

# Intensification of sorption enhanced steam methane reforming for production of high purity hydrogen

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Doctoral thesis extended abstract

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## Summary

The present doctoral thesis was focused in the development of a novel reforming process, by combining in-situ CO<sub>2</sub> capture with chemical looping concept. The proposed process, namely *Sorption Enhanced Chemical looping Steam Methane Reforming (SE-CL-SMR)*, provides a path for intensified conversion of natural gas directly to high-purity hydrogen with reduced energy demands. In order to overcome significant obstacles towards ensuring the proposed proof-of-concept, a series of research activities were conducted, including thermodynamic calculations, advanced materials development and testing in bench-scale apparatuses. Initially, a detailed thermodynamic analysis of the proposed process was conducted to determine the window of optimum operating parameters. The calculations ensured that SE-CL-SMR can lead to increased H<sub>2</sub> purity and lower energy demands, resulting in superior performance compared to conventional reforming process.

Furthermore, research was focused on the development and extensive evaluation of CaO-based CO<sub>2</sub> sorbents and NiO-based oxygen transfer materials identified the best materials for implementation. On this task, the development of mixed CaO-based sorbents that exhibit significant stability was performed. Among the studied structural promoters, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> resulted in the most stable sorbents. The improved stability of these materials was ascribed to the formation of the mixed phases Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaZrO<sub>3</sub>. The best performing sorbent (CaO/CaZrO<sub>3</sub>) was further tested in fixed and fluidized bed reactor units, with the material exhibiting very high carbonation conversion under all investigated conditions. Regarding the NiO-based oxygen transfer materials, the different support materials showed their significant impact on both NiO reduction and selectivity towards H<sub>2</sub> production. Conventional reforming experiments at low temperature (650°C) demonstrated satisfactory performance of reduced NiO on Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub>, NiAl<sub>2</sub>O<sub>4</sub> or MgAl<sub>2</sub>O<sub>4</sub>. The most promising materials were tested under chemical looping steam methane reforming conditions for twenty redox cycles. Among the studied materials, NiO/ZrO<sub>2</sub> exhibited good activity with high initial CH<sub>4</sub> conversion (>80%) and minimal deactivation after 20 redox cycles.

The developed materials were evaluated under the determined optimal conditions of the proposed scheme, providing experimentally the proof-of-concept of the SE-CL-SMR process. Further on, a comprehensive parametric analysis was performed to ensure that production of high purity hydrogen (up to 99%) with reduced energy demands is feasible. The process was further demonstrated with continuous cyclic tests. The materials exhibited excellent stability without deterioration in performance for up to 30 cycles, corresponding to more than 30 h under reaction conditions. The results derived from this work are expected to significantly advance progress towards future commercialization of the proposed concept.

## Introduction

### *State of the art*

Decreasing availability of fossil resources, together with the environmental issues related to the fossil-derived greenhouse gas emissions, have dictated the necessity for further improvements in the efficiency of energy production processes as well as the transition towards sustainable resources. In this context, hydrogen is heavily supported as an energy carrier, as it is expected to play a key role in the necessary transition from fossil fuels to a sustainable energy future. Likewise, hydrogen demands as a primary industrial gas are continuously increasing in the petroleum refining, mainly driven by clean fuel regulations.

Hydrogen however, is produced almost entirely from fossil fuels. Steam reforming of methane (SMR), the dominant large-scale technology for hydrogen production, accounts for almost 50% of the worldwide production. It has been widely practiced for several decades as an effective means for converting hydrocarbons into hydrogen in the presence of steam. Although a mature and well-established technology, it still remains very energy intensive, involving multiple steps and severe operating conditions (temperatures in the range of 800–900°C and elevated pressures of 20–30 atm) [1]. In steam reforming process the overall carbon footprint is very high, due to secondary streams that contain CO<sub>2</sub>, such as the flue gases from the reforming furnace. Moreover, despite the CO<sub>2</sub> separation system after the PSA unit, quantities of CO<sub>2</sub> are also vented during the purging of the PSA columns. Apart from the challenges in the hydrogen production process, one should also take in to account that the global consumption of hydrogen is forecast to increase in the upcoming years. This growth is mainly driven by clean fuel regulations, enacted to address environmental and pollution concerns. Moreover, due to its CO<sub>2</sub>-free combustion, hydrogen is heavily supported as the energy carrier of the future and is expected to play a key role in the necessary transition from fossil fuels to a sustainable energy future.

