

Chemical-looping methane hydrogen production performance of Cu, La, Ce modified $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carrier

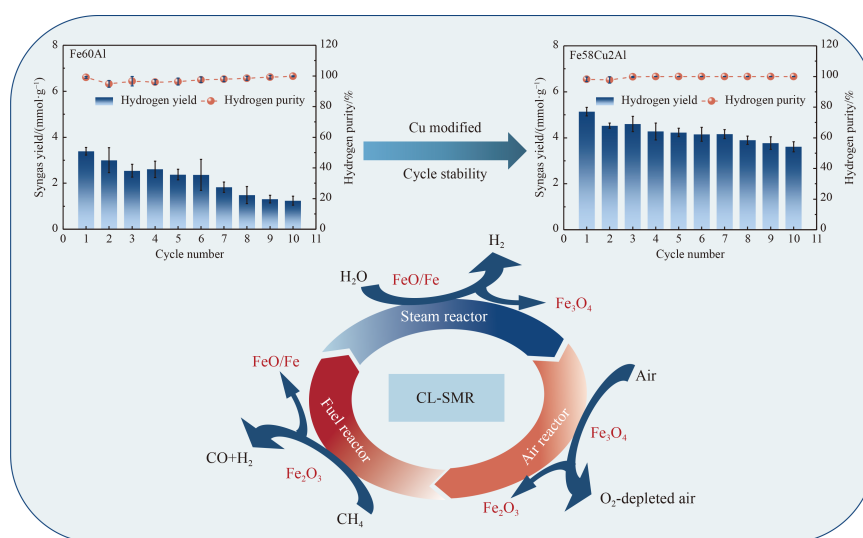
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Abstract: Chemical looping methane steam reforming (CL-MSR) has garnered significant attention owing to its ability to sequentially produce syngas with high selectivity and high-purity hydrogen through redox cycling. To overcome the limitations of single iron-based oxygen carriers, including poor cycling stability, low reactivity and susceptibility to sintering, this study employed a dip-coating method to modify $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carriers

by incorporating three distinct metal additives: Cu, La and Ce. The composite oxygen carriers were systematically characterized and evaluated under redox conditions to investigate the structure-activity relationships between the physicochemical properties, reactivity, and hydrogen production performance. Results revealed that the spinel-phase CuFe_2O_4 exhibited higher reactivity than the perovskite-phase LaFeO_3 and CeO_2 , promoting the deeper reduction of Fe_2O_3 . Fe58Cu2Al exhibited an oxygen storage capacity as high as 6.5 mmol/g. During the CH_4 reaction stage, Fe58Cu2Al achieved the highest oxygen loss of 12.1 g/100 g oxygen carrier, accompanied by a syngas yield of 5.15 mmol/g—1.33 times and 1.59 times greater than that of Fe60Al . In the hydrogen production stage, the 2% Cu-modified oxygen carrier demonstrated optimal performance, yielding 5.13 mmol/g of hydrogen, which was 1.51 times that of the pristine sample. Even after ten cycles, the H_2 yield remained at 3.61 mmol/g, surpassing the single-cycle output of the pristine sample and the H_2 purity consistently exceeded 98%.

Key words: chemical looping; iron-based oxygen carrier; metal promoter; hydrogen purity



Hydrogen is an important energy carrier and industrial feedstock with a high calorific value of 142 MJ/kg and zero carbon emissions during its utilization. It has extensive applications in crude oil refining, ammonia synthesis, methanol production, and metal casting, underscoring its essential role in clean energy technologies and the emerging

hydrogen economy^[1-2]. However, as a secondary energy source, hydrogen must be produced from other energy feedstocks^[3]. Currently, approximately 99% of hydrogen is derived from fossil fuels, with steam methane reforming (SMR) being the dominant method for large-scale industrial hydrogen production^[4-6]. SMR involves multiple steps

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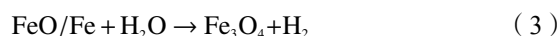
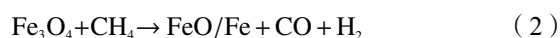
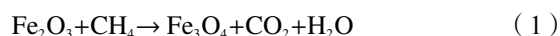
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including desulfurization, steam reforming, condensation, water-gas shift conversion, decarbonization, and pressure swing adsorption. Despite its technological maturity, SMR is still hampered by high complexity, high costs, significant energy consumption, and substantial carbon emissions, which constrain their long-term viability for hydrogen production^[7–8]. Consequently, there is an urgent need to develop cleaner, more efficient, and more sustainable hydrogen production technologies^[9]. Chemical looping steam methane reforming (CL-SMR) is a hydrogen production technology that enables the generation of high-quality syngas during the methane reduction stage and high-purity hydrogen in the steam oxidation stage. Characterized by a simplified process layout and low energy requirements, this approach enhances energy-conversion efficiency while reducing carbon emissions^[10–11]. A schematic of the process is illustrated in Figure 1. CL-SMR comprises three interrelated steps: methane reduction, steam oxidation, and air oxidation, mediated by metal oxides (oxygen carriers)^[12]. In the methane reduction stage, the oxygen carrier is reduced by methane to produce a high-quality syngas suitable for Fischer-Tropsch synthesis. In the steam oxidation stage, the oxygen carrier is oxidized by steam to yield high-purity hydrogen. And in the air oxidation stage, the oxygen carrier undergoes complete oxidation by anhydrous air before returning to the methane reduction stage to continue the cyclic reaction^[13–14]. As the core intermediate in CL-SMR, oxygen carriers still face challenges despite years of development because they exhibit low reactivity, limited hydrogen yield, low hydrogen purity, and poor cycling stability. Therefore, the development of non-toxic, low-cost oxygen carriers with high reactivity and cycle stability is critical for advancing CL-SMR technology. Over recent decades, researchers have investigated various metal oxides as oxygen carriers, such as Fe^[15–16], Cu^[17–18], Ni^[19–20], Mn^[21] and Co-based oxides^[22–23], as well as their mixed oxides^[24–25]. Among these, iron-based oxygen carriers are currently among the most predominant materials used in CL-SMR, owing to their low cost, environmental friendliness, high oxygen storage capacity, and favorable thermodynamic properties in reactions involving methane and steam^[26–27]. The reduction-oxidation cycle of iron-based oxygen carrier Fe₂O₃ in CL-SMR proceeds as follows: in the fuel reactor, Fe₂O₃ is reduced by CH₄ to Fe₃O₄ (Reaction 1), followed by

further reduction of Fe₃O₄ by CH₄ to FeO or Fe (Reaction 2). In the steam reactor, reduced FeO or Fe are reoxidized by high-temperature steam to produce hydrogen and regenerate Fe₃O₄, as shown in Reaction (3). Subsequently, Fe₃O₄ is completely oxidized back to Fe₂O₃ by air in the air reactor, as shown in Reaction (4), closing the chemical looping hydrogen production cycle.



However, pure Fe₂O₃ suffers from limitations such as low reactivity, tendency to carbon deposition, susceptibility to sintering at high temperatures, and poor cycle stability^[28]. To address these challenges, performance enhancement can be achieved by modifying the oxygen carrier through loading with inert supports or doping with other metal ions. Refractory materials such as Al₂O₃, ZrO₂, TiO₂, SiO₂, CeO₂ and MgAl₂O₄ are commonly used as inert supports for Fe₂O₃ to enhance its sintering resistance and improve cycling stability^[29–36]. Among these, Al₂O₃ is widely adopted as an inert support in oxygen carrier synthesis because of its abundant availability and low cost^[37]. Furthermore, incorporating other metal additives into iron-based oxygen carriers to form bimetallic oxygen carriers can further enhance carrier reactivity and reduction depth through metal-ion interactions^[38–39]. As shown in Table 1, several researchers have modified iron-based oxygen carriers by adding metal additives such as Cu, Ca, Zn and Mg to Fe₂O₃/Al₂O₃ oxygen carriers. These studies demonstrate that metal additives enhance hydrogen yield and cycling stability of Fe₂O₃/Al₂O₃ oxygen carriers. Qin et al.^[40] and Li et al.^[41] report that incorporating low concentration of Cu metal additives into iron-based oxygen carriers significantly promotes methane conversion and enhances the reactivity and regenerative capacity of the iron-based oxygen carrier, noting that Cu ions facilitates oxygen ion migration within the oxygen carrier and reduces the activation energy of the CH₄ reduction reaction.

