SOLAR FUELS FROM CHEMICAL LOOPING CYCLES WITH PEROVSKITE CATALYST IN AN INNOVATIVE FLUIDIZED BED REACTOR

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Abstract
The production of solar fuels with renewable energy sources is considered a fundamental cornerstone to reach the goal of net-zero emissions by 2050. Water splitting through Chemical Looping cycles sustained by Concentrated Solar Thermal (CST) energy can be a valuable alternative to electrolysis. In the transitional phase toward a carbon-free industry model, Chemical Looping cycles can combine the use of natural or bio- gas to reduce energy requirements. The research in this field follows two parallel lines: the optimization of oxygen carriers and the development of solar reactors. In this study, a laboratory synthesized perovskite is tested in an innovative solar reactor based on fluidized bed technology.

Introduction
Concentrated Solar Thermal (CST) technology uses solar radiation as a heat source, by concentrating solar rays with an array of sun-tracking mirrors (heliostats) [1]. In the last decade the application of CST to power generation has spread over the world, reaching a total capacity of 6.2 GW in 2020 [2]. The application of CST to the production of solar fuels would mark a significant progress, leading to the decarbonization of different industrial sectors.
Chemical Looping cycles generally involve a metal oxide, that is cyclically reduced and oxidized, acting as an oxygen carrier [3]. Solar energy can sustain the endothermic reduction step, by which oxygen (O_2) is released:

$$MO_x \rightarrow MO_{x-y} + y/2\ O_2 \tag{1}$$

Then, the reduced oxide reacts with water vapor (H_2O) or carbon dioxide (CO_2), producing hydrogen (H_2) or carbon monoxide (CO) and getting oxidized back:

$$MO_{x-y} + y\ H_2O \rightarrow MO_x + y\ H_2 \tag{2}$$

$$MO_{x-y} + y\ CO_2 \rightarrow MO_x + y\ CO \tag{3}$$

By summing the two reaction steps, the overall result is the decomposition of $H_2O \backslash CO_2$. The reduction step typically occurs at temperatures of 1000-1500°C that can technically be reached in a solar reactor. Extremely low O_2 partial pressures are required, usually obtained by vacuum pumping or inert gas sweeping. By introducing methane (CH_4) in the reduction step, the reaction temperature can be lowered below 1000°C and no energy needs to be spent to keep a low O_2 partial pressure:

$$MO_x + y\ CH_4 \rightarrow MO_{x-y} + 2y\ H_2 + y\ CO \tag{4}$$
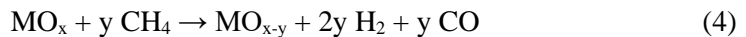
The overall process, known as Chemical Looping Reforming, is endothermic [4]. Compared to traditional steam/dry reforming, the reaction heat is supplied by CST energy rather than by the combustion of a fuel, so it yields an energy gain. An additional advantage is that the oxidation step produces a pure stream of H_2 or CO (Eq. (2–3)), ready for any use without need of downstream gas conditioning operations.

The research of suitable oxygen carriers is a key aspect in the development of this process. Feasible reduction temperatures, high re-oxidation rates and good stability over cycles are generally desired properties [5]. Perovskites are non-stoichiometric oxides characterized by the presence of two cations and represented with the formula ABO_3. They have excellent properties, due to a stable crystal phase that keeps unchanged throughout the process. Besides, redox properties can be suitably modified by partial substitution of the A and B cations [6].

The development of solar reactors is a complementary key aspect [7]. Recently a lanthanum (La) – iron (Fe) perovskite, in which strontium (Sr) partially replaces La, has been tested for Chemical Looping Reforming under both fixed and fluidized bed conditions [8]. A high selectivity toward partial oxidation of CH_4 was obtained. Fluidized bed experiments showed faster kinetics, but $9\%_w$ of the bed mass was lost probably due to fragmentation and elutriation.

In this study, the same perovskite is tested in an innovative Directly Irradiated Fluidized Bed Reactor (DIFBR) [9] and the results are compared with those obtained in a conventional fluidized bed. The effects of a support of γ-allumina are also investigated with the aim of optimizing the mechanical properties of the oxygen carrier.