It becomes evident that a novel technology for large-scale hydrogen production with high efficiency, low energy requirements and low carbon footprint is required. At this direction, process intensification is considered as one the most effective ways, with research efforts focused in the recent decades on several new, intensified reforming concepts for hydrogen production that operate at milder conditions, with increased efficiency, lower carbon footprint and lower production costs, such as membrane assisted reforming [2,3], sorption enhanced reforming [4–6] and chemical looping reforming [7–9].

Sorption enhanced steam methane reforming (SE-SMR), has recently attained a growing interest in the scientific community [10–12]. The SE-SMR process combines the reforming reaction system (reforming & water gas shift reactions – *Eq. 1 & 2*) in a single vessel by introducing a high-temperature solid sorbent material. Capture of CO<sub>2</sub> directly at its production in this reaction configuration, overcomes the equilibrium limitations of the reforming and WGS reactions and leads to significant improvement of the reactant conversion. In addition, increased hydrogen selectivity is attained in a single step, as a result of shifting the equilibrium of the overall reaction to the product side (*Le Chatelier's principle*). This leads to process intensification, as it decreases the size of downstream separation stages or even eliminates the need for them.

Among the potential sorbents for the SE-SMR process, probably the most attractive materials are CaO-based solids due to their wide availability, low cost, high theoretical CO<sub>2</sub> sorption capacity and fast carbonation/calcination kinetics [13]. In addition to the above benefits, the use of a CaO-based sorbent in the reformer has another significant advantage. The heat generated by the strongly exothermic sorbent's carbonation reaction (*Eq. 3*) can be consumed in-situ for the highly endothermic reforming reaction (*Eq. 1*), alleviating the need for direct fuel combustion. Moreover, the reaction

enhancement enables lower operation temperatures (600–700°C), reducing problems associated with high process energy requirements and poor energy integration within the plant.



As the sorbent is effectively consumed in the reformer, the process is inherently dynamic in operation, requiring a regeneration step. Regeneration however requires a high amount of energy in order to heat the solid and drive the endothermic  $\text{CaCO}_3$  calcination (reverse reaction 3). The formed  $\text{CaCO}_3$  can be decomposed at higher temperatures (>800°C) in the presence of a suitable sweep gas, producing a pure  $\text{CO}_2$  stream ready for sequestration or further use.

In order to overcome the energy penalty in SE–SMR process, addition of a second solid looping cycle based on chemical looping reforming has been proposed [14,15]. *Lyon and Cole (General Electric)* [15] were the first to propose the use of chemical looping concept, which involves oxidation of a fuel with oxygen from a solid oxygen transfer material (OTM), as an interesting concept for autothermal  $\text{H}_2$  generation through reforming processes. In chemical looping reforming, the methane/steam feed and the air feed are not mixed as in conventional autothermal reforming. Oxygen is instead provided by an OTM which is reduced in the presence of  $\text{CH}_4$ . Re-oxidation of the OTM with air in a subsequent regeneration cycle is highly exothermic and provides the heat to drive the endothermic reforming reactions in the methane/steam cycle. Pure oxygen production plant, which is needed in conventional autothermal reforming, is avoided and undiluted high purity  $\text{H}_2$ , with small quantities of  $\text{CO}_2$  and  $\text{CO}$ , can then be produced. Lyon and Cole went one step further and additionally proposed the coupling of sorption enhanced reforming with the chemical looping reforming concept. This combined intensified process is known as *Sorption Enhanced Chemical Looping Steam Methane Reforming (SE–CL–SMR)*. In this case, the exothermic sorbent carbonation reaction provides the necessary heat for the endothermic steam reforming reaction during the reforming cycle, while regeneration of the sorbent is driven by the OTM re-oxidation in the regeneration cycle. The coupling of both endothermic and exothermic reactions in one single step favors a better thermal integration, as heat is directly transferred from the oxygen transfer material to the calcium carbonate during regeneration stage without the need for intermediate heat exchange devices.