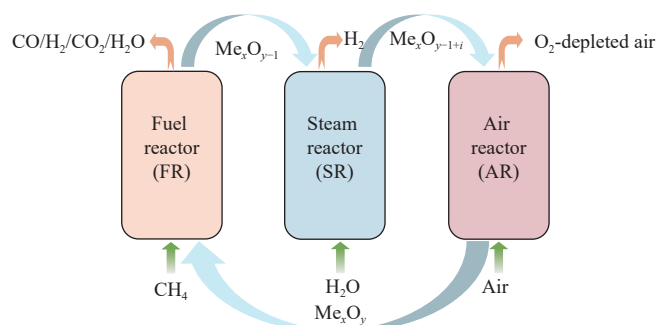


Fig. 1 Schematic diagram of the CL-SMR hydrogen production process

Table 1 Hydrogen production performance of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carriers modified with different metal additives

Oxygen carrier	Reactor	Fuel	Temperature / $^{\circ}\text{C}$	Hydrogen yield / $(\text{mmol}\cdot\text{g}^{-1})$	Syngas yield / $(\text{mmol}\cdot\text{g}^{-1})$	Cycle number	Ref.
Fe	Fixed bed reactor	5% CH_4	800	0.93	—	1	[45]
Fe	Fixed bed reactor	Biomass gas	850	~ 1.4	—	10	[46]
Fe/Al	Fixed bed reactor	5% CH_4	900	2.45	—	10	[37]
Fe/Al	Fixed bed reactor	Biomass gas	850	~ 1.3	—	10	[46]
Ca-Fe/Al	Fixed bed reactor	5% CH_4	850	3.16	6.94	10	[47]
Zn-Fe/Al	Fixed bed reactor	CO	850	2.23	—	20	[48]
Mn-Fe/Al	Fixed bed reactor	5% CO_2	800	2.1	—	20	[49]
Mg-Fe/Al	Fluidized bed reactor	5% CH_4	900	1.0	~ 0.9	10	[16]
Cu-Fe/Al	Fixed bed reactor	5% CH_4	900	2.88	—	10	[37]
Cu-Fe/Al	Fixed bed reactor	CO	850	10.59 mL/g	—	12	[50]
Cu-Fe/Al	Fixed bed reactor	Biomass gas	850	~ 3	—	5	[51]

Furthermore, Ce is frequently employed as a metal additive to enhance oxygen carrier performance. Gao et al.^[42] incorporated Ce into NiFe_2O_4 oxygen carriers, observing a substantial increase in hydrogen yield and cycling stability. Subsequently, Ma et al.^[43] employed Ce to modify hematite and observed that Ce-modified hematite exhibited substantially higher hydrogen yield and purity compared to natural hematite. Gu et al.^[44] demonstrated that using Ce and La separately to modify natural iron ore enhanced its reactivity and hydrogen production. These findings collectively indicate that the three metal additives, Cu, La and Ce, contribute to improving the performance of the oxygen carriers.

In this study, Cu, La and Ce metal additives were employed to modify $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carriers. The reduction reaction performance, lattice oxygen transfer capability, and hydrogen production efficiency of different oxygen carriers in the CL-SMR process were investigated using a fixed-bed reactor at 800 $^{\circ}\text{C}$. The pristine sample and the optimally modified oxygen carrier were further subjected to multi-cyclic tests to assess their cyclic stability and anti-coking properties. These findings provide valuable theoretical insights and experimental foundation for the development of high-performance iron-based oxygen carriers.

1 Materials and methods

1.1 Oxygen carrier preparation

The oxygen carrier particles were prepared using a one-step impregnation method. $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carriers were modified with three additives: Cu, La and Ce. The mass ratio of the metal oxide (Me_xO_y) to the inert carrier (Al_2O_3) was 6:4, resulting in an original mass ratio of $\text{Fe}_2\text{O}_3:\text{Al}_2\text{O}_3 = 6:4$, denoted as Fe60Al in the text. $\text{Fe}_2\text{O}_3:\text{Me}_x\text{O}_y:\text{Al}_2\text{O}_3 = 5.8:0.2:4$. Thus, the oxygen carriers modified with Cu, La and Ce additives were denoted as Fe58Cu2Al, Fe58La2Al and Fe58Ce2Al, respectively. The Al_2O_3 used in this experiment was 99.9% metal-basis, α -

phase, 30 nm and hydrophilic. The corresponding nitrates for the metal oxides included $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (AR), $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (AR), $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (AR) and $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (AR). Stoichiometric amounts of the metal nitrate precursors were dissolved together with the α - Al_2O_3 carrier in deionized water to form an impregnation solution. This mixture was stirred continuously in a water bath at 55 $^{\circ}\text{C}$ until complete solvent evaporation. The resulting wet material was then transferred to an oven and dried at 100 $^{\circ}\text{C}$ for 24 h. The dried samples were then calcined in a muffle furnace under a programmed temperature regime. First, the sample was heated at 10 $^{\circ}\text{C}/\text{min}$ to 550 $^{\circ}\text{C}$, held for 60 min, and then heated at the same rate to 950 $^{\circ}\text{C}$ and held for 180 min. Finally, particles sized between 20–40 mesh were selected by sieving and used as oxygen carrier particles for subsequent reactivity tests.

1.2 Oxygen carrier characterization

The crystalline phases of the oxygen carriers were identified by X-ray diffraction (XRD) to analyze their physical structure. The X-ray tube was operated at 40 kV and 40 mA with a scanning angle (2θ) ranging from 10 $^{\circ}$ to 90 $^{\circ}$. The XRD patterns were recorded at 0.05 $^{\circ}$ intervals at a scanning rate of 5($^{\circ}$)/min. Scanning electron microscopy (SEM) was employed to observe the microstructure of the oxygen carrier and energy-dispersive X-ray spectroscopy (EDX) was used to examine the elemental distribution. X-ray photoelectron spectroscopy (XPS) was utilized to determine the chemical states of the metal ions and oxygen, with the XPS spectrum referenced to the carbon peak at 284.8 eV. To evaluate the reduction performance of the oxygen carrier, hydrogen temperature-programmed reduction (H_2 -TPR) was conducted on a chemisorber. Before each reduction test, 0.1 g of the oxygen carrier was purged with high-purity N_2 for 10 min. Subsequently, TCD signals were recorded from 10 to 900 $^{\circ}\text{C}$ at a constant rate of 10 $^{\circ}\text{C}/\text{min}$ under a 10% H_2/Ar flow (50 mL/min). To characterize the carbon buildup after ten cycles of testing, temperature-programmed oxidation (O_2 -TPO) was performed using a chemical adsorption instrument. The

sample was heated from 10 to 920 °C at a constant rate of 10 °C/min under an oxygen atmosphere and the testing was coupled with gas chromatography-mass spectrometry (GC-MS) to monitor changes in O₂, CO and CO₂ curves.

1.3 Experimental procedures

In this study, a fixed-bed reaction evaluation system was employed to test the redox performance and cyclic stability of the oxygen carriers. As shown in Figure 2, the system primarily consists of an inlet unit, water vapor unit, reactor unit, quartz gas-liquid separation unit, and gas monitoring unit.

To investigate the reaction performance of four oxygen carriers with CH₄ at different temperatures (CH₄-TPR), 1.0 g of 20–40 mesh granulated sample was weighed and loaded into a quartz reaction tube (14 mm inner diameter, 550 mm length) in the following sequence: quartz wool-oxygen carrier-quartz wool. Under a nitrogen atmosphere with a flow rate of 150 mL/min, the sample was heated to 200 °C at a rate of 10 °C/min and held for 20 min to remove adsorbed water and other impurities from the surface of the oxygen carrier. Subsequently, the gas atmosphere was switched to a reducing gas containing 5% CH₄ by volume, at a flow rate of 150 mL/min. Heating was continued at a rate of 5 °C/min to 950 °C, and real-time changes in CH₄, CO₂, CO and H₂ concentrations in the tail gas were monitored using a flue gas analyzer.

