



# Catalyst evaluation for high-purity H<sub>2</sub> production by sorption-enhanced steam-methane reforming coupled to a Ca/Cu process



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## HIGHLIGHTS

- Catalyst applicability on SE-SMR coupled to a Ca/Cu process was evaluated.
- Parameters such as temperature, space velocity and cyclability were assessed.
- Catalyst deactivation was only apparent after 200 oxidation-reduction cycles.
- Positive results at optimal conditions support further development of the process.

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## ABSTRACT

The operational limits of a commercial nickel-based catalyst under the conditions of a sorption-enhanced steam-methane reforming process coupled to a Ca/Cu chemical loop are investigated for high-purity H<sub>2</sub> production in a cyclic operation. The performance of the reforming catalyst is tested by means of a high number of oxidation-reduction-reforming cycles. After 100 oxidation-reduction cycles, this catalyst retains its exceptional reforming activity. The methane conversion values are close to the thermodynamic equilibrium under very demanding conditions: temperature between 500 °C - 700 °C and mass hourly space velocity of 8.8 kgCH<sub>4</sub> h<sup>-1</sup> kgcat<sup>-1</sup>. After 200 cycles, the sample shows reduction in its reforming activity in line with a lower dispersion of the Ni species. Sintering of Ni nanocrystals is evidenced during the oxidation-reduction multi-cycles. The performance of the catalyst after 200 oxidation-reduction cycles mixed with a CaO-based CO<sub>2</sub> sorbent is studied under optimal conditions calculated for the sorption-enhanced reforming process coupled to a Ca/Cu cycle (temperature of 650 °C, steam/methane ratio of 4, sorbent/catalyst ratio of 4 and space velocity of 0.75 kgCH<sub>4</sub> h<sup>-1</sup> kgcat<sup>-1</sup>). Remarkably, an equilibrium value over 92 vol.% H<sub>2</sub> concentration is achieved, highlighting this catalyst as a promising candidate for the next steps of the process development.

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## 1. Introduction

Hydrogen production worldwide is currently at a rate of more than 50 million tonnes per year [1], and its demand for both chemical and energy industries is expected to increase in the medium to long term [2]. Steam-methane reforming (SMR) is the most commonly used process for the production of hydrogen; however, this process emits high levels of CO<sub>2</sub>, an average of close to 7 kgCO<sub>2</sub> kgH<sub>2</sub><sup>-1</sup> [3], which is a by-product of the reforming process and the additional combustion of CH<sub>4</sub> required by the steam reformer. Therefore, SMR does not meet market requirements of low CO<sub>2</sub>

emission levels and high-energy efficiency [4]. CO<sub>2</sub> capture is currently seen as a promising way to decrease global CO<sub>2</sub> emissions, and there is great interest worldwide in developing new CO<sub>2</sub> capture technologies for the purpose of reducing the energy penalty. The sorption-enhanced steam-methane reforming (SE-SMR) process for hydrogen production, may fulfil this need. The concept behind this process is based on the use of a reforming catalyst in combination with a selective regenerable solid sorbent to remove CO<sub>2</sub> in situ from the reaction zone [5]. This way, most of the 15–20% CO<sub>2</sub> present in the effluent gases from the SMR process can be captured. Additionally, CO<sub>2</sub> removal from the gas phase in the reaction zone shifts the equilibrium of the reversible reactions of SMR and water gas shift (WGS), enhancing hydrogen production from approximately 80% to 95% (dry basis) [6] based on Le Chatelier's principle. Other potential advantages of SE-SMR when compared to

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SMR have been already pointed out in the literature, such as the reduction in reaction temperature, lower by-product formation, elimination of WGS reactor, etc. [7], which is why this process has received much attention over the last two decades [8,9]. However, the SE-SMR process requires the addition of a sorbent regeneration stage in order to be able to perform cyclically once the CO<sub>2</sub> sorbent is saturated. Accordingly, the SE-SMR process has been studied in different configurations, such as fixed bed under atmospheric or high pressure, and in fluidized and bubbling bed systems [10]. Nevertheless, combined strategies for hydrogen production with CO<sub>2</sub> capture focused on reducing the associated costs and energy penalty are still at a very early stage of development.

J. C. Abanades et al. [11] have developed a process that uses the well-known principals of SE-SMR for H<sub>2</sub> production with CaO/CaCO<sub>3</sub> chemical loop, coupled to a second Cu/CuO chemical loop that solves the problem of endothermic CaCO<sub>3</sub> calcination [12]. There has been an intense work in the recent years for the further development of the Ca/Cu looping process for H<sub>2</sub> production and or power generation compiled in a recent overview by Fernandez and Abanades [13]. The initial works presented the conceptual design of the process [11,14] and relevant works have been focused on reactor modelling [7,15–17] and process integration [18–21] to demonstrate the implementation of the concept on large-scale H<sub>2</sub> production process. Reaction stages involving Ca and Cu solids have been experimentally studied at laboratory scale [22,23] and simultaneous CuO reduction/CaCO<sub>3</sub> calcination up to TRL4 [24]. The experimental studies on SER stage under relevant conditions of the process are currently scarce nevertheless high H<sub>2</sub> production efficiencies have been corroborated for a mixture of CO<sub>2</sub>-sorbent with fresh or aged reforming catalyst at different mass hourly space velocities and pressures [25]. The basic Ca/Cu looping process consists of a sequence of three main reaction steps (see Fig. 1), which are adiabatically carried out in fixed-bed reactors operating in parallel at different reaction steps to make a continuous looping operation feasible. Narrow and precise operating windows have been defined for the conceptual design of the process [7,14,15]. Accordingly, the optimal operation conditions calculated for the reforming stage are 650 °C–750 °C, 5 bar–15 bar, a steam to carbon ratio of 3–6 and a mass flow velocity (CH<sub>4</sub>+steam) of 3.5 kg m<sup>-2</sup> s<sup>-1</sup>. The high exothermicity of Cu oxidation permits the generation of an exit gas stream at a high temperature of 830 °C to allow energy recovery [14] and the calcination reaction, together with the exothermic reduction of CuO, is carried out at a high temperature ranging between 850 °C and 870 °C. One of the actual challenges is to find appropriate materials that withstand the