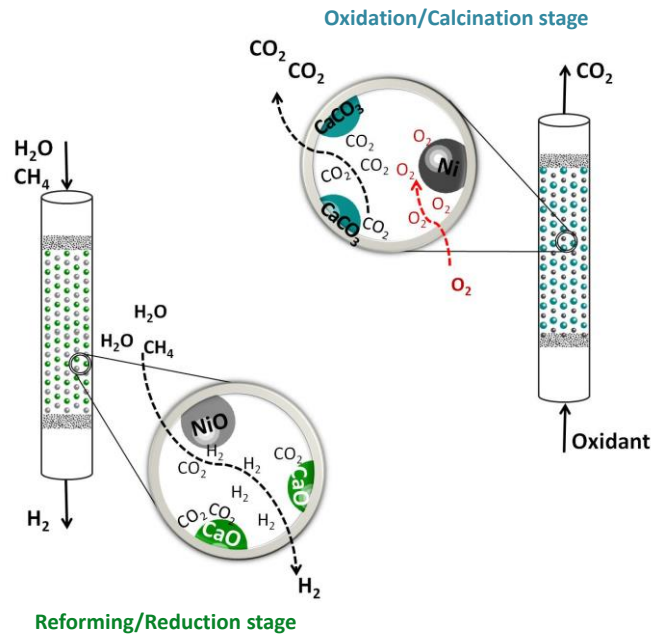
As discussed above,  $\text{CaO}$ -based  $\text{CO}_2$  sorbents are the most established materials used in sorption enhanced processes. Among the various metal oxides studied as potential OTMs,  $\text{NiO}$  appears to be the most promising candidate for chemical looping reforming processes as apart from the high oxygen transfer capacity, metallic  $\text{Ni}$  displays excellent catalytic properties for steam methane reforming and water gas shift reactions [16,17].

The two stages can operate either under fixed-bed configuration, where at least two reactors run alternately under reforming and regeneration conditions, or under circulating fluidized bed conditions in two interconnected reactors, with the OTM and the  $\text{CO}_2$  sorbent particles as bed material. The reforming reactor would contain a suitable  $\text{CaO}$ -based sorbent together with a  $\text{NiO}$ -based OTM as bed materials. In the regenerator, an oxidant flow (e.g. air, steam, pure  $\text{O}_2$  or  $\text{CO}_2$ ) would be used as sweep gas to facilitate  $\text{CO}_2$  removal from the saturated sorbent. The complete reaction scheme is provided through *Eq. 4–12* in Table 1 at both consecutive stages shown in Figure 1. During reforming stage, in addition to the reforming, WGS and carbonation reactions,  $\text{NiO}$  is reduced by partial and total oxidation reactions of  $\text{CH}_4$  (*Eq. 6 & 7*). Reduction by the produced reformat gas ( $\text{H}_2$ ,  $\text{CO}$ ) and more likely by  $\text{H}_2$ , due to its high partial pressure in the system, cannot be excluded. In the second step,  $\text{Ni}$  is reoxidized to  $\text{NiO}$ , providing the required heat for  $\text{CaCO}_3$  calcination.

## Introduction

**Table 1:** Overall reaction scheme during SE–CL–SMR process

Reduction/Reforming Stage		
$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow 3\text{H}_2 + \text{CO},$	$\Delta H_{298\text{K}} = 206\text{kJ/mol}$	(4)
$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2,$	$\Delta H_{298\text{K}} = -41\text{kJ/mol}$	(5)
$\text{CH}_4 + \text{NiO} \leftrightarrow \text{CO} + \text{H}_2 + \text{Ni},$	$\Delta H_{298\text{K}} = 203\text{kJ/mol}$	(6)
$\frac{1}{4}\text{CH}_4 + \text{NiO} \leftrightarrow \frac{1}{4}\text{CO}_2 + \frac{1}{2}\text{H}_2\text{O} + \text{Ni},$	$\Delta H_{298\text{K}} = 31\text{kJ/mol}$	(7)
$\text{H}_2 + \text{NiO} \leftrightarrow \text{H}_2\text{O} + \text{Ni},$	$\Delta H_{298\text{K}} = -2\text{kJ/mol}$	(8)
$\text{CO} + \text{NiO} \leftrightarrow \text{CO}_2 + \text{Ni},$	$\Delta H_{298\text{K}} = -43\text{kJ/mol}$	(9)
$\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3,$	$\Delta H_{298\text{K}} = -178\text{kJ/mol}$	(10)
Oxidation/Regeneration stage		
$\text{Ni} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{NiO},$	$\Delta H_{298\text{K}} = -240\text{kJ/mol}$	(11)
$\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2,$	$\Delta H_{298\text{K}} = +178\text{kJ/mol}$	(12)