To investigate the effect of different additives on the performance of Fe₂O₃/Al₂O₃ oxygen carriers in CL-SMR, isothermal single-cycle reaction experiments were conducted on the four prepared oxygen carriers. The single-cycle experiment comprised three stages: reduction, hydrogen production, and reoxidation. After loading the oxygen carrier particles (1.0 g) into a quartz reaction tube, the sample was heated at a rate of 15 °C/min to a constant temperature of 800 °C under a 150 mL/min flow of N₂ gas. Subsequently, the gas was switched to a mixture of 5% CH₄/N₂. The oxygen carrier then reacted with CH₄ and was reduced. To fully investigate the performance of the oxygen carrier, two reduction durations were applied: one

corresponding to the time required for complete reduction of the oxygen carrier, and the other fixed a 25 min for the oxygen carrier and CH₄ to react. Following the reduction reaction, N₂ was purged at a flow rate of 150 mL/min to prevent gas cross-contamination during hydrogen production. Following N₂ purging, pure water was delivered via a high-pressure liquid-transfer pump at a flow rate of 0.015 mL/min. Water was heated to vaporize within the heating zone. The vapor was then carried by nitrogen carrier gas (flow rate: 150 mL/min) into the reactor, where it oxidized the oxygen carrier while simultaneously producing high-purity hydrogen. Following the hydrogen production, the system was again purged with at 150 mL/min. Subsequently, a 15% O₂/N₂ mixture was introduced at a flow rate of 150 mL/min to ensure complete oxidation of the oxygen carrier. A flue gas analyzer continuously monitored the outlet gas during the reaction process.

1.4 Data processing

To facilitate the comparison of the reaction performance differences among various oxygen carriers, the following metrics were selected to evaluate their performance in the chemical looping hydrogen production process from methane. The corresponding calculation methods are as follows.

The reduction depth of oxygen carriers was characterized based on the oxygen loss in the reduction stage:

$$m_0 = 32 \times \frac{\int_0^t c_{\text{CH}_4\text{in}} \times dt \times F_{\text{in}} - \int_0^t c_{\text{CH}_4\text{out}} \times dt \times F_{\text{out}} + \int_0^t c_{\text{CO}_2\text{out}} \times dt \times F_{\text{out}}}{R_g} + 16 \times \frac{\int_0^t c_{\text{COout}} \times dt \times F_{\text{out}} - \int_0^t c_{\text{H}_2\text{out}} \times dt \times F_{\text{out}}}{R_g} \quad (5)$$

CH₄ conversion efficiency in the reduction phase:

$$x_{\text{CH}_4} = \frac{\int_0^t c_{\text{CH}_4\text{in}} \times dt \times F_{\text{in}} - \int_0^t c_{\text{CH}_4\text{out}} \times dt \times F_{\text{out}}}{\int_0^t c_{\text{CH}_4\text{in}} \times dt \times F_{\text{in}}} \quad (6)$$

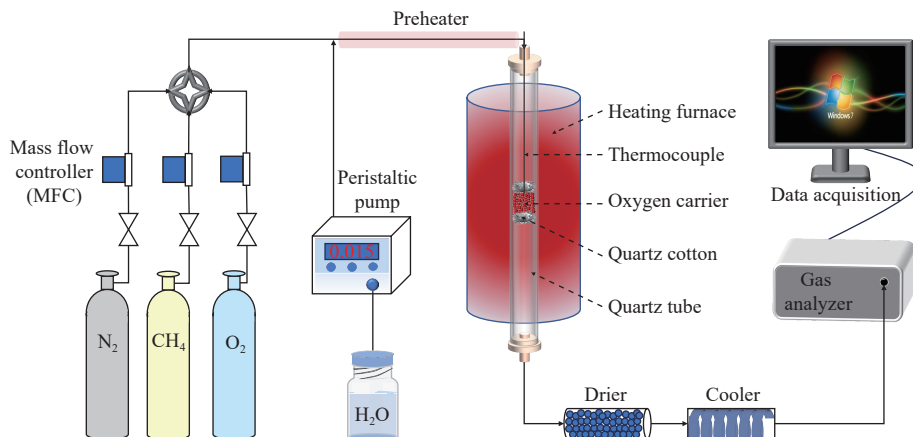


Fig. 2 Schematic diagram of the fixed-bed reactor for chemical looping hydrogen production

Syngas production in the reduction stage:

$$y_{sg} = \frac{\int_0^t c_{CO-out} \times dt \times F_{out} + \int_0^t c_{H_2-out} \times dt \times F_{out}}{R_g \times m_{oc}} \quad (7)$$

H₂/CO ratio in the reduction stage:

$$R = \frac{\int_0^t c_{H_2-out} \times dt \times F_{out}}{\int_0^t c_{CO-out} \times dt \times F_{out}} \quad (8)$$

H₂ production in the hydrogen production stage:

$$y_{H_2} = \frac{\int_0^t c_{H_2-out} \times dt \times F_{out}}{R_g \times m_{oc}} \quad (9)$$

H₂ purity in the hydrogen production stage:

$$P_{H_2} = \frac{\int_0^t c_{H_2-out} \times dt \times F_{out}}{\int_0^t c_{CO-out} \times dt \times F_{out} + \int_0^t c_{CO_2-out} \times dt \times F_{out} + \int_0^t c_{H_2-out} \times dt \times F_{out}} \quad (10)$$

where m_0 is the amount of oxygen loss, g; m_{oc} is the mass of oxygen carrier, g; c_{CH_4-in}/c_{CH_4-out} is the inlet/outlet methane concentration at any time t , %; c_{CO_2-out} is the outlet CO₂ concentration at any time t , %; c_{CO-out} is the outlet CO concentration at any time t , %; c_{H_2-out} is the outlet H₂ concentration at any time, %; F_{in}/F_{out} is the inlet/outlet gas flow rate at any time t , mL/min; R_g is the gas constant (22.4 L/mol) in the ideal state; x_{CH_4} is the efficiency of CH₄ conversion, %; y_{sg} , y_{H_2} are the yields of syngas, H₂, respectively, mmol/g; P_{H_2} is the H₂ purity, %.

2 Results and discussion

2.1 Characterization of oxygen carriers

2.1.1 XRD characterization of fresh oxygen carriers

Figure 3 shows the XRD patterns of the four fresh oxygen carrier particles. The pattern of Fe60Al displays only the characteristic diffraction peaks of Fe₂O₃ and Al₂O₃ phases, with no additional phase detected, indicating no solid solution reaction occurred between Fe₂O₃ and Al₂O₃. The addition of Cu, La and Ce results in new crystalline phase structures. Specifically, Fe58Cu2Al exhibits a new spinel-type phase, identified as CuFe₂O₄. CuFe₂O₄ exhibits higher reactivity than Fe₂O₃, enhancing the reduction reaction performance of the oxygen carrier and promotes deep reduction. The XRD pattern of Fe58La2Al reveals a perovskite-type oxide phase, LaFeO₃. Following Ce doping, only the CeO₂ phase is observed in Fe58Ce2Al, indicating the stable nature of CeO₂ and the absence of reaction with Fe₂O₃.

2.1.2 H₂-TPR curves of oxygen carriers

Figure 4 shows the H₂-TPR profiles of the oxygen carriers modified with different additives. As seen in the

figure, all four oxygen carriers exhibit three distinct H₂ reduction peaks. The undoped Fe60Al oxygen carrier displays three reduction peaks at 450, 720 and 900 °C, representing the progressive reduction of iron oxide. The reduction peak at 450 °C corresponds to Fe₂O₃ → Fe₃O₄, the peak at 720 °C to Fe₃O₄ → FeO, and the peak after 850–900 °C to FeO → Fe. Upon Cu addition, the first reduction peak shifted leftward, lowering the reduction temperature from 450 to 350 °C, whereas the second peak shifted slightly rightward. In contrast, La and Ce doping shifted the first reduction peak to the right, increasing the reduction temperature, while both the second reduction peaks shifted slightly to the right. This indicates that La and Ce doping increase the reaction temperature of the oxygen carrier, whereas Cu doping enhances the reactivity of the carrier and lowers the reaction temperature. The oxygen storage capacities of Fe60Al, Fe58Cu2Al, Fe58La2Al and Fe58Ce2Al oxygen carriers measured by H₂-TPR at 0–800 °C were 7.0, 6.5, 5.7 and 6.2 mmol/g, respectively. Compared to the oxygen storage capacity (OSC) of 557 μmol/g reported for CeO₂–ZrO₂ materials by Yentekakis et al.^[52], all four oxygen carriers exhibited higher storage capacities, with the unmodified Fe60Al showing the highest OSC among the tested carriers. The H₂-TPR profiles reveal that Fe58Cu2Al exhibits the lowest reaction temperature, indicating superior reducibility. Furthermore, combined with the XPS analysis in Figure 5 and Table 2, Fe58Cu2Al possesses the highest surface oxygen content, suggesting superior reactivity among the oxygen carriers.

