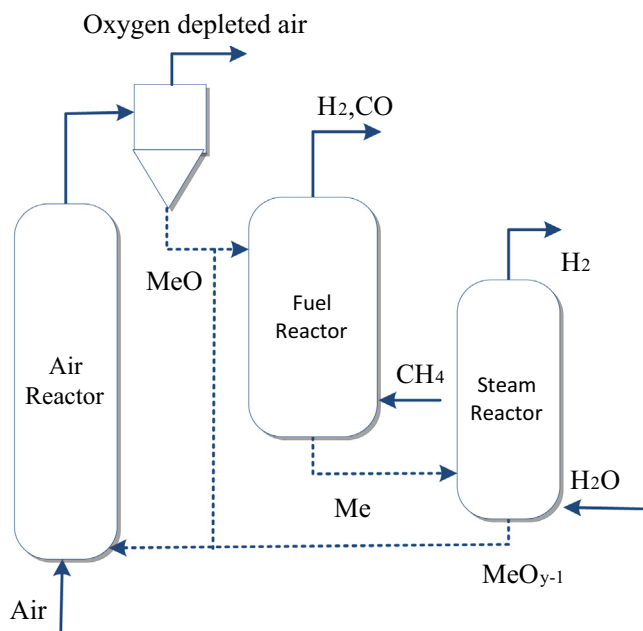


Fig. 1. CL-SMR for syngas and hydrogen production.

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