**Figure 1.** Sorption Enhanced Chemical Looping Steam Methane Reforming concept*Problem addressed*

Apart from the initial work by *Lyon and Cole* [15] which included the basic concept and preliminary experiments, only a few publications have been devoted to the study of the process and specifically to the energy efficiency during regeneration stage. The major challenge in all cyclic processes is the stability of the materials and, in this case, especially of the CaO–based sorbent. Even though pure CaO derived from natural sources such as limestone is a very attractive material, due to low cost and wide availability, it suffers from sintering and intense loss of capacity over multiple cycles. Even though this loss can be well tolerated for the cheap limestone, provided relatively high make up rates in the case of utilizing the sorbent for post–combustion CO<sub>2</sub> capture applications such as carbonate looping, this may not be the case for a more complex process such as SE–CL–SMR. The reactivity of the sorbent should be compatible with that of the OTM/reforming catalyst, in order to provide a sufficient materials management over multiple reforming/regeneration cycles and render the process

economically viable. From the above, it can be deduced that significant breakthroughs with regards to materials development and evaluation under relevant conditions and process optimization are still ahead, in order to establish this intensified concept as a key route for sustainable hydrogen production.

The aim of this doctoral thesis was the development of a novel efficient, low-carbon process for hydrogen production via sorption enhanced chemical looping methane reforming. In order to address this challenge, this dissertation systematically delved into several aspects through a series of research activities, including computational analysis, material preparation and evaluation under the conditions of the proposed process concept. Initially, preliminary design and thermodynamic calculations were conducted in order to determine the optimum window of operating parameters. For the next step, having as a guideline that the key for the successful implementation of the process is the identification of effective materials, extensive work was conducted on the development of advanced CO<sub>2</sub> sorbents and oxygen transfer materials with enhanced reactivity and stability. A particularly important aspect of this thesis was also the development of hybrid multi-functional catalytic materials, possessing good oxygen transfer characteristics, significant reforming activity and stable CO<sub>2</sub> sorption capacity. The structural and morphological properties of the developed materials can play a crucial role in their performance in the target reactions. Therefore, reaction tests were supplemented with detailed characterization of the materials before and after the tests in order to elucidate possible modifications occurring under the investigated conditions. The developed materials were evaluated under the determined optimal conditions of the proposed scheme, providing experimentally the proof-of-concept of the SE-CL-SMR process. Further on, a comprehensive parametric analysis was performed in order to ensure that production of extra pure hydrogen (up to 99%) with reduced energy demands is feasible through a compact operating scheme. The results derived from this work are expected to significantly advance progress towards future commercialization of the sorption-enhanced chemical looping steam methane reforming concept, as well as the scientific understanding of the phenomena occurring in the combined process. The key points of this thesis are summarized below.

## Key Innovations, Implementations and Results

### *Thermodynamic analysis of SE-CL-SMR process*

Since the reactions taking place in the combined reforming process are thermodynamically limited, it was considered important to initially determine the window of optimum operating parameters and detect the advantages and disadvantages of the concept compared to sorption enhanced reforming and the conventional steam reforming process. The effect of different parameters, such as reactor temperature, pressure, H<sub>2</sub>O/CH<sub>4</sub> ratio, CaO/CH<sub>4</sub> ratio and CaO/NiO ratio was investigated. Moreover, the use of different sweep gases and oxidants for the re-oxidation/calcination cycle, like pure oxygen, air, steam and CO<sub>2</sub>, was specifically addressed. Conventional steam reforming (SMR) and sorption enhanced steam reforming (SE-SMR) were also investigated for comparison reasons [18].

The results of thermodynamic analysis showed significant advantages of both sorption enhanced processes compared to conventional steam reforming for H<sub>2</sub> production at lower temperatures. The reason for the improved performance of the sorption enhanced processes is the addition of the CaO sorbent in the reforming reactor, leading to higher methane conversion at low temperatures (~650°C) and to higher product purity. Moreover the in-situ capture of the produced CO<sub>2</sub> and the release of a sequestration-ready CO<sub>2</sub> stream during the regeneration stage minimize the steps and the cost of the overall process. However, the main issue with the simple sorption enhanced reforming process is the heat required for the regeneration of the sorbent. The addition of NiO, in the case of sorption enhanced chemical looping steam methane reforming, leads to minimization of thermal requirements of the process, demonstrating the superiority of this process compared to conventional SMR and SE-SMR.

