

Lanthanide-Based Perovskite Enhance Syngas Production for a Low-Carbon Future through Chemical Looping Dry Reforming of Methane

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ABSTRACT

Chemical looping dry reforming of methane (CL-DRM) has emerged as a promising approach, providing a pathway to mitigate greenhouse gas emissions by simultaneously converting methane and carbon dioxide into valuable syngas. In this study, we focus on the utilization of lanthanide-based perovskite oxygen carriers to enhance the performance of CL-DRM for syngas production. We investigate the influence of various operational parameters, including temperature, reactant gas ratio, and oxygen carrier composition, on the reactivity performance. The results reveal that the $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ oxygen carrier exhibited excellent activity in promoting the CL-DRM reactivity. Furthermore, this oxygen carrier showed high selectivity towards syngas production (CO selectivity > 99%, $\text{H}_2/\text{CO}=2$). These findings suggest that $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ perovskite oxygen carriers hold great potential for sustainable syngas production, contributing to the transition to a low-carbon future.

Keywords: chemical looping, dry reforming of methane, syngas, perovskite

NONMENCLATURE

Abbreviations

CL-DRM	Chemical looping dry reforming of methane
WMO	World Meteorological Organization
XRD	X-ray diffraction

1. INTRODUCTION

The World Meteorological Organization (WMO) released the latest edition of its Greenhouse Gas

Bulletin, pointing out that the concentration of carbon dioxide and methane in 2021 will be 149% and 262% of the pre-industrial level in 1750, respectively[1]. Urgent action is needed to reduce greenhouse gas emissions and prevent further increases in global temperatures in the future. Greenhouse gases in the atmosphere can be reduced by capturing CO_2 before, during and after the combustion of fossil fuels[2–4], as well as CH_4 from petrochemical, biogas, landfill gas, flue gas and direct air capture sources[5–7]. The dry reforming of methane is further utilized to convert the captured greenhouse gas into syngas for the synthesis of downstream chemical raw materials[8–10]. Due to the endothermic nature of the dry reforming of methane, this conversion requires a suitable catalyst to induce the conversion. Nickel-based materials are favored because they are cheap and relatively abundant[11,12]. However, the inactivation caused by carbon deposition has hindered the commercial application of these catalysts[10,11,13–15]. The researchers developed a new method of chemical looping dry reforming of methane[16–18]. First, in a reduction reactor, CH_4 reacts with oxygen carriers to produce H_2 and CO . Then in the oxidation reactor, the incoming CO_2 restores the oxygen carrier and produces CO . This method avoids catalyst deactivation due to long-term catalysis. At the same time, the direct contact between CH_4 and CO_2 is avoided, and the synthesis gas selectivity is improved by inhibiting the reverse water gas conversion reaction[19–21]. As the oxygen transport medium of the redox cycle, the reactivity of the oxygen carrier determines the reaction performance of CL-DRM. The perovskite ABO_3 has attracted much attention due to its low reactive energy barrier and adjustable redox properties[18]. Among all kinds of perovskite oxides, LaFeO_3 perovskite, as a representative of perovskite metal oxides, has been widely studied in chemical

looping reactions due to its high oxygen storage capacity and strong lattice oxygen mobility[22,23]. Research further shows that the properties of LaFeO₃ can be further regulated by partial A or B cation substitution[24–27].

In this study, a sol-gel method is used to synthesize a B-doped LaFe_{0.8}Al_{0.2}O₃ oxygen carrier for CL-DRM. By optimizing the reaction time, temperature and other parameters, the goal of generating a synthesis gas with high purity and ideal H₂/CO ratio is achieved.

2. METHODOLOGY

2.1 Synthesis of oxygen carriers

LaFe_{0.8}Al_{0.2}O₃ oxygen carrier was prepared by sol-gel method[28]. The precursor nitrate solution, including La(NO₃)₃·6H₂O, Fe(NO₃)₃·9H₂O and Al(NO₃)₃·9H₂O, was dissolved in deionized water according to the stoichiometric ratio. Later, citric acid was added to the solution at the ratio of citric acid: metal cation = 2.5. Then add ammonia water to make the pH of the solution = 7. The obtained solution was stirred at 80°C to slowly concentrate into a viscous gel. The resulting gel was placed in an oven at 150°C for 12 hours to obtain a dry solid nitrate mixture. It is then calcined in a Muffle furnace at 450°C for 4 hours to remove the organic matter and finally calcined in 1200°C air for 4 hours. After grinding, a fresh perovskite sample LaFe_{0.8}Al_{0.2}O₃ was obtained. The LaFeO₃ oxygen carrier used in the control group was also synthesized by the above method.