typical Ca/Cu process conditions and are able to work in multi-cyclic operation (oxidation-reduction/calcination-reforming cycles). A focus on the evolution of every material involved in the process in a high number of these multiple cycles is required before furthering the development of the technology.

With regard to catalysts applicable to the SE-SMR process coupled to a Ca/Cu cycle, commercial SMR catalysts developed to be applied at high temperature and pressure (typically 800 °C–900 °C and 15 atm–20 atm) [3] have been used successfully in SE-SMR processes [26–40]. In these studies, the reforming step was carried out at remarkably reduced temperatures and pressures (400 °C–750 °C and 1 atm–15 atm) [26–40]. For the sorbent regeneration step, these studies changed temperature and reaction atmospheres to calcination conditions (550 °C–1000 °C, and steam, diluted air or inert gas) [8,27,36–41]. Periodical changes in the catalyst environment produce enlargement and reduction of molar volumes from reduced metallic Ni<sup>0</sup> to oxidized NiO [10,36], which can negatively affect catalyst performance. Likewise, catalysts can suffer from carbon formation and oxidation by steam effect [42], formation of spinels [43], agglomeration of Ni crystallites [36], and Ni crystallite growth [37,42]. Although catalyst stability is a key parameter for the potential development of the process, there is little information regarding the effect of reforming-regeneration cycling on the activity of commercial catalysts for SMR [27,36–40]. In relation to the high number of cycles, Lysikov et al. [36] studied the influence of RedOx cycling in a pristine catalyst consisting of nano-sized nickel oxide with an average diameter of 5–10 nm and reported an increase in the active component of up to 100–200 nm after 100 cycles. Lopez-Ortiz and Harrison [37] reported a different increase in the Ni crystallites with regard to size and growth pattern depending on the regeneration temperature under an inert atmosphere. For the first 5 cycles the active phase presented a similar increase for both regeneration temperatures of 800 °C and 950 °C, to 25.4 nm and 26.3 nm, respectively. However, an additional increase occurred at 950 °C with diameters reaching 32.2 nm in the 15th cycle, compared to the increase in the crystallite produced by regeneration at 800 °C, to 27.2 nm after 25 cycles.

The aim of the present research was to study the limits for application of a commercial catalyst provided by Johnson Matthey<sup>®</sup> (HiFUEL<sup>®</sup> R110) under conditions of SE-SMR coupled with a Ca/Cu chemical loop. The experiments were initially performed without sorbent to allow close monitoring of the reforming activity and the evolution of catalyst properties after multi-cyclic oxidation-reduction tests. To our knowledge, this is the first time in the literature that an evaluation has been made of catalyst performance during the cyclic operation of the SE-SMR process involving reforming-oxidation-reduction stages. The material was placed in an atmospheric fixed bed reactor system and endured consecutive stages of oxidation at 850 °C under O<sub>2</sub> rich atmosphere and reduction at 850 °C with H<sub>2</sub>, in an attempt to mimic the different stages defined in the process under study. Catalyst performance was evaluated under different conditions of temperature and mass hourly space velocity (MHSV). The catalyst was subsequently cycled through 200 oxidation-reduction steps in order to study its SMR catalytic stability and its performance in a proper SE-SMR process with a sorbent.

## 2. Experimental

A commercial SMR Ni-based catalyst with 15.9–20.0 wt% Ni content, as determined by element analysis within this current study, and supported on CaAl<sub>2</sub>O<sub>4</sub> was supplied by Johnson Matthey, HiFUEL<sup>®</sup> R110. This solid was received in a 4-hole quadrilobe pellet form, and was crushed and sieved to a particle size between 100 μm and 200 μm for the experiments.

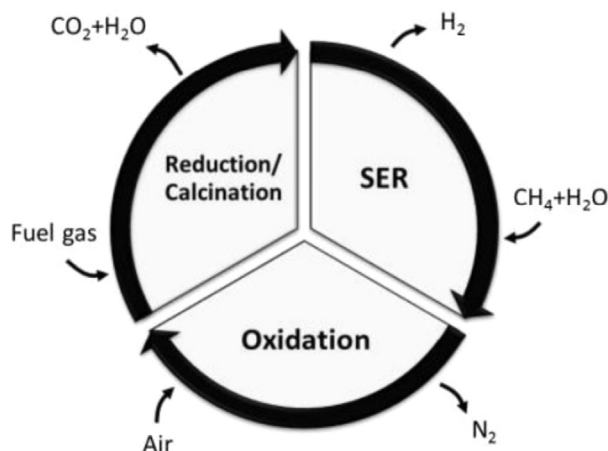


Fig. 1. H<sub>2</sub> production Ca/Cu looping process concept from Grasa et al. [25].

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