Investigation of the type of oxidant which can be used for re-oxidation/regeneration showed that only air or pure O<sub>2</sub> can be used to reduce the energy requirements of the SE-CL-SMR process up to 33% compared to the SE-SMR, and up to 53% compared to the conventional SMR, when the optimum operating conditions for each process are used. The choice between air or pure oxygen is a matter of techno-economic evaluation. Use of air requires the use of separate reactors for re-oxidation and calcination (resulting therefore in increased equipment cost and less efficient heat integration), whereas use of oxygen requires an air separation unit. The use of CO<sub>2</sub> or steam aggravates the energy balance as nickel re-oxidation is endothermic in these cases.

A negative effect from NiO addition in the sorption enhanced chemical looping steam methane reforming process is decrease in hydrogen production (due to reaction of part of methane with NiO to CO<sub>2</sub>), up to 11% for a NiO/CaO ratio of 0.7. For this ratio however the process's regeneration stage can run essentially under autothermal conditions. The optimum operating windows according to thermodynamics are summarized in Table 2.

**Table 2:** Optimum operating conditions of SE-CL-SMR process

Reforming cycle	Regeneration cycle
Temperature: 550–650°C	Temperature: 850–900°C
Pressure: 1–4 atm	Pressure near atmospheric
Steam/Carbon ratio: 3	Type of oxidant: air or oxygen
CaO/Carbon ratio: 0.8–1	
NiO/CaO ratio: 0.2–0.7	

### *Materials development and preliminary testing*

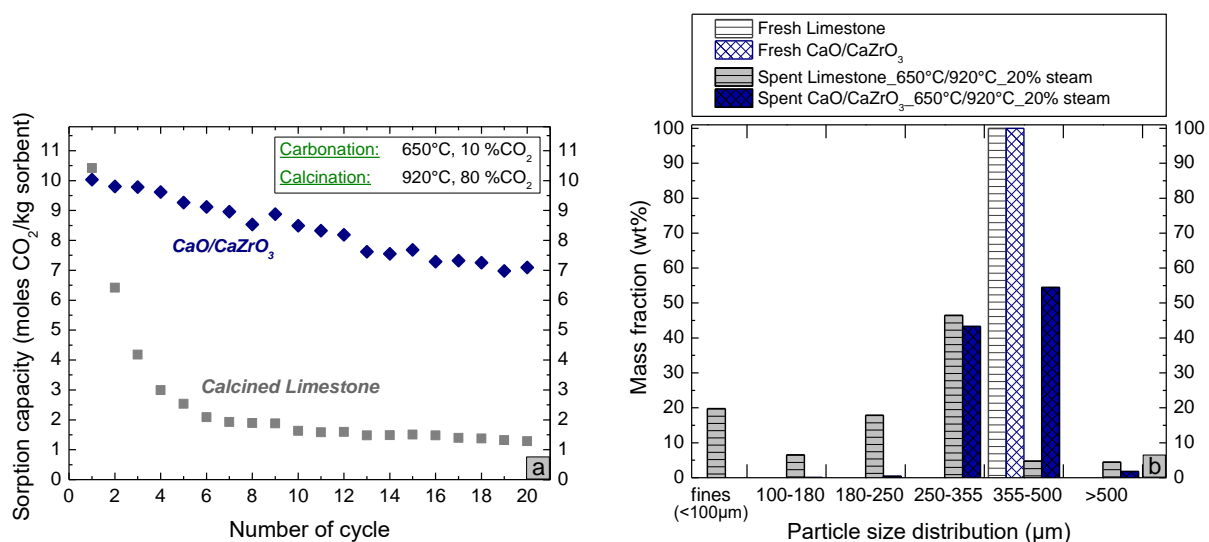
Taking into consideration that the key for the successful commercialization of the process is the identification of effective materials, extensive work was conducted on the development, performance evaluation and detailed characterization of two series of materials with enhanced reactivity and stability: **CaO-based CO<sub>2</sub> sorbents** and **NiO-based oxygen transfer materials**.