2.2 Experimental set

The CL-DRM was tested in a fixed-bed quartz tube reactor, as shown in Fig. 1. Each test was loaded with a 200 mg oxygen carrier and the reaction flow rate was fixed at 30 mL·min⁻¹. In an Ar atmosphere, the temperature is heated to 900°C at a heating rate of 10 °C·min⁻¹. After the temperature stabilized for 10 minutes, 10% CH₄ in Ar flow was injected into the reduction step. Then, 10% CO₂ in the Ar stream was introduced in the oxidation step. To avoid mixing of reactants and reaction products, Ar purging was used for 10 min between reduction and oxidation reactions. The outlet uses mass spectrometry (Pfeiffer OmniStar) to monitor changes in gas concentration, while the cyclic reaction products are collected with airbags and quantitatively analyzed using chromatography (Agilent 8890). The reactant conversion and H₂/CO ratio are calculated using the following formula:

$$X_{CH_4} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \quad (1)$$

$$S_{CO} = \frac{F_{CO,out}}{F_{CO,out} + F_{CO_2,out}} \quad (2)$$

$$\frac{H_2}{CO} = \frac{F_{H_2,out}}{F_{CO,out}} \quad (3)$$

where F stands for molar flow rate.

Similarly, the average CO₂ conversion during the CO₂ oxidation step can be calculated using the following equations:

$$X_{CO_2} = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \quad (4)$$

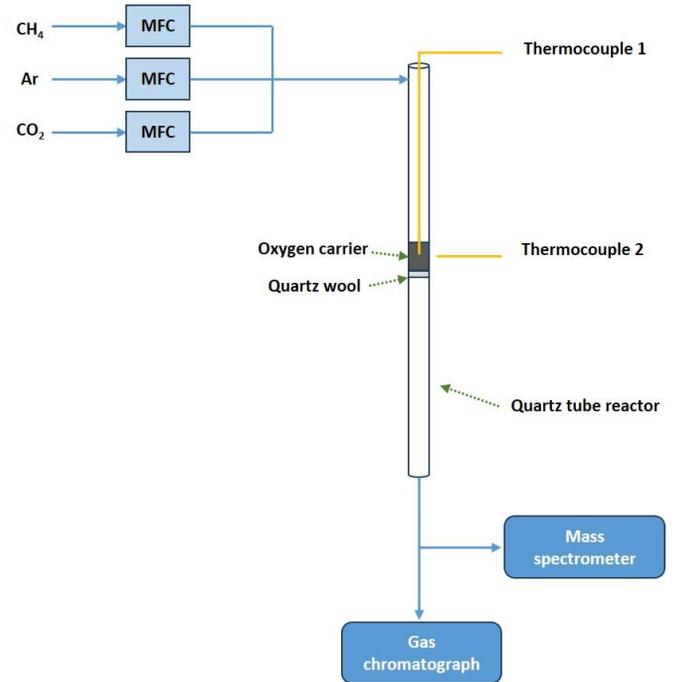


Fig. 1. The diagram of experimental system.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction of oxygen carriers

The phase structure and composition analysis were performed using an X-ray diffractometer (XRD, Bruker X). Fig. 2 shows the XRD pattern of the prepared fresh oxygen carriers. The XRD diffractograms recorded on the LaFeO₃ sample are consistent with the ICDD No.01-088-0641, and the doped LaFe_{0.8}Al_{0.2}O₃ is consistent with the characteristic peak of LaFeO₃. No impurities such as Fe₂O₃, La₂O₃, Al₂O₃ and other single metal oxides exist, it can be considered that the prepared oxygen carrier has good crystallization.

3.2 The effect of reaction time

To determine the maximum reaction capacity of oxygen carrier and raw gas, methane is injected for 4, 5, and 6 min respectively, which is equivalent to 12, 15, and 18 mL CH₄. The oxidation step entry time is consistent with the reduction step time. As can be seen from Fig. 3(a), when methane is introduced into the reduction step for

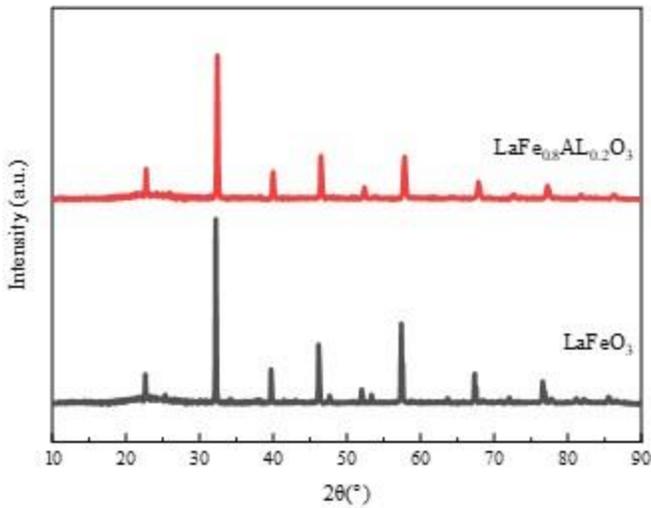


Fig. 2 XRD patterns of fresh oxygen carriers.