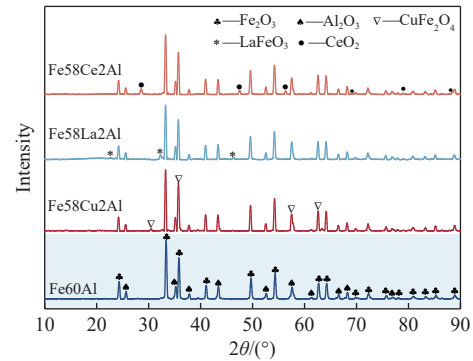


Fig. 3 XRD patterns of fresh oxygen carriers

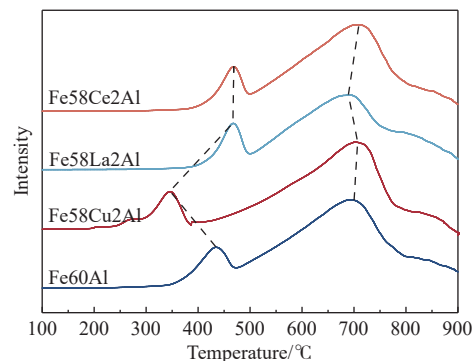


Fig. 4 H₂-TPR profiles of fresh oxygen carriers

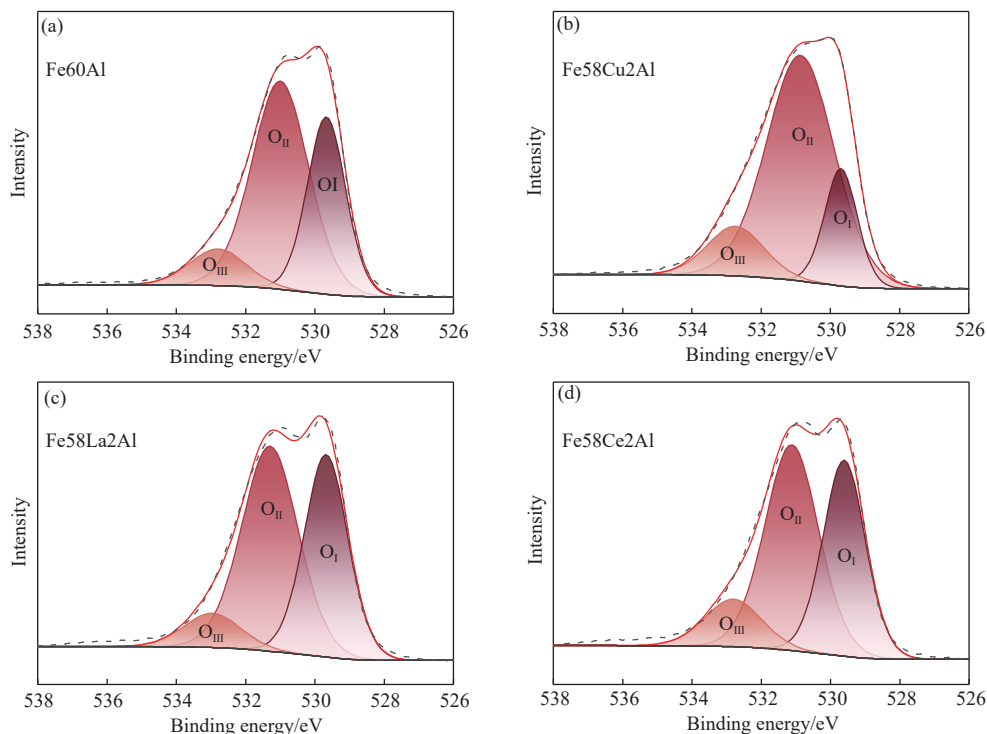


Fig. 5 XPS O 1s spectra of fresh oxygen carriers

Table 2 XPS analysis of oxygen element characteristics on the surface of fresh oxygen carriers

Oxygen carrier	O 1s binding energy/eV			O 1s percentage/%			O_{II}/O_I
	O_I	O_{II}	O_{III}	O_I	O_{II}	O_{III}	
Fe60Al	529.67	531.00	532.79	32.98	56.97	10.05	1.73
Fe58Cu2Al	529.69	530.86	532.74	17.52	69.69	12.79	3.98
Fe56La2Al	529.67	531.29	532.96	39.43	51.90	8.67	1.32
Fe54Ce2Al	529.60	531.12	532.80	38.58	50.20	11.22	1.30

2.1.3 XPS characterization of oxygen carriers

To further investigate the effects of Cu, La and Ce doping on the surface properties of iron-based oxygen carriers, XPS characterization was performed on the four fresh oxygen carriers, and the results are shown in Figure 5. Figures 5 (a)–(d) present the O 1s spectra of Fe60Al, Fe58Cu2Al, Fe58La2Al and Fe58Ce2Al oxygen carriers, respectively. Each spectrum can be deconvoluted into three oxygen species: lattice oxygen (O_I) at a binding energy of 529.6–530 eV, surface-adsorbed oxygen (O_{II}) at 530–532 eV and physically adsorbed oxygen (O_{III}) near 532.5–533.5 eV, the latter comprising surface hydroxyl and/or carbonate species. Typically, surface oxygen exhibits higher reactivity than lattice oxygen. This study employed the O_{II}/O_I ratio to characterize the oxygen activity of the oxygen carriers^[53]. As shown in Figure 5 and Table 2, Cu doping reduced the lattice oxygen content while increasing the surface oxygen content, leading to a higher O_{II}/O_I ratio. In contrast, doping with both La and Ce increased the lattice oxygen content, reduced the surface oxygen content, and led to a lower O_{II}/O_I ratio. This indicates that Cu doping enhances the reactivity of the oxygen carrier.

2.1.4 CH_4 -TPR curves for oxygen carriers

Figure 6 shows the variation profiles of outlet gas composition for different oxygen carriers during CH_4 temperature-programmed reduction (CH_4 -TPR). As shown in the figure, the outlet gases from all four oxygen carriers contained CH_4 , CO_2 , CO and H_2 , exhibiting similar variation trends. Analysis of the gas composition changes provides direct insight into the reaction activity of the oxygen carriers. Upon reaching a certain temperature, methane underwent complete oxidation with highly reactive surface oxygen species, initially producing CO_2 . As the reaction progresses, CO_2 exhibits its first peak. Subsequently, with continued temperature rise, methane reacted with surface oxygen while simultaneously initiating partial oxidation involving lattice oxygen, yielding CO and H_2 . When the temperature continues to increase, methane achieves an optimal reaction with the oxygen carrier, resulting in a peak for both CO_2 and CO . Subsequently, as the temperature increased further, methane began to crack, resulting in a decline in CO_2 and CO concentrations and a rapid increase in H_2 . Figure 6(a) shows the CH_4 -TPR profile of Fe60Al.

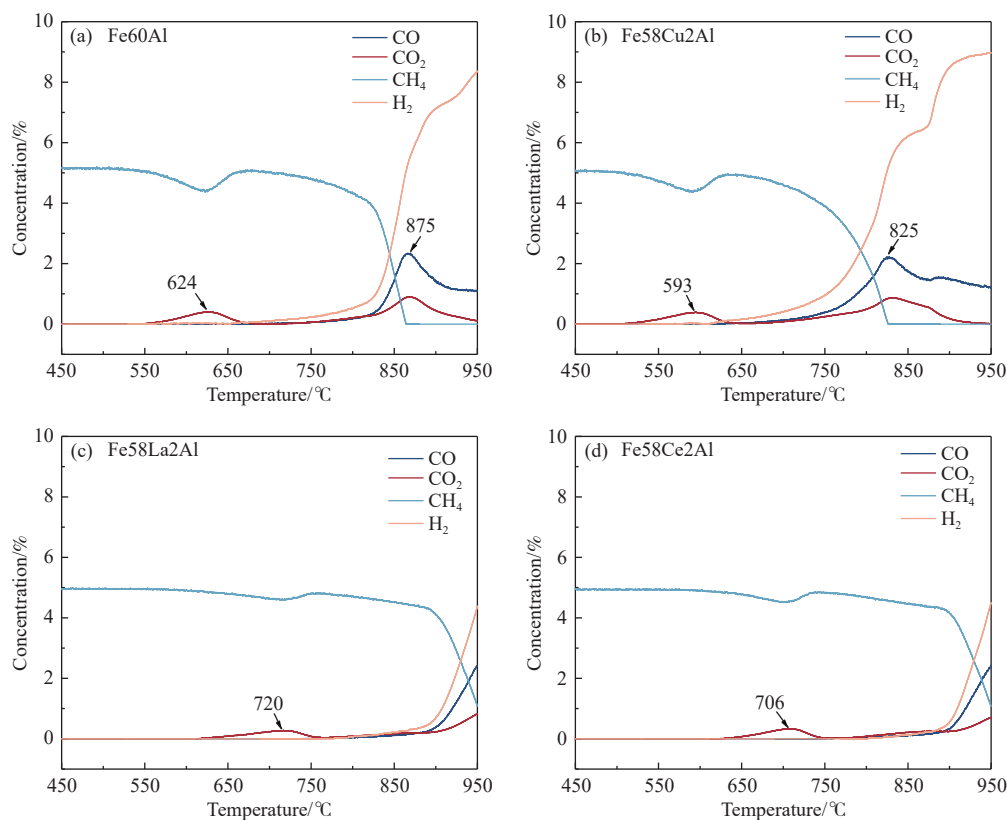


Fig. 6 Variation of outlet gas composition during CH₄ temperature-programmed reduction over different oxygen carriers

