Utilizing γ-Al_2O_3-Supported Perovskites in Methane Chemical Looping Cycles

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Abstract

The production of solar fuels using renewable energy is a key objective in achieving carbon neutrality. Chemical Looping (CL) cycles powered by Concentrated Solar Thermal (CST) energy offer a promising alternative to electrolysis for splitting H_2O and CO_2 to generate synthesis gas (H_2 and CO). In this context, the development of efficient oxygen carriers is crucial. Perovskite-based materials, particularly those modified through cationic substitution, are being explored to enhance redox performance and stability in CL processes. In this work, an innovative material with chemical formula $La_{0.6}Sr_{0.4}Mn_{0.4}Fe_{0.6}O_3$, has been synthetized by partial substitution of Fe with Mn. Reactive CL tests were performed in a fluidized bed.

Material preparation

The catalyst was prepared by impregnating γ-Al_2O_3 particles, whose size range was between 200-400 μm, with an aqueous solution. The solution was obtained dissolving stoichiometric amounts of manganese (II) nitrate tetrahydrate, strontium nitrate, hydrated lanthanum nitrate and non-hydrated iron (III) nitrate in double-distilled water. The solution was agitated, dried at 110°C and then calcined at 920°C [1]. The choice of a supported catalyst was dictated to have particle mechanical properties such as to withstand the continuous particle-particle and particle-wall interactions in fluidized bed (FB). The prepared material was tested in a FB reactor using the experimental setup illustrated in Fig.1. The experimental setup consists of a tubular quartz FB reactor with an inner diameter of 10 mm, placed inside a cylindrical electric furnace. The material loaded during the tests is approximately 1.0 g. Temperatures were monitored by four K-type thermocouples. A transducer monitored the pressure drop upstream the reactor. It was also used to estimate the minimum fluidization velocity of the catalyst, by measuring pressure drops data as a function of the inlet gas velocity. A value of 5.30 cm/s was computed at room temperature in air. In the experimental rig, a three-way valve is positioned upstream the reactor to send the gas flow either directly to the reactor, or through a thermostatically controlled bath, set at a temperature of 50°C, to feed steam into the bed. Outlet gases pass through a filter, then to a condenser to collect the condensed

steam and, finally, to the analyser. Five isothermal cycles were conducted at 850°C and at a fluidization velocity of 21.9 cm/s. Each cycle includes: i) a reduction step with a mixture of CH_4 at 5% in N_2, during which supported perovskite particles are reduced to a $La_{0.6}Sr_{0.4}Mn_{0.4}Fe_{0.6}O_{3-\delta}$ state with the contextual production of CO/H_2; ii) an oxidation step with H_2O, during which the catalyst active phase returns its original form and H_2 is produced; iii) a final step in air for complete catalyst reoxidation is performed even to oxidize carbon deposits if formed during step i) [2].

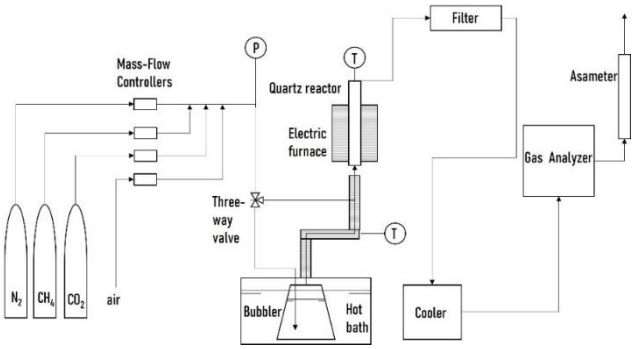

Figure 1. Sketch of the experimental set-up.

Results and Discussion

Fig. 2 shows the results obtained during the experimental tests. For each test, a fixed mass of fresh material was used. Fig. 2(A and D) depict the evolution of δ during the reduction phase, indicating that the oxygen reduction capacity of catalyst active phase stabilizes around 0.8 over time. Fig. 2(B and E) present the selectivity towards CO as a function of δ during this phase, while, as well, Fig. 2 (C and F) show the selectivity towards CO_2 over δ. Upon exposure to H_2O and O_2, catalyst particles are fully reoxidized, and the cycling is highly reproducible with no noticeable loss in reactivity.