5 min, CO_2 is detected at the exit for a short period at the beginning of the reaction. And then it is wholly a partial oxidation reaction that generates CO and H_2 . In the oxidation step, only the oxidation product CO is produced. According to the chromatographic quantitative analysis as shown in Fig. 3 (b), with the extension of reaction time, the increased H_2/CO ratio indicates the occurrence of methane cracking reaction. Under the condition of a reaction time of 5 min, the conversion rate of methane is greater than 90%, and an ideal proportion of syngas is generated. In all cases, the selectivity of CO is greater than 99%, indicating that $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ has high selectivity for methane reaction.

It is also noted that the conversion rate of CO_2 in the oxidation step is lower than that of CH_4 in the reduction step. This is because the incoming CO_2 is not only used to oxidize the oxygen carrier but also to remove the carbon deposits generated in the reduction step. After the above analysis, it is determined that the reaction time of the experiment was fixed at 5 min.

3.3 The effect of temperature

Fig. 4 shows the performance of $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ oxygen carrier for CL-DRM at different temperatures. The effect of reaction temperature on reaction performance is obvious. At 800 and 825°C, the reactivity of oxygen carriers is very low, and the complete and partial oxidation reactions of methane mainly occur. From 850 to 925°C, the reaction performance increased significantly. The methane conversion rate increased from 37.0% at 850°C to 95.9% at 925°C, and the CO selectivity remained near 100%. And the theoretical $\text{H}_2/\text{CO}=2$ synthesis gas is generated, which also indicates that the reaction is almost wholly methane partial oxidation. The directional conversion of methane to high-quality syngas is realized.

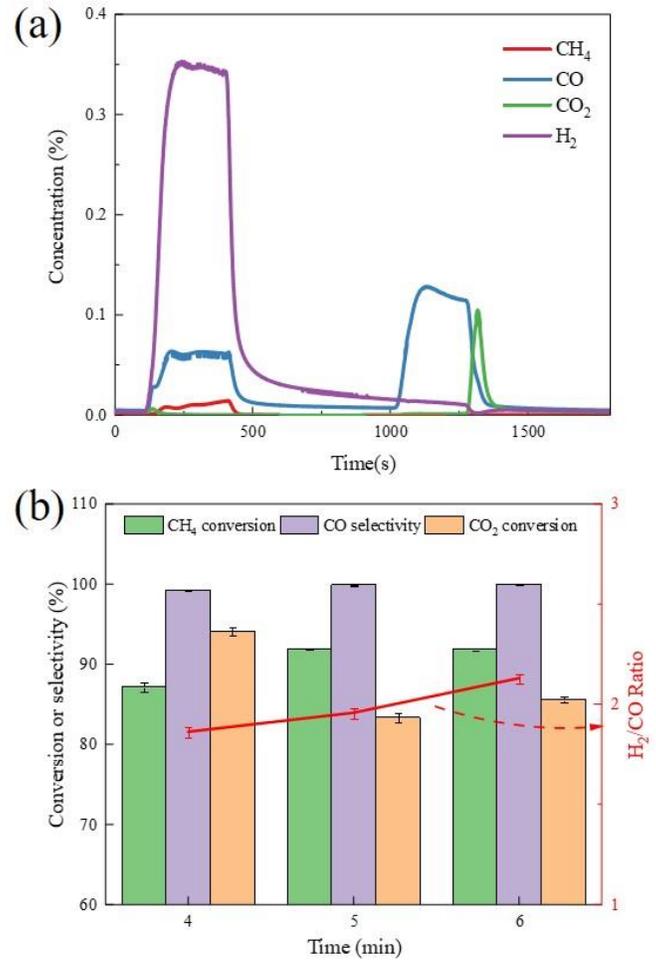


Fig. 3. (a) The outlet gas concentration under 5min reaction time. (b) Methane conversion /Carbon dioxide conversion, carbon monoxide selectivity and hydrogen/carbon monoxide ratio of different reaction time.