There are two reduction peaks with the first one of CO₂ formed at 624 °C and the other at 875 °C. Figure 6(b) shows two CO₂ peak for Fe58CuAl at 593 and 825 °C. Figures 6(c) and (d) present the CH₄-TPR profiles for Fe58La2Al and Fe58Ce2Al, respectively, with first CO₂ peak at 720 and 706 °C. Notably, no second CO₂ peak appeared, even at 950 °C, for Fe58La2Al and Fe58Ce2Al. This indicates that the addition of La and Ce suppress the reactivity of the oxygen carrier, whereas the addition of Cu enhances the reactivity of the oxygen carrier and lowers its reaction temperature of the oxygen carrier.

2.2 Performance evaluation of oxygen carriers

2.2.1 Patterns of changes in export gas composition

A single-cycle experiment was conducted at 800 °C, when hydrogen purity reached $\geq 98\%$ and $H_2/CO \geq 2.5$, to terminate the reduction stage reaction. Figure 7 illustrates the variation in outlet gas composition during the methane reduction-oxidation experiments using different oxygen carriers. The initial reaction between the oxygen carrier and CH₄ is highly vigorous, causing a sharp increase in CO₂ content. After approximately 3–5 min, CH₄ content rose while CO₂ declined, accompanied by the appearance of CO and H₂. As shown in Figures 7(a)–(d), for Fe60Al, Fe58Cu2Al, Fe58La2Al and Fe58Ce2Al, a decrease in CH₄ content was observed at 31, 28, 80 and 81 min, respectively,

alongside a gradual increase or decrease in CO and a sharp rise in H₂ content, indicating the onset of CH₄ cracking. Thus, by comparing the reaction times, the reactivity ranking of the different oxygen carriers is Fe58Cu2Al > Fe60Al > Fe58La2Al > Fe58Ce2Al. The methane concentration changes in Figure 7 reveal that Fe58Cu2Al exhibits the lowest methane concentration, followed by Fe60Al, with Fe58La2Al and Fe58Ce2Al show the highest concentrations. This indicates that the Fe58Cu2Al oxygen carrier achieves the highest methane conversion.

To better evaluate the reactivity of each oxygen carrier under controlled conditions, isothermal reactions with CH₄ were conducted at 800 °C for 25 min. The variation in gas composition at the reactor outlet is shown in Figure 8. As shown in Figures 8(c) and (d), after 25 min of reaction, the Fe58La2Al and Fe58Ce2Al oxygen carriers reacted slowly with CH₄, resulting in a high CH₄ concentration of 4.6% and a low H₂ concentration during the hydrogen production stage. This indicates that both oxygen carriers exhibit relatively low reactivity. Comparing Figures 8(a) and (b), it is observed that during the CH₄ reduction stage, the reaction activities of Fe58Cu2Al and Fe60Al were higher than those of Fe58La2Al and Fe58Ce2Al. Notably, Fe58Cu2Al achieved a lower CH₄ concentration than Fe60Al, while its H₂ and CO concentrations are significantly higher than Fe60Al. Furthermore, Fe58Cu2Al exhibited a high H₂ concentration during the hydrogen production stage. In summary, for the 25 min reduction period, the Fe58Cu2Al oxygen carrier demonstrate optimal reaction performance.

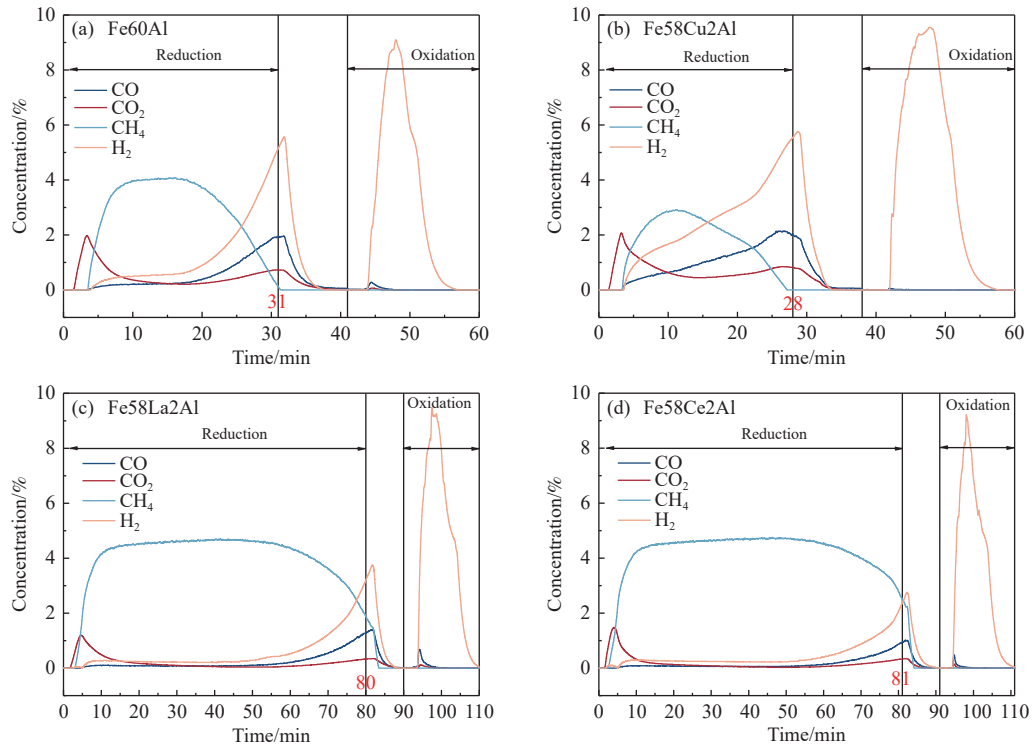


Fig. 7 Time evolution of gas concentration during a single CL-SMR cycle over different oxygen carriers at 800 °C

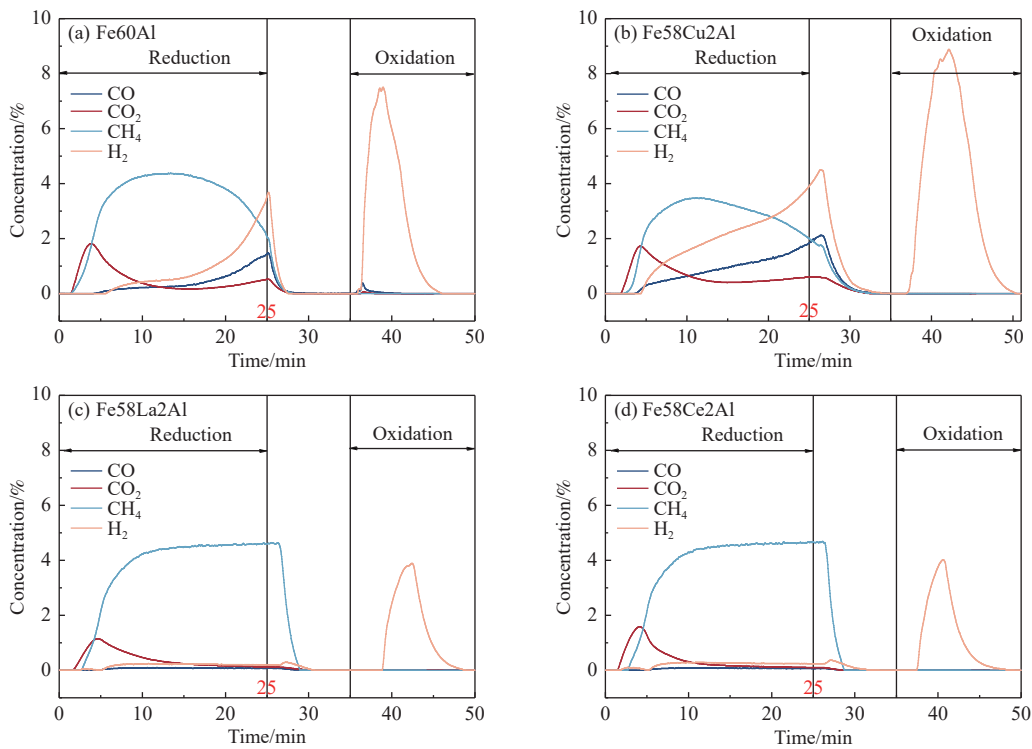


Fig. 8 Time evolution of gas concentration during a single cycle after 25 min of methane reaction over different oxygen carriers under isothermal conditions at 800 °C