#### CaO-based CO<sub>2</sub> sorbent materials

Regarding the first group of materials, the development of mixed CaO-based CO<sub>2</sub> sorbents with inert structural promoters that exhibit significant stability was performed [19]. Different synthesis parameters were investigated. The type of combustion agent used during the synthesis influenced greatly the surface area and consequently, the CO<sub>2</sub> sorption capacity of the prepared CaO. Citric acid was identified as the most suitable combustion agent, resulting in the formation of CaO with the highest initial capacity and was further used for the development of the promoted sorbents. Among the different inert materials studied as structural promoters, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> resulted in the preparation of the sorbents with the most stable performance, with a sorption capacity higher than 9 moles CO<sub>2</sub>/kg of sorbent, corresponding to more than 78% carbonation conversion after 100 cycles in a thermogravimetric analyzer. Among the different inert materials studied as structural promoters, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> resulted in the most stable sorbents. The improved stability of these materials was ascribed to the formation of the mixed phases Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaZrO<sub>3</sub> as identified by X-ray diffraction, which create a strong framework that inhibits CaO grain growth during multi-cyclic experiments.

In addition to the intensification of thermodynamically limited processes, CaO-based sorbents can be also used for post-combustion CO<sub>2</sub> from the flue gases via *Carbonate Looping*. In this contest, the best performing CaO/CaZrO<sub>3</sub> sorbent was further evaluated in thermogravimetric analyzer and also a bench-scale unit equipped with fixed and fluidized bed reactors to determine its performance over various operating conditions. The material demonstrated superior performance, with high carbonation

conversion recorded during pre-breakthrough region (60–85%) under all investigated conditions. The addition of steam led to higher conversions, due to enhanced diffusion of  $\text{CO}_2$  through the formed layer of  $\text{CaCO}_3$ , while significantly improving the stability of the sorbent, resulting to <16% deactivation after 20 consecutive cycles. Characterization of the spent material with SEM showed that in the presence of steam, the morphology of the material was reconstructed, resulting in generation of additional pores during calcination in each cycle. The material demonstrated also an excellent performance with enhanced attrition resistance even under severe calcination conditions (a high  $\text{CO}_2$  partial pressure of 0.8 at  $920^\circ\text{C}$ ) as shown in Figure 2, maintaining more than 70% of its initial sorption capacity after 20 cycles, a value more than 5 times higher compared to natural limestone [20].



**Figure 2.**  $\text{CO}_2$  sorption capacity during pre-breakthrough period versus number of cycles (a) and particle size distribution before and after carbonate looping cycles (b) under severe calcination conditions for limestone and  $\text{CaO}/\text{CaZrO}_3$  sorbent (carbonation:  $650^\circ\text{C}$ , 10%  $\text{CO}_2/3.2\% \text{O}_2/20\% \text{H}_2\text{O}/\text{N}_2$ ; calcination:  $920^\circ\text{C}$ , 20%  $\text{H}_2\text{O}/\text{CO}_2$ ).

### NiO-based oxygen transfer materials/reforming catalysts

A series of NiO-based oxygen transfer materials over different commercial and lab-synthesized supports were developed. Their assessment included testing of the OTMs in their reduced form as reforming catalysts, as well as their evaluation in continuous reduction/reforming and re-oxidation cycles under *Chemical Looping Steam Methane Reforming (CL-SMR)* conditions [21].

Different support materials showed their significant impact on both NiO reduction and selectivity towards high  $\text{H}_2$  production. Conventional reforming experiments at low temperature ( $650^\circ\text{C}$ ) with pre-reduced OTMs demonstrated satisfactory performance of NiO supported on commercial  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{CeO}_2\text{-ZrO}_2\text{-La}_2\text{O}_3$  and lab-synthesized  $\text{NiAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$ , initial methane conversions in the 80–87% range and less than 10% decrease in conversion after 10 h time-on-stream. On the other hand, NiO/ $\text{SiO}_2$  and NiO/ $\text{TiO}_2$  exhibited low initial activity and rapid deactivation. Post-reaction characterization of representative active and inactive materials revealed that the most probable reason for deactivation is reoxidation of metallic Ni by steam during reaction on titania and silica supports.

The materials demonstrating the best catalytic activity were further tested for 20 cycles under *Chemical Looping Steam Methane Reforming* conditions. The OTMs exhibited high initial  $\text{CH}_4$  conversion, similar to that attained during conventional reforming. This result is important as it proves that NiO can indeed be reduced by  $\text{CH}_4$  in the presence of steam. The product concentration profiles during the reduction/reforming step showed that the reformat gas evolves almost simultaneously with the introduction of the  $\text{CH}_4$ /steam feed, indicating that reforming reactions occur as soon as some metallic nickel is formed on the surface of the solid. In terms of cyclic reactivity, NiO supported on  $\text{ZrO}_2$  showed the most promising results, in terms of both stability and NiO reducibility.