Experimental methods

The experimental apparatus, outlined in Fig. 1, is the same used in previous studies [9] with some modifications. The reactor is made of stainless steel and thermally insulated with multiple layers of rock wool blanket. It is composed by two coaxial tubes connected at the bottom of a conical receiver (upper diameter 120 mm). A fluidizing gas stream is fed to the inner tube (riser, internal diameter 10 mm), through a nozzle and lifts the solid reactant up to the receiver. The solid falls in the outer tube

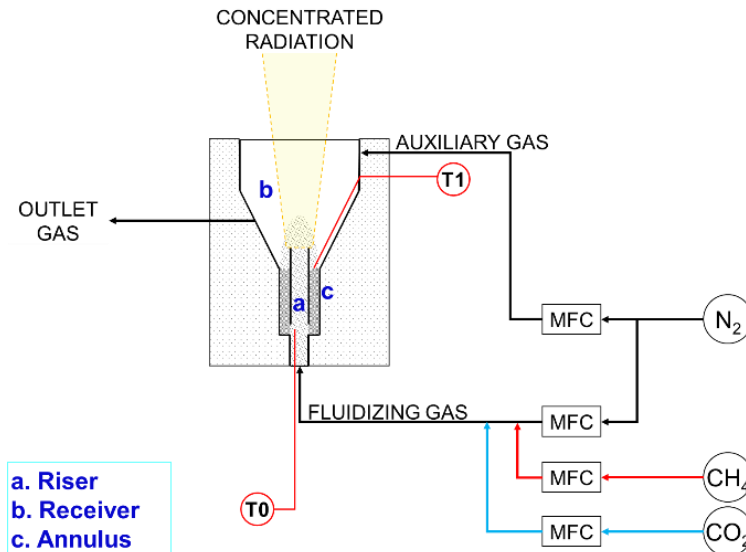(the annulus) and then is recycled to the riser through four holes drilled in the riser wall.

Figure 1. Experimental set-up.

The top of the receiver is sealed by a transparent quartz window, to let in solar radiation. An auxiliary stream can be fed to the receiver through a lateral tube for the protection of the window. The reactor is operated with a bed inventory of 10 g of sand-like particles. The fluidizing and reacting gases are fed from gas cylinders through mass flow controllers. Bed temperature is measured with two K-type thermocouples: one located inside the riser at the same height of the four orifices (T0), the other in the receiver at the inlet of the annulus (T1). A LabView application sets the mass flow controllers, monitors and records reactor temperatures. A high-flux solar simulator directly radiates the particles in the receiver. The power of the lamp can be varied within 2–7 kW_e with 1 kW_e steps.

The synthetized perovskite material has chemical formula $La_{0.6}Sr_{0.4}FeO_3$. A pure sample is prepared starting from an aqueous solution of nitrate salts by evaporation and calcination at 1000°C. Another perovskite sample is also prepared on a support of γ-allumina (Al_2O_3) by impregnation, evaporation and calcination at 920°C. The mass fraction of the perovskite in the supported catalyst is about 30%.

The performance of the two samples is investigated by carrying out several cycles for different inlet gas velocities. A reaction cycle consists of three steps: reduction with methane (CH_4), oxidation with carbon dioxide (CO_2) and then with oxygen (O_2). The lamp power is regulated in order to keep the T1 temperature in the range 880-900°C during the reaction steps. The supported sample is tested also in an electrically heated conventional fluidized bed for comparison. Fluidized bed tests were conducted in a 10 mm quartz tube at a temperature of 850°C taken as the mean between the T0 and T1 temperature and a gas velocity of 0.5 m/s.

Results

Figure 2 shows the temperature and gas concentration profiles during a typical reaction cycle performed in the DIFBR. The favored products of the reduction step are H_2 and CO, except for an initial peak of CO_2 and for carbon (C) that forms as perovskite full conversion is achieved. The oxygen carrier is totally re-oxidized after the steps with CO_2 and O_2, and cycles are repeatable showing no decrease in reactivity.
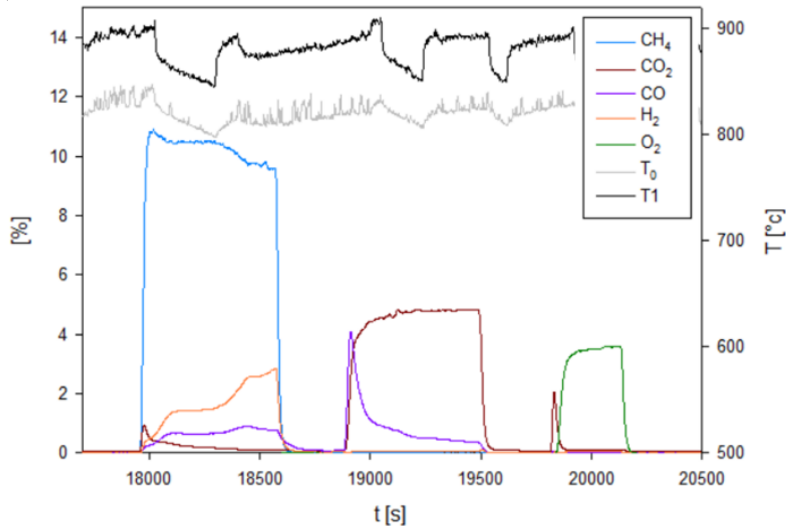

Figure 2. Concentration profiles of main gaseous species, and temperature, during a typical reaction cycle.