2.2.2 Lattice oxygen transfer mechanism

Figure 9 shows the oxygen loss of different oxygen carriers during the methane reduction reaction stage, clearly illustrating the oxygen loss changes of the four oxygen

carriers, Fe60Al, Fe58Cu2Al, Fe58La2Al and Fe58Ce2Al, after reacting with CH₄ for 25 min. The results indicate that the oxygen loss of all four carriers increased continuously throughout the reaction. During the initial 3 min of the reaction, the oxygen loss curves of different carriers

overlap, indicating that the addition of Cu, La and Ce metal additives has a negligible impact on the initial stage of the CH_4 reduction reaction. However, as the reaction progressed, the oxygen loss of Fe58Cu2Al was significantly higher than that of the other three oxygen carriers. This is attributed to the formation of CuFe_2O_4 within the oxygen carrier, which participated in the oxygen transfer process and possessed higher reactivity than Fe_2O_3 . After 25 min, the oxygen loss rates for Fe60Al, Fe58Cu2Al, Fe58La2Al and Fe58Ce2Al are 9.1, 12.1, 7.6 and 7.2 (g/100 g oxygen carrier), respectively. It can be observed that the oxygen loss rates of Fe58La2Al and Fe58Ce2Al are relatively close and both lower than that of Fe60Al, whereas the oxygen loss rate of Fe58Cu2Al is 1.33 times that of Fe60Al. Therefore, the Fe58Cu2Al oxygen carrier possesses the optimal reactivity.

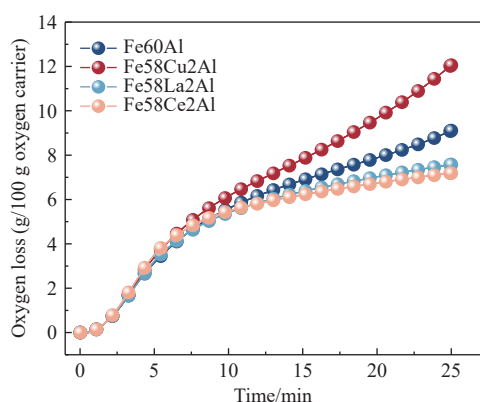


Fig. 9 Oxygen loss during the methane reduction reaction stage for different oxygen carriers

2.2.3 Reduction performance

Figure 10 compares the reduction performance of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carriers doped with Cu, La and Ce additives. As shown in Figure 10(a), at identical reaction times of 31 min, 28 min, 80 min, and 81 min, respectively, the corresponding synthesis gas yields over Fe60Al, Fe58Cu2Al, Fe58La2Al, and Fe58Ce2Al oxygen carriers were 3.24 mmol/g, 5.15 mmol/g, 4.17 mmol/g, and 3.03 mmol/g, while the methane conversions were 41.7%, 59.1%, 15.6%, and 14.6%, respectively. The results indicate that La and Ce doping do not significantly enhance the oxygen carrier performance, whereas the introduction of Cu markedly enhances the reaction activity. The syngas yield and methane conversion of Fe58Cu2Al were 1.59 times and 1.42 times higher than those of Fe60Al, respectively. As shown in Figure 10(b), when the reduction reaction time was fixed at 25 min, the performance of all four oxygen carriers decreased to varying degrees. Specifically, the syngas production of Fe58La2Al and Fe58Ce2Al dropped to 0.39 and 0.45 mmol/g, respectively, indicating that La- and Ce-modified oxygen carriers exhibited slow reaction rates and low activity during the CH_4 reduction stage. In contrast, Fe60Al and Fe58Cu2Al produced syngas at 1.88 and 4.23 mmol/g, respectively, with the latter being 2.25 times higher than the former. These values represent 10.85-fold and 9.4-fold increases over the La- and Ce-modified systems, respectively, further confirming the promoting effect of Cu on oxygen carrier activity.

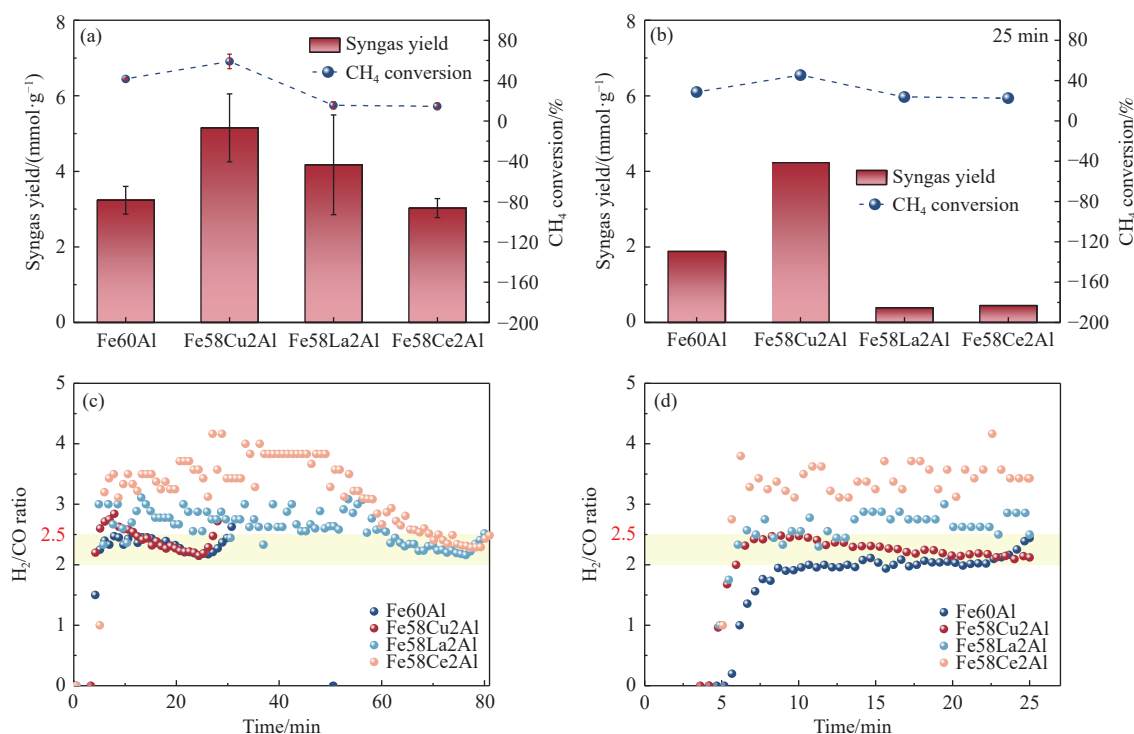


Fig. 10 Reduction performance of different oxygen carriers during methane reaction stage: (a), (c) Reduction reaction time when H_2/CO ratio ≥ 2.5 ; (b), (d) Reduction reaction time of 25 min

As shown in Figures 10(c) and (d), the H_2/CO ratios of Fe58La2Al and Fe58Ce2Al fluctuate considerably during reduction and consistently exceeded 2.5, whereas those of Fe60Al and Fe58Cu2Al remained stable between 2 and 2.5. In summary, the overall reduction performance of the four oxygen carriers can be ranked as follows: Fe58Cu2Al > Fe60Al > Fe58La2Al > Fe58Ce2Al.