*Experimental Proof-of-Concept of SE-CL-SMR process*

The feasibility of the intensified reforming process was demonstrated experimentally over a mixture of the most promising CO<sub>2</sub> sorbent and OTM [22]. Production of a high purity H<sub>2</sub> stream in a single step with reduced energy requirements was demonstrated by utilizing a calcium loop of the Zr-promoted CaO sorbent and a second chemical loop of NiO/ZrO<sub>2</sub> OTM. Very high H<sub>2</sub> concentration of ~95% was achieved at 650°C for a CH<sub>4</sub>/steam feed ratio of 3. During the initial stage of the regeneration of the solids in air, the heat generated by Ni reoxidation was adequate to sharply increase the temperature of the reactor and decompose an adequate amount of the saturated CaCO<sub>3</sub> without external heat supply.

The process was further demonstrated with a continuous experiment of 20 cycles. The materials exhibited excellent stability without deterioration in their performance for 20 consecutive cycles, corresponding to more than 60 h of testing. Post-reaction characterization results were in line with the stable performance of the two solids, showing that the used CO<sub>2</sub> sorbent retains almost completely the surface area and porous characteristics of the fresh material. On the other hand, the surface area of the OTM underwent significant reduction after reaction, without however deterioration of its catalytic performance. Considering the very high loading of NiO (40 wt.%), the material is expected to be more prone to sintering. As high amounts of OTM are required to provide heat for the sorbent regeneration, it is anticipated that sintering would not affect the performance of the material in the actual process.

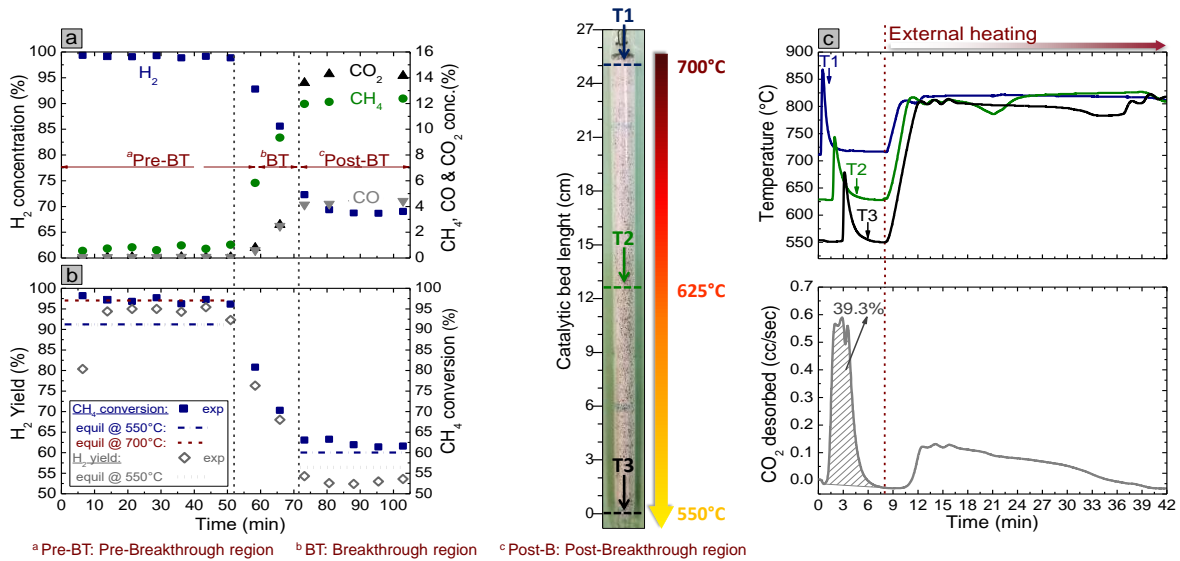
A comprehensive parametric analysis was performed in order to determine the optimum operating conditions towards maximization of H<sub>2</sub> purity and yield and minimization of the thermal requirements of the process. The presence of the CO<sub>2</sub> sorbent in the reactor facilitated H<sub>2</sub> production, resulting in high H<sub>2</sub> concentration, close to equilibrium, over the entire range of the investigated parameters. Even under more realistic conditions from the viewpoint of industrial application, (low S/C ratios, high GHSVs), the materials displayed excellent performance, with maximum H<sub>2</sub> purity being achieved.