The maximum conversion degree of CH_4 mainly depends on the contact time (τ) between the reacting solid and the fluidizing gas (Fig. 3):

$$\tau = m_{perovskite} / Q \tag{5}$$

where $m_{perovskite}$ is the mass of perovskite in the fluidized bed and Q is the fluidizing gas flowrate. Contact times with the supported perovskite are lower than with the pure perovskite because it contains less reacting material for an equal bed inventory. Conversion degrees are coherently lower. On the other hand, the pure perovskite is very fragile and a mass loss of up to $30\%_w$ is reported for the test in DIFBR, whereas no significant loss of mass is reported for the supported perovskite.

Apparently, conversion degrees in the conventional fluidized bed are higher. However, if contact times in the solar reactor are recalculated by considering only the mass inside the riser (i.e., that effectively in contact with the gas), the data appear closer as shown in Fig. 4.

Finally, Figure 5 compares the maximum selectivity toward CO for the studied cases. Selectivity is higher for the solar reactor than for the conventional fluidized bed.
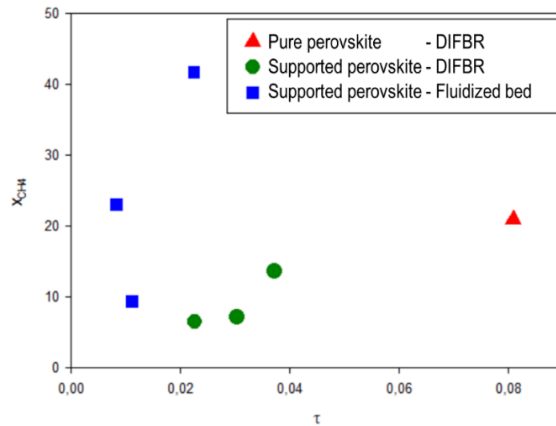
Figure 3. Maximum conversion of CH_4 (X_{CH4}) vs. contact time (τ [g h NL^{-1}]), considering the whole bed inventory for DIFBR.
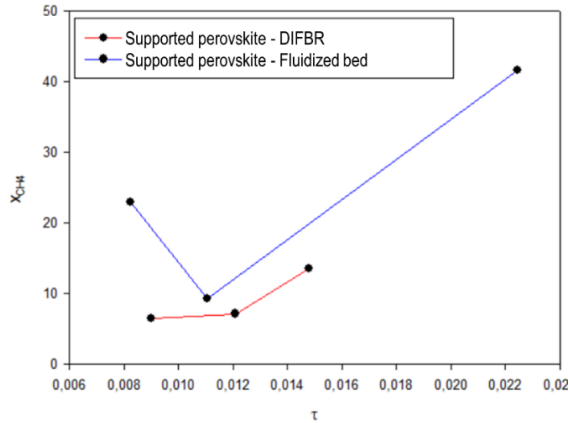
Figure 4. Maximum conversion of CH_4 (X_{CH4}) vs. contact time (τ [g h NL^{-1}]), considering only the riser inventory for DIFBR.
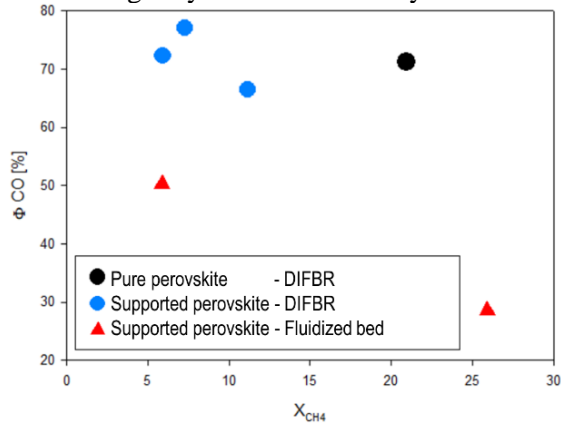
Figure 5. Maximum selectivity toward CO (Φ CO) vs. maximum conversion of CH_4 (X_{CH4}).

Conclusions

The $La_{0.6}Sr_{0.4}FeO_3$ perovskite is tested for Chemical Looping Reforming of CH_4 under simulated solar radiation in an innovative solar reactor. The results confirm that catalyst has a good stability and a good selectivity toward synthesis gas. The use of an alumina support improves the mechanical strength of the oxygen carrier and can be advised for use in fluidized bed reactors. On the other hand, the contact time must be optimized to improve CH_4 conversion. Selectivity toward synthesis gas is found to be higher for the solar reactor than for a conventional fluidized bed under equivalent operating conditions.

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