Fig. 3 illustrates the progression of CO_2 and CO selectivity throughout the reaction process. These graphs provide insight into the number of moles of CO_2 and CO generated per cycle during the methane reduction phase. It is worth to note that, just after the methane feeding, the reaction pathway initially favours the formation of CO_2. However, as the process progresses, the selectivity of the reaction pathway changes: the CO_2 selectivity gradually decreases to zero, while CO is steadily produced.

The incorporation of γ-Al_2O_3 as a support material has enhanced the mechanical robustness of the perovskite structure. This improvement is especially relevant for FB applications, where resistance to attrition and particle fragmentation is typically a fundamental requirement. The results obtained in this study serve as a first step for the development of efficient CL methane reforming technologies aimed at solar fuel production using a Directly Irradiated Fluidized Bed Reactor (DIFBR) [2].

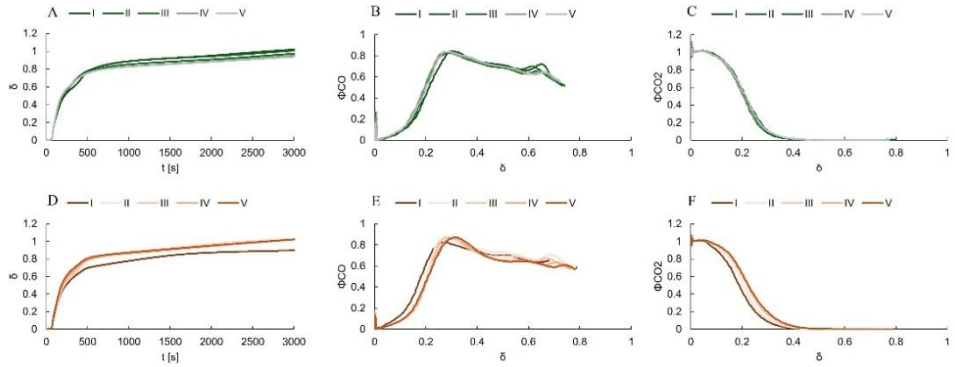

Figure 2. (A-D) variation of δ over time for each cycle for two tests; (B-E) CO selectivity over δ; (C-F) CO_2 selectivity over δ.

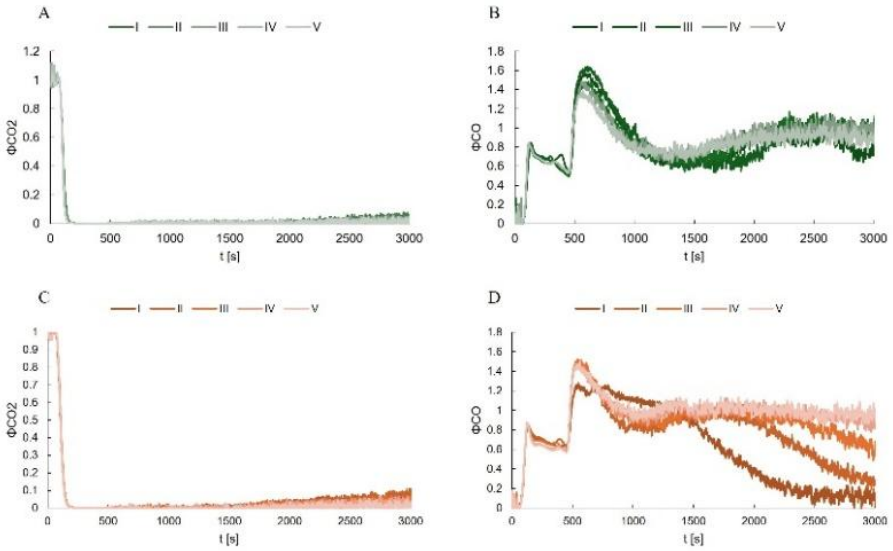

Figure 3. (A-B) variation of CO_2 selectivity over time; (B-D) CO selectivity variation over time.

References

1. Luciani G., Landi G., Aronne A., Di Benedetto A., "Partial substitution of B cation in La0. 6Sr0. 4MnO3 perovskites: A promising strategy to improve the redox properties useful for solar thermochemical water and carbon dioxide splitting", *Solar Energy*.171:1–7 (2018).
2. Tregambi C., Padula S., Galbusieri M., Coppola G., Montagnaro F., Salatino P., Troiano M., Solimene R., "Directly irradiated fluidized bed reactor for thermochemical energy storage and solar fuels production", *Powder Technology.* 366:460–9 (2020).