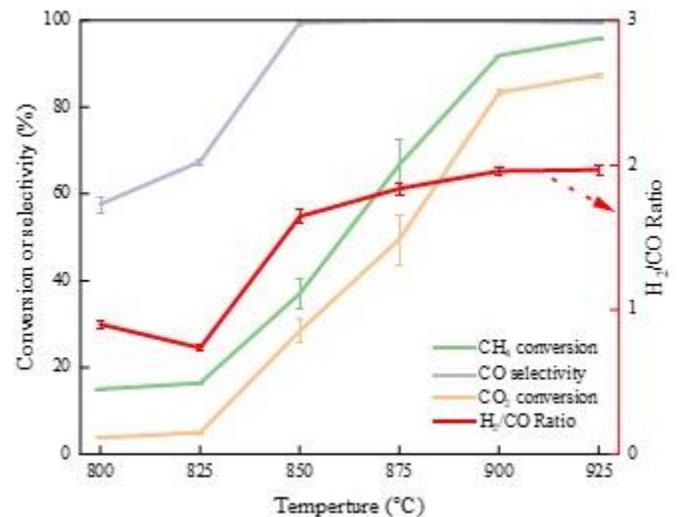


Fig. 4. Methane conversion /Carbon dioxide conversion, carbon monoxide selectivity and hydrogen/carbon monoxide ratio of different reaction temperatures.

3.4 The comparison between $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ and LaFeO_3

Fig. 5 compares the reaction performance of doped $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ with LaFeO_3 at 900°C . It can be seen from the concentration of the reaction outlet in Fig. 5 (a) that the outlet contains a large amount of methane. Fig. 5 (b) shows that the methane conversion rate of doped $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ is 10 times that of LaFeO_3 . Compared to LaFeO_3 's 91.0% CO selectivity, $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ achieves a CO selectivity of 99.9% and produces an ideal ratio of syngas. This shows that Al doping can greatly improve the performance of oxygen carriers.

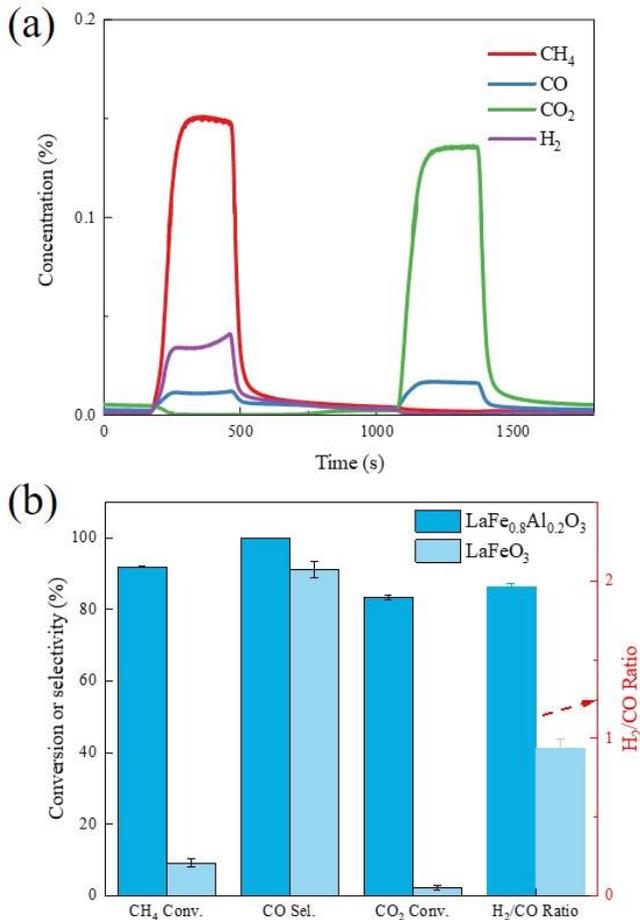


Fig. 5. (a) The outlet gas concentration of LaFeO_3 . (b) Methane conversion /Carbon dioxide conversion, carbon monoxide selectivity and hydrogen/carbon monoxide ratio of different oxygen carriers.

4. CONCLUSIONS

In this study, $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ perovskite oxygen carrier was synthesized by the sol-gel method, and its performance for CL-DRM was tested in a fixed bed reactor. The effect of reaction time and reaction temperature on reaction performance is tested, and the optimal reaction time of 5min is determined to achieve partial oxidation of methane. The reaction temperature also has a huge impact on the reaction type of methane.

At least above 850°C , partial oxidation of methane becomes the main reaction, which has high selectivity for CO. In all, the use of $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ perovskite oxygen carriers at a reaction temperature of 900°C achieves a methane conversion of 91.9%, a CO selectivity of nearly 100%, and the generation of an ideal ratio of syngas ($\text{H}_2/\text{CO}=2$) in the reduction step. In addition, the conversion of CO_2 to CO is also achieved in the oxidation step. In conclusion, this study achieves low-carbon conversion of methane and reuse of carbon dioxide through the CL-DRM. However, further stability test and scale-up studies are necessary to explore the commercial viability of the oxygen carrier for CL-DRM process.

ACKNOWLEDGEMENT

The authors would like to acknowledge the support by National Natural Science Foundation of China (NSFC) grant (No.52176026 and No. 52241601, No.51888103).

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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