2.2.4 Hydrogen production performance

Figure 11 compares the hydrogen yields and purity levels of the four oxygen carriers after one cycle. As shown in Figure 11(a), when the oxygen carriers Fe60Al, Fe58Cu2Al, Fe58La2Al and Fe58Ce2Al had reaction times of 31, 28, 80 and 81 min, respectively, during the reduction stage, the corresponding hydrogen yields during the hydrogen generation stage were 3.39, 5.13, 5.31 and 4.41 mmol/g, respectively, with hydrogen purity exceeding 98% for all. After the oxygen carriers were fully reduced during the reduction stage, the hydrogen yields of Fe58Cu2Al, Fe58La2Al and Fe58Ce2Al exceeded that of Fe60Al by 1.51, 1.57 and 1.3 times, respectively. However, the reaction times for Fe58La2Al and Fe58Ce2Al were considerably long to achieve these yields. As shown in Figure 11(b), when the reaction time for all four oxygen carriers during the reduction phase was set to 25 min, the hydrogen yields of Fe58La2Al and Fe58Ce2Al decreased significantly to 1.11 and 1.05 mmol/g, respectively, both lower than the 2.23 mmol/g achieved by Fe60Al. In contrast, Fe58Cu2Al exhibited a hydrogen yield of 3.69 mmol/g, which was markedly higher than those of the other three oxygen carriers. This indicates that Cu incorporation not only enhances methane conversion efficiency but also boosts hydrogen yield, attributable to the increased reactivity imparted by Cu. Comparing the hydrogen production rates of the various oxygen carriers in Table 1, the Fe58Cu2Al oxygen carrier developed in this study exhibits one of the highest hydrogen yields reported, reaching 5.13 mmol/g.

2.3 Cycling performance

To investigate the effect of Cu modification on the cyclic

stability of Fe_2O_3/Al_2O_3 oxygen carriers, ten cycles of experiments were conducted on two oxygen carriers: Fe60Al and Fe58Cu2Al. Their redox performances are shown in Figure 12. Both oxygen carriers maintained a hydrogen purity above 98% throughout ten cycles. Figures 12(a) and (b) show that for Fe60Al, the methane conversion, syngas yield, and hydrogen yield decreased with increasing cycle number. Methane conversion dropped from 41.7% in the first cycle to 22.6% in the tenth cycle, syngas yield decreased from 3.24 to 0.87 mmol/g and hydrogen yield fell from 3.39 to 1.24 mmol/g. This indicates that the oxygen carrier exhibits an overall low performance and poor cycling stability. In contrast, Figures 12(c) and (d) demonstrate superior cycling performance for Fe58Cu2Al compared to Fe60Al. Methane conversion decreased from 59.1% in the first cycle to 44.1% in the tenth cycle, while syngas yield decreased from 5.15 to 3.45 mmol/g, respectively, and the hydrogen yield decreased from 5.13 to 3.61 mmol/g. This indicates that the oxygen carrier exhibits an overall higher cycling performance and good cycling stability. Comparative analysis revealed that after ten cycles, Fe58Cu2Al maintained a higher methane conversion, syngas yield, and hydrogen yield than Fe60Al after a single cycle. Evidently, the addition of Cu enhances the reaction performance of the oxygen carrier and improves its cycling stability.

To further elucidate the factors underlying the performance differences in oxygen carriers after ten cycles, SEM-EDS analyses were conducted on the Fe60Al and Fe58Cu2Al oxygen carriers after ten cycles, as shown in Figure 13. Figure 13(a) clearly shows severe particle agglomeration and poor dispersion in the Fe60Al oxygen carrier after ten cycles. In contrast, Figure 13(b) shows only slight agglomeration and good dispersion in the Fe58Cu2Al oxygen carrier after ten cycles. This improvement can be attributed to the $CuFe_2O_4$ spinel formed by the addition of Cu, which enhances the sintering of the oxygen carrier. Figures 13(c) and (d) show EDS mapping of Fe60Al and Fe58Cu2Al, respectively. The images reveal a uniform elemental distribution across both the oxygen carriers, confirming that the single-dip method promotes particle interactions and facilitates the formation of a homogeneous phase.

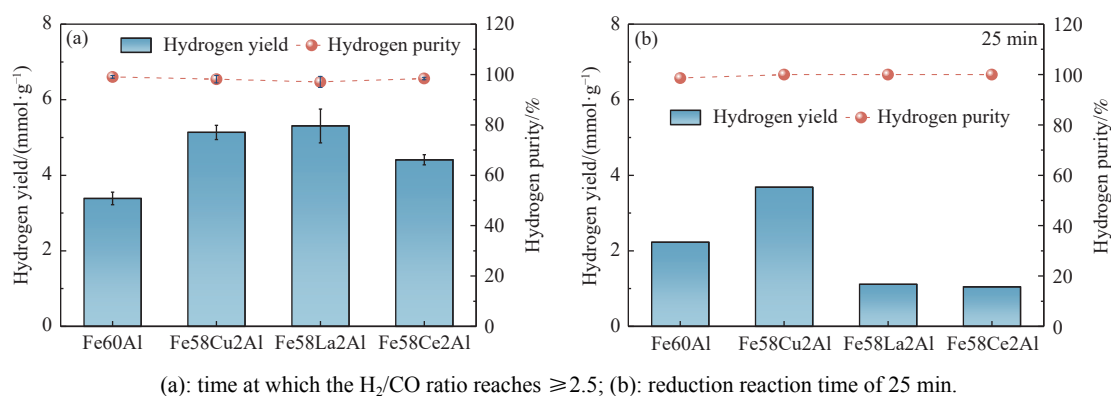


Fig. 11 Hydrogen production performance of different oxygen carriers during the oxidation stage

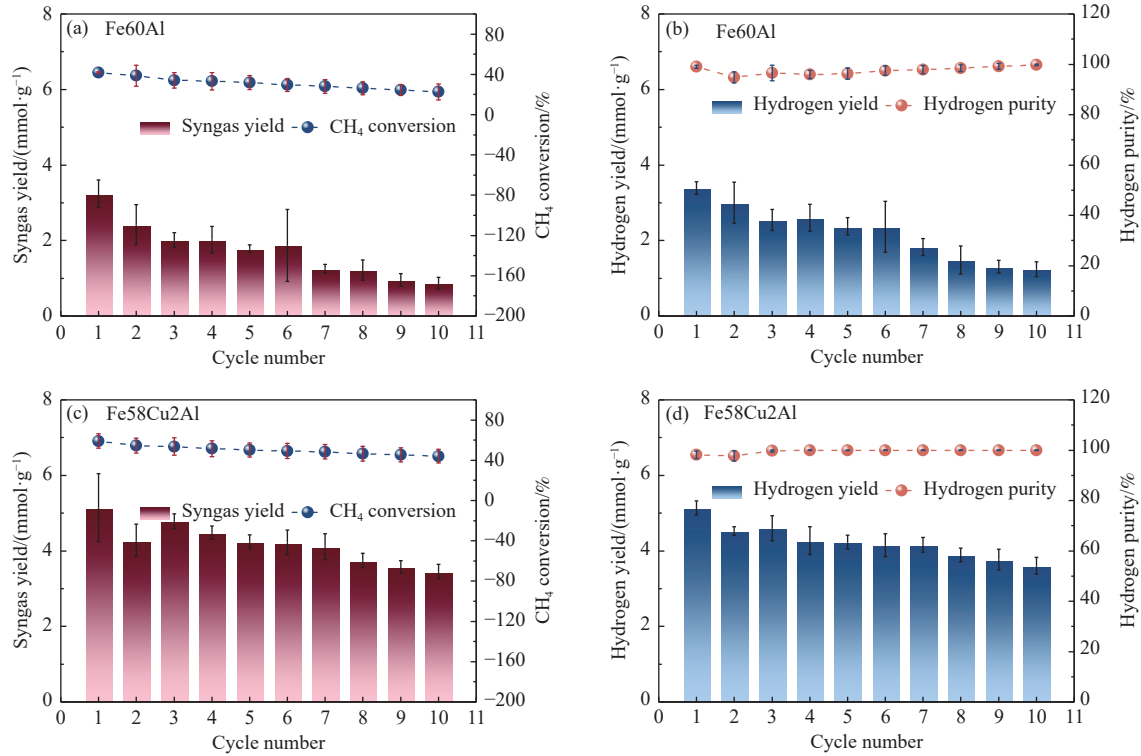


Fig. 12 Cyclic performance evaluation of different oxygen carriers over ten redox cycles: (a), (b) Fe60Al oxygen carrier; (c), (d) Fe58Cu2Al oxygen carrier

