



CO₂/H₂O splitting by thermochemical cycles with perovskite-based catalysts for storage of solar energy

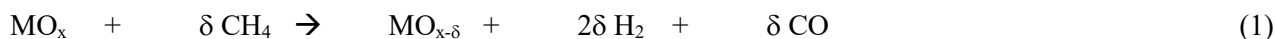
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1. Introduction

Extensive research is in progress on Concentrating Solar Thermal (CST) technologies able to convert the solar energy in electricity or in industrial process heat. ThermoChemical Energy Storage (TCES) of concentrated solar radiation in high-value carriers is currently widely pursued to increase dispatchability of solar energy. An ambitious strategy aims at converting the H₂O and CO₂ molecules into H₂ and CO in two step reaction cycles by using metal oxides systems, which act as chemical carriers at relatively high temperatures (1200–1500 °C). In a first endothermic step, the metal oxide is thermally reduced at high temperature, with the consequent release of O₂. The reduced metal oxide is then oxidized back with H₂O/CO₂ to eventually produce H₂/CO. Several metal oxides have been tested, but the overall efficiency is strongly affected by the high temperature required for the endothermal step. An alternative reaction scheme involves the use of a reducing agent like methane to lower the thermodynamic barrier of the reduction step as in the following:



Reaction (2), namely the CO₂ splitting/utilization, can be alternatively performed with H₂O to produce H₂. With this hybridization, the overall process shifts from a solar-thermal splitting cycle to a solar chemical looping reforming of methane with CO/H₂ production. The energy content of the resulting gas is increased up to about 25% with respect to the original methane stream. In this study, the methane-reforming and CO₂ splitting cycle has been investigated in both a fixed bed and fluidized bed solar reactor using as metal oxide a perovskite material (ABO₃) made of a mixture of La and Sr as “A” cation and Fe as “B” cation.

2. Methods

The perovskite material was synthesized following the procedure developed in a previous study [1], to obtain a perovskite powder (La_{0.6}Sr_{0.4}FeO₃, 200–300 μm). Material performance over cycling was investigated in a fixed bed reactor under isothermal conditions at 920, 1000 and 860 °C, using a mixture of CH₄ and N₂ for the reduction step and a mixture of CO₂ and N₂ for the oxidation step. Some isothermal cycles at 920 °C were also performed using a mixture of H₂O and N₂ for the oxidation step. The same kind of experiments are on going in a solar fluidized bed reactor heated by a concentrated solar power simulator [2].

3. Results and discussion

Figure 1 shows the reduction of material in temperature ramp using the 5%_v CH₄:N₂ stream and the following oxidation during CO₂ splitting.

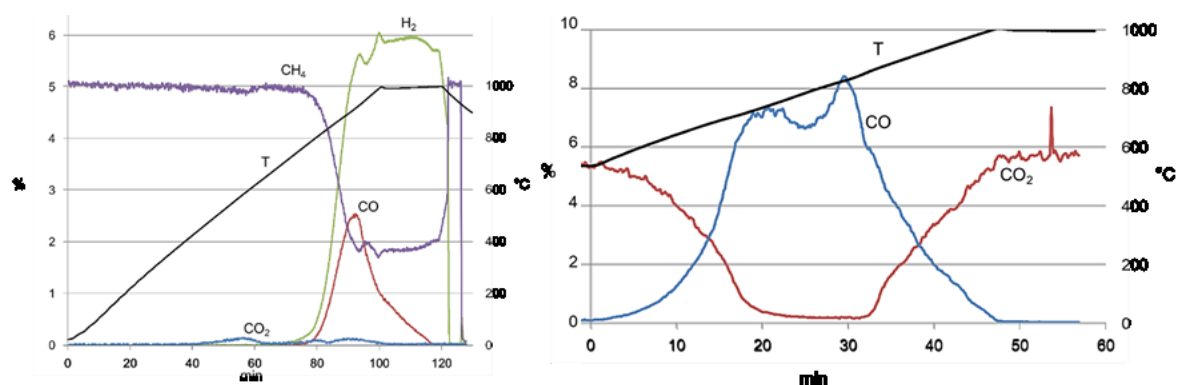


Figure 1. A) Reduction of the perovskite in 5 %_v CH₄/N₂ stream; B) CO₂ splitting of reduced perovskite in 5 %_v CO₂/N₂.

During the reduction step with methane, 10 L/h of a 5 %_v CH₄/N₂ mixture at ambient temperature were fed to a 0.477 g fixed bed of perovskite. At about 800 °C the reaction starts to take place with high selectivity of the reaction towards the products of partial oxidation and with limited conversion of CH₄. This means that probably the reaction is kinetically controlled by oxygen diffusion from the bulk of the material towards the surface. Increasing further the temperature, CO concentration decreases keeping more or less constant both CH₄ conversion and H₂ concentration. As a consequence, as the material is progressively reduced, CH₄ decomposition takes place in parallel with reforming. From these results a value of δ for reaction (1) can be computed of 1.5, that corresponds to the total reduction of iron from Fe⁺³ to Fe⁰. The formation of Fe⁰ may be responsible for the catalytic decomposition of CH₄. During the oxidation step with carbon dioxide, 10 L/h of a 5 %_v CO₂/N₂ mixture were fed at ambient temperature. The reaction starts just above the initial temperature of 550 °C and no kinetic limitations to the reaction above 700 °C appear, as the conversion of CO₂ is almost complete. Then conversion falls down as the material is progressively reoxidized. The molar ratio between CO and converted CO₂ is sometimes greater than unity and this points out that gasification of deposited carbon according to the Boudouard reaction occurs in parallel to perovskite oxidation. The regeneration of the material can be considered complete and the deposited carbon is completely converted to CO too. TP reduction and oxidation profiles clearly show that CO₂ splitting kinetics is faster than CH₄ reduction. Reduction/oxidation cycles were performed at 860 °C with the same feed conditions. The reduction steps were interrupted in order to limit the decomposition of methane. This resulted in a minor reduction degree (around 50%). The cycles showed good material repeatability and stability. Reduction/oxidation cycles were performed as well at 920 and 1000 °C. No changes in selectivity were observed, but the reaction rates changed. The reduction steps lasted about 15 min at 860 °C, whereas they took almost 10 min to reach the same reduction degree at higher temperatures. An inverse relation with temperature was observed for the rate of the oxidation steps: at 860 °C they lasted 15 min, whereas they required 20 min at higher temperatures at least. Some cycles were performed at 920 °C, using H₂O instead of CO₂ for the oxidation steps. This time the reduction steps were limited to 6 min for a reduction degree of about 40%. The rates of the reaction with H₂O were remarkably higher than those with CO₂, as the oxidation steps lasted 6-7 min.

4. Conclusions

Preliminary results of chemical looping reforming of methane with the perovskite material show good reactivity at relatively low temperatures and a potential global yield of about 0.3 Nm³ of syngas per kg with H₂:CO ratios of 1 or 3 depending on whether CO₂ or H₂O is splitted during the oxidation step. Experimental tests for solar chemical looping reforming of methane with CO/H₂ production are currently ongoing.

References

- [1] G. Luciani, G. Landi, A. Aronne, A. Di Benedetto, Sol. Energy 171 (2018) 1–7
- [2] C. Tregambi, S. Padula, M. Galbusieri, G. Coppola, F. Montagnaro, P. Salatino, R. Solimene Powder Tech (2019)