Temperature was identified the most crucial parameter during reforming stage. Higher temperatures resulted in lower H<sub>2</sub> purity due to thermodynamic limitations of the exothermic carbonation reaction, while decrease of the reactor's temperature, even though favored the CO<sub>2</sub> capture, resulted in lower CH<sub>4</sub> conversion. In order to raise these limitations to produce extra pure H<sub>2</sub>, ready for direct industrial application without further processing, a different fixed bed reactor configuration was investigated by employing multiple zones of descending temperature along the length of the materials bed. Thus by facilitating both the catalytic steam reforming reaction at the high-temperature section (~700°C) and the exothermic WGS and carbonation reactions at the low-temperature bottom part (~550°C), it was possible to further increase the purity of the produced H<sub>2</sub> stream.

The composition of the reformat gas on dry basis during the reforming stage is shown in Figure 3a. During the pre-breakthrough period, where NiO reduction, reforming and water gas shift reactions are carried out simultaneously with *in-situ* CO<sub>2</sub> capture, very high H<sub>2</sub> 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 CO<sub>2</sub> concentrations as low as 0.05%, with no further purification of the produced H<sub>2</sub> 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, CO<sub>2</sub> and CH<sub>4</sub> and decrease of H<sub>2</sub> concentration. Although almost complete CH<sub>4</sub> conversion is reached from the beginning of the reforming stage, H<sub>2</sub> yield is relatively low (82%) during the first ~10min, indicating that during this short period part of CH<sub>4</sub> is consumed for NiO reduction. After complete NiO reduction, the reactor runs under conditions of simple SE-SMR process with higher H<sub>2</sub> yield (~95%), which is somehow higher than the thermodynamically dictated (91%) (Figure 3b). The higher temperature in the upper part (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 sorbent regeneration (Figure 3c).



**Figure 3.** Product concentration (a), CH<sub>4</sub> conversion and H<sub>2</sub> yield (b) versus time during the reforming stage and temperatures and CO<sub>2</sub> desorption profiles as a function of time during the regeneration stage (c).

In order to achieve optimal heat integration during regeneration stage different approaches were adopted. Increase of the NiO/CaO ratio in the materials bed up to 0.8 demonstrated that around 45% of the saturated sorbent can be decomposed by the heat from Ni reoxidation which is generated and utilized in-situ. The type of oxidant and the residence time of the feed stream in the reactor have a significant effect on the amount of sorbent material that can be regenerated without providing external heat to the reactor. For higher space velocities, an increase in regeneration's degree of autothermicity was observed. The use of pure O<sub>2</sub> can cover up to 55% of the heat requirements of the regeneration stage even at low space velocities compared to air, producing a pure CO<sub>2</sub> stream ready for sequestration. Moreover, the option of operating the regeneration stage of the process under substantially autothermal conditions was studied. This was made possible by partially regenerating the CO<sub>2</sub> sorbent. In this case, the regeneration took place for a short period of time and only with the heat supplied by the reoxidation of Ni. The ability of the sorbent to effectively remove the produced CO<sub>2</sub> during reforming stage was not affected, despite the fact that almost 2/3 of the material was already in carbonate form during the initiation of this step. The materials exhibited excellent stability without deterioration for up to 30 cycles, corresponding to more than 30 h under these reaction conditions.

Regarding the materials synthesis, a novelty of this thesis was the development of hybrid multi-functional materials that combine good oxygen transfer characteristics, significant reforming activity and stable CO<sub>2</sub> sorption capacity. The OTM/sorbent hybrid materials demonstrated very high catalytic activity and sorption capacity, producing of high purity H<sub>2</sub> comparable to that of the experiment with the mechanical mixture. The use of multifunctional materials is very promising as it can reduce the complexity and the volume of the reactor and consequently the cost of the SE-CL-SMR process.

The main results obtained in the present thesis revealed that there are significant advantages of the proposed process compared to conventional steam reforming. The SE-CL-SMR process is an innovative integrated single-stage route for high purity H<sub>2</sub> production with inherent CO<sub>2</sub> capture. The reformer can operate under nearly auto-thermal conditions, with very low overall carbon footprint, as the overall reaction is performed at lower temperature and most of the required heat is generated by CaO carbonation. The re-oxidation of the reduced oxygen transfer material can cover a large part of the heat required for the endothermic sorbent calcination.

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