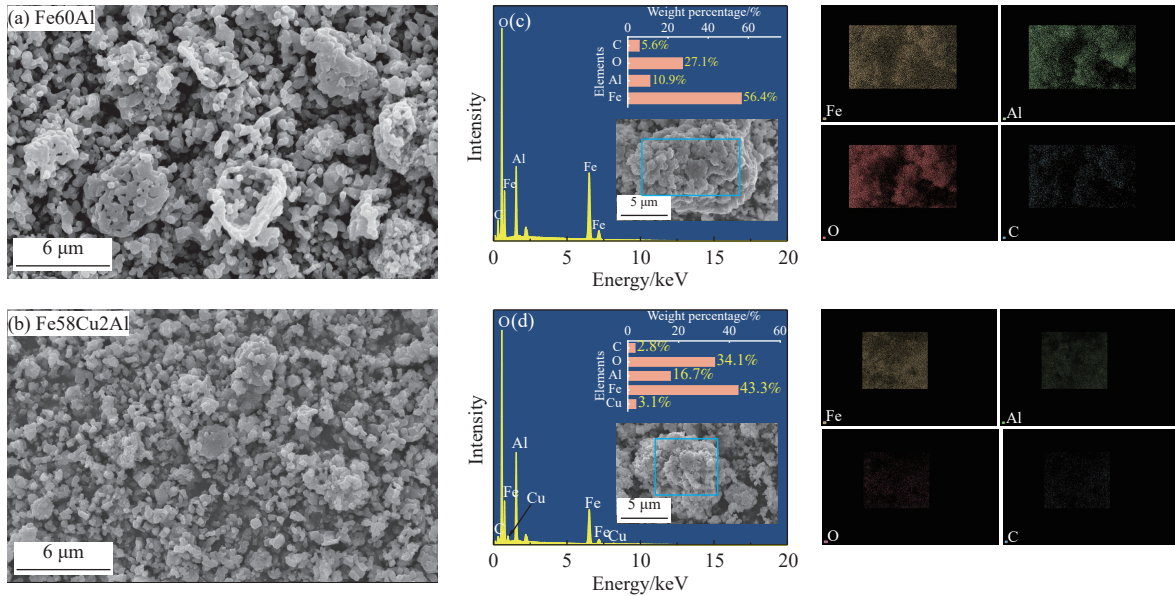


Fig. 13 SEM images and corresponding EDS mapping of oxygen carriers after ten cycles: (a), (c) Fe60Al; (b), (d) Fe58Cu2Al

A comparison of the weight percentages of carbon in both oxygen carriers reveals that carbon deposition on the Fe60Al oxygen carrier accounted for 5.6% of its total elemental content, whereas the carbon content in Fe58Cu2Al was only 2.8%. Consequently, after ten cycles, the Fe60Al oxygen carrier exhibited severe carbon deposition, with accumulation levels significantly higher than those on the Fe58Cu2Al oxygen carrier. This demonstrates that the Fe58Cu2Al oxygen carrier exhibits superior sintering resistance and coking resistance,

contributing to its maintained high performance after ten cycles.

To further analyze the carbon deposition on the oxygen carriers after ten cycles, O₂-TPO tests were conducted on the spent Fe60Al and Fe58Cu2Al oxygen carriers after ten cycles, as shown in Figure 14. Figure 14(a) presents the comparative O₂-TPO reaction profiles for the two oxygen carriers. The figure clearly shows that when the temperature exceeded 900 °C, a pronounced oxygen consumption peak accompanied by a corresponding CO signal was observed.

At this point, carbon deposits within the oxygen carrier react with oxygen to form CO. Furthermore, the carbon deposition reaction rate profiles (Figure 14(b)) demonstrates that the Fe60Al oxygen carrier exhibited a significantly higher carbon deposition reaction rate than the Fe58Cu2Al

oxygen carrier. The CO production of the Fe60Al oxygen carrier was 1.5 times that of the Fe58Cu2Al oxygen carrier, indicating that the Fe58Cu2Al oxygen carrier possessed superior anti-carbon deposition properties and exhibited outstanding cyclic performance.

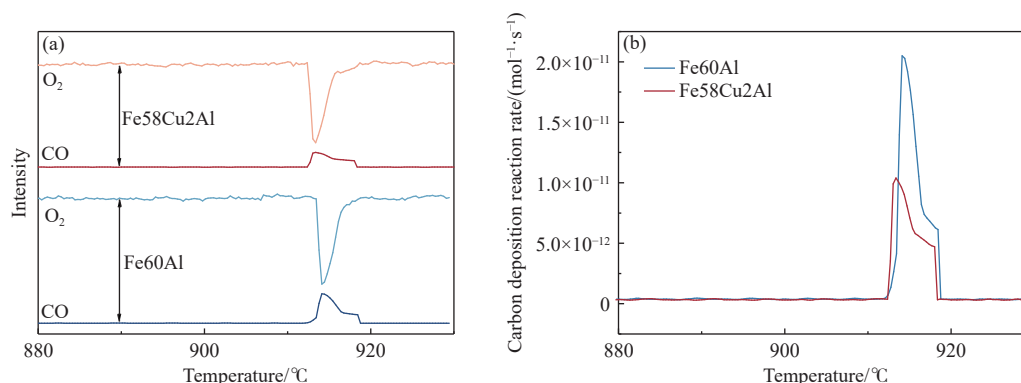


Fig. 14 O₂-TPO curves of carbon deposits on Fe60Al and Fe58Cu2Al oxygen carriers after ten cycles

3 Conclusions

In this study, four oxygen carriers—Fe60Al, Fe58Cu2Al, Fe58La2Al and Fe58Ce2Al—were prepared *via* the impregnation method. Their performance in hydrogen production *via* CL-SMR was evaluated in a fixed-bed reactor. The main conclusions are summarized as follows:

The incorporation of the three additives resulted in the formation of three new phases: CuFe₂O₄, LaFeO₃ and CeO₂, respectively. The oxygen loss rates of the oxygen carriers during the CH₄ reduction reaction stage at 25 min were in the order Fe58Cu2Al > Fe60Al > Fe58La2Al > Fe58Ce2Al. The addition of Cu increased the oxygen content on the oxygen carrier surface, significantly enhancing the reactivity of the oxygen carriers.

The Fe58Cu2Al oxygen carrier achieved the highest hydrogen yield in the first cycle, reaching 5.13 mmol/g with a purity exceeding 98%, which is 1.51 times that of Fe60Al. Under a 25 min reduction reaction time, the reduction and oxidation performances of the four oxygen carriers ranked as follows: Fe58Cu2Al > Fe60Al > Fe58La2Al > Fe58Ce2Al.

After ten cycles, Fe58Cu2Al maintained a hydrogen yield of 3.61 mmol/g, surpassing the single-cycle yield of Fe60Al (3.39 mmol/g). Furthermore, Fe58Cu2Al demonstrated superior dispersion and resistance to coking compared to Fe60Al after ten cycles, confirming its excellent cyclic stability.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Cu、La、Ce 改性 Fe₂O₃/Al₂O₃ 氧载体的化学链甲烷制氢性能研究

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摘 要: 化学链甲烷蒸汽重整制氢技术因能够在氧化还原过程中分步生产高选择性的合成气和高纯度的氢气而备受关注。针对单一的铁基氧载体存在循环稳定性差、反应活性较低和易烧结等问题, 本工作采用浸渍法分别掺杂 Cu、La、Ce 三种不同的金属助剂对 Fe₂O₃/Al₂O₃ 氧载体进行改性。对复合氧载体进行了表征和氧化还原循环实验, 研究了不同氧载体物理化学性能与反应活性及制氢性能的构效关系。研究表明, 尖晶石相 CuFe₂O₄ 相较于钙钛矿 LaFeO₃ 和 CeO₂ 具有更高的反应活性, 促进 Fe₂O₃ 的深度还原。Fe₅₈Cu₂Al 的储氧量可达 6.5 mmol/g, 在 CH₄ 反应阶段 Fe₅₈Cu₂Al 的失氧量最高达到 12.1 g/100 g 氧载体, 合成气产量达 5.15 mmol/g, 分别是 Fe₆₀Al 的 1.33 倍和 1.59 倍。在制氢阶段中 2%Cu 改性的氧载体效果最佳, 氢气产量达 5.13 mmol/g, 是原样的 1.51 倍, 且十次循环以后 H₂ 产量为 3.61 mmol/g, 仍高于原样一次循环的氢气产量, 且 H₂ 纯度均高于 98%。

关键词: 化学链; 铁基氧载体; 金属助剂; 氢气纯度

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