



# Evaluation of process variables on the performance of Sorption Enhanced Methane Reforming



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## HIGHLIGHTS

- Calcination at oxidizing conditions does not affect the catalyst performance.
- Calcination using CO<sub>2</sub> and steam does not affect the sorbent performance.
- The SER step can operate at a relatively high mass hourly space velocity.
- It is possible to work at low H<sub>2</sub>O/CH<sub>4</sub> ratios and at sorbent-to-catalyst ratio of 8.
- Effective catalyst activity is promoted by the sorbent due to Le Chatelier principle.

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## ABSTRACT

The joint performance of a synthetic Ca-based sorbent and a 10%wt.NiO/NiAl<sub>2</sub>O<sub>4</sub> catalyst is tested under Sorption Enhanced Reforming (SER) of CH<sub>4</sub> in a fixed bed reactor. The effects of the mass hourly space velocity (MHSV, mol CH<sub>4</sub> h<sup>-1</sup> (g<sub>catalyst</sub> + g<sub>sorbent</sub>)<sup>-1</sup>), the sorbent-to-catalyst proportion (Z) for diverse steam-to-methane ratios (S/C) and the behavior of cycled solids under different regeneration conditions (by calcination under inert, oxidant, with steam and CO<sub>2</sub> atmospheres) are studied.

An H<sub>2</sub> concentration close to equilibrium (≈95 vol.% for S/C = 3.2) is achieved working at both lower (0.01 mol CH<sub>4</sub> h<sup>-1</sup> (g<sub>catalyst</sub> + g<sub>sorbent</sub>)<sup>-1</sup> or 769 h<sup>-1</sup>) and higher MHSV (0.04 mol CH<sub>4</sub> h<sup>-1</sup> (g<sub>catalyst</sub> + g<sub>sorbent</sub>)<sup>-1</sup> or 3000 h<sup>-1</sup>). The practical operation window for the combination of the sorbent and catalyst used should be below 0.044 mol CH<sub>4</sub> h<sup>-1</sup> g<sub>sorbent</sub><sup>-1</sup> and around 0.44 mol CH<sub>4</sub> h<sup>-1</sup> g<sub>catalyst</sub><sup>-1</sup>. The stabilities of both solids (sorbent and catalyst) working cyclically are demonstrated, despite the demanding and realistic regeneration environments used. Thus, H<sub>2</sub> purity close to equilibrium (≈88 vol.% for S/C = 2) is attained under SER conditions and no carbon deposition is found. In summary, the results obtained confirm the good joint performance of the synthesized solids in the SER process even when working under demanding conditions.

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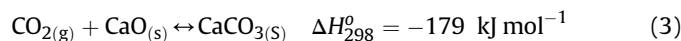
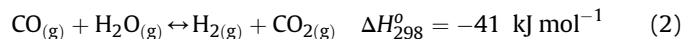
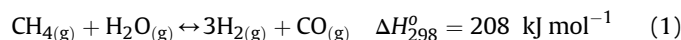
## 1. Introduction

Steam Methane Reforming (SMR) is the most well-established process for large scale hydrogen production [1–5]. Nevertheless, due to its high CO<sub>2</sub> production and severe operational conditions, it is necessary to develop new alternative and more efficient processes. In this context, Sorption Enhanced Reforming (SER) is a process that improves the traditional SMR, producing high purity H<sub>2</sub> and drastically lowering CO<sub>2</sub> emissions. This is possible by using

in the same reactor a reforming catalyst and a CO<sub>2</sub> acceptor which removes the CO<sub>2</sub> as soon as it is formed by reforming and water gas shift reactions. So, this process involves the reforming reaction, water gas shift reaction and the CO<sub>2</sub> capture by the CaO-based sorbent in a single step (Eqs. (1)–(3), respectively). At the same time, the CO<sub>2</sub> removal by the sorbent shifts the equilibrium to favor the formation of high H<sub>2</sub> concentrations, in accordance with the Le Chatelier principle (i.e., according to equilibrium calculations, at 650 °C, 1 atm. and at steam to methane ratio of 3.2, H<sub>2</sub> concentrations around 94.6 vol.%, dry basis, d.b. are expected, while CO and CO<sub>2</sub> remain at about 2.6 vol. %, d.b. and 1.8 vol.% d.b., respectively [6]).

