

Production of extra pure H₂ in a single step via an energy efficient methane reforming process by coupling Calcium and Chemical Looping

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Highlights

- Experimental demonstration of low energy sorption enhanced chemical looping reforming.
- An extra pure H₂ stream (~99%) is produced in a single step.
- CaO/CaZrO₃ sorbent demonstrates high capacity and remarkable stability in multiple cycles.
- Ni reoxidation can cover substantial part of the heat for sorbent calcination.

1. Introduction

Sorption enhanced chemical looping steam methane reforming (SE-CL-SMR) is an alternative method for the efficient production of pure hydrogen in a single step (~95%), combining chemical looping steam methane reforming with in-situ CO₂ capture [1]. In this process, the reformer contains a CO₂ sorbent and an oxygen transfer material (OTM). In the first step of this cyclic process, the oxide is reduced by CH₄ and catalyzes the reforming reaction of CH₄. The CO₂ formed is captured by the sorbent shifting the equilibrium of reforming and WGS towards the production of pure H₂. The reaction proceeds under near autothermal conditions due to the heat released by the strongly exothermic carbonation. In a second step, the saturated sorbent is regenerated, with the energy provided by the exothermic OTM re-oxidation. Aiming at further increase of H₂ purity, the use of a fixed bed reactor with multiple zones of descending temperature along the reactor length has been proposed, in order to facilitate both catalytic steam reforming at the high-temperature section and the exothermic WGS and carbonation reactions at the low-temperature part of the reactor [2]. Herein, we demonstrate experimentally the feasibility of the SE-CL-SMR process with varying reactor temperature profile over a mechanical mixture of a NiO/ZrO₂ OTM with a CaO/CaZrO₃ sorbent for high purity H₂ production with low thermal demands.

2. Methods

Material synthesis: The NiO-based OTM was prepared via wet impregnation using a commercial ZrO₂ support with 40wt% NiO loading [3]. The CaO-based sorbent was prepared via sol-gel auto-combustion route, using citric acid as combustion agent and CaZrO₃ as structural promoter, with 66wt% CaO concentration [4].

SE-CL-SMR experiments: The SE-CL-SMR experiments were conducted in fixed bed flow reactor using a mechanical mixture of NiO/ZrO₂ with CaO/CaZrO₃ at fixed NiO/CaO ratio. For these tests, the materials were initially exposed to CH₄/steam with S/C=3 and GHSV=350 h⁻¹. Reforming step was carried out with the temperature profile of the reactor ranging from 550 to 700°C as shown in the schematic representation of material bed included in Fig. 1. After sorbent saturation, the feed was switched to pure oxygen for reoxidation of Ni and regeneration of CaCO₃ at higher temperature (800°C).

3. Results and discussion

The composition of the reformate gas on dry basis during the reforming stage for the OTM/sorbent mechanical mixture is shown in Fig. 1a. During the pre-breakthrough period, where NiO reduction, reforming and water gas shift reactions are carried out simultaneously with in-situ CO₂ capture, very high H₂ concentration was observed (~99%), due to the lower temperature at the bottom of the reactor that facilitates carbonation and WGS reaction to higher extent. At this low temperature (550°C) it was possible to attain CO

and CO₂ concentrations as low as 0.05%, with no further purification of the produced H₂ stream required. Pre-breakthrough period was followed by a transitional period, where the sorbent was gradually saturated (breakthrough period) leading to an increase of CO, CO₂ and CH₄ and decrease of H₂ concentration. Although almost complete CH₄ conversion is reached from the beginning of the reforming stage, H₂ yield is relatively low (82%) during the first ~10min, indicating that during this short period part of CH₄ is consumed for NiO reduction. After complete NiO reduction, the reactor runs under conditions of simple SE-SMR process with higher H₂ yield (~95%), which is somehow higher than the thermodynamically dictated (91%) at 550°C (Fig. 1b). The higher temperature in the upper part of the bed (700°C) explains this deviation. After CaO saturation, the reformat gas obtained at the exit of the reactor has composition that approaches that of conventional reforming (post-breakthrough). When the flow was switched to oxygen and for almost 9 minutes no additional external heating was applied to the reactor, since the heat generated by Ni reoxidation was more than enough to sharply increase the temperature of the solid and supply almost 40% of the heat requirements for the strongly endothermic sorbent regeneration reaction (Fig. 1c).

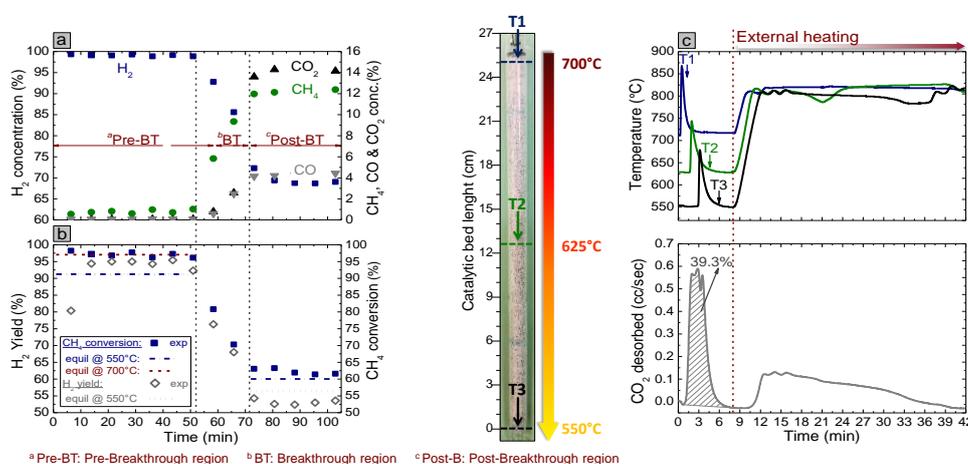


Figure 1. Product concentration (a), CH₄ conversion and H₂ yield (b) as a function of time during the reforming stage and temperatures and CO₂ desorption profiles as a function of time during the regeneration stage (c).

The stability of the materials under cyclic SE-CL-SMR operation was tested for 30 reforming/regeneration cycles. During this test, the regeneration step was carried out without applying additional external heating for a short period (~10min) which was enough for the complete reoxidation of the OTM and the partial calcination of the sorbent (40%). Thus, the sorbent returned in the reforming step in a partially regenerated state in the subsequent cycles while regeneration proceeded under autothermal conditions. The materials exhibited excellent stability without deterioration in their performance. Similarly high H₂ purity and pre-breakthrough duration were recorded for 30 cycles (not shown for brevity).

4. Conclusions

The combined experiment over OTM/CO₂ sorbent mechanical mixture demonstrated the feasibility and high potential of the proposed process. During the reforming step, the use of multiple temperature zones resulted in almost complete CH₄ conversion and production of extra pure H₂ (~99%). During the initial stage of regeneration, the heat generated by Ni reoxidation was adequate to sharply increase the temperature of the solid, causing the decomposition of a substantial part of the saturated CaCO₃ without external heating.

References

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Keywords

Ca–Ni looping; Sorption enhanced chemical looping reforming; High-purity hydrogen; High energy efficiency.