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Besides, the energy required by the endothermic reforming reaction (Eq. (1)) is compensated for by the exothermic water gas shift (Eq. (2)) and carbonation reactions (Eq. (3)). It is therefore not necessary to provide the supplementary energy required in traditional SMR [3,4,7].

Once the sorbent is saturated it must be regenerated in an additional step by the calcination of  $\text{CaCO}_3$  to  $\text{CaO}$  at a high temperature that depends on the  $\text{CO}_2$  partial pressure [8]. Thus, SER is a looping process in which reforming-carbonation and calcination stages take place successively. Due to the continuous changes between such steps, it is necessary to have a mixture of solids able to operate under abrupt cyclic variations of temperature and chemical environment. In this way, the catalyst should be active at low temperatures ( $\approx 600 \text{ }^\circ\text{C}$ – $700 \text{ }^\circ\text{C}$ ) in the reforming-carbonation step, but also maintain its activity after the calcination step where the solid is submitted to higher temperatures ( $\approx 900 \text{ }^\circ\text{C}$ ) in an oxidizing medium. In the same way, the sorbent should maintain a constant  $\text{CO}_2$  capture capacity throughout the cycles even under severe operational conditions such as high calcination temperatures [9] and  $\text{CO}_2$  partial pressures inside the calciner [8,10].

The SER process has been experimentally studied in different configurations: in a fixed bed under high pressure [11–16] and also under atmospheric pressure [16–22], and in bubbling [23,24] and circulating fluidized bed systems [25]. Several of these experimental works showed the importance of analyzing the influence of the cyclic operation between the reforming-carbonation and calcination steps [14,22–28] on the process performance. Nevertheless, only a few have considered the effect of including  $\text{O}_2$  during the calcination step [14,23], that could oxidize the catalyst, or studied the influence of the partial pressure of  $\text{CO}_2$ , that could cause sorbent deactivation [29–31].

A promising catalyst for use in the multi-cyclic SER process is NiO supported over  $\text{NiAl}_2\text{O}_4$ . This material avoids some of the disadvantages of the  $\text{NiO}/\text{Al}_2\text{O}_3$  catalysts, currently the most commonly used in steam reforming, such as the loss of active Ni to form  $\text{NiAl}_2\text{O}_4$  in the presence of oxygen at high calcination temperatures or due to the formation of  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  by interaction between the catalyst support and the CaO based sorbent [6,14,32].  $\text{NiO}/\text{NiAl}_2\text{O}_4$  has previously been used by other authors as a SER catalyst although generally at high NiO loads (60%) [23,25]. However, in a previous work developed by our group, satisfactory results were obtained when using a charge of only 10% NiO under SER conditions [33]. Regarding the  $\text{CO}_2$  sorbent, some promising candidates are CaO based sorbents doped with Al, which show a good performance after several carbonation/calcination cycles. This has been attributed to the formation of mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) [34] that helps to retard the thermal sintering of the sorbent [35]. In a previous work, a synthetic sorbent prepared by a physical mixture of CaO and calcium aluminate cement [6] presented a residual  $\text{CO}_2$  capture capacity of around  $0.2 \text{ g CO}_2 \text{ g}_{\text{calcined sorbent}}^{-1}$  after 60 calcination–carbonation cycles ( $875 \text{ }^\circ\text{C}$  and  $100 \text{ vol.}\% \text{N}_2$ – $650 \text{ }^\circ\text{C}$  and  $15 \text{ vol.}\% \text{CO}_2$  in  $\text{N}_2$ , respectively), higher than natural CaO-based sorbents [9,27,28,36].

In order to run the process using reforming catalyst and  $\text{CO}_2$  sorbent simultaneously, it should be ensured that both the reforming and carbonation reactions occur successfully. Thus, it is important to take into account that carbonation kinetics are

determinant in the SER process because the carbonation reaction rate is slower than the reforming kinetics [37]. Therefore, the space velocity has been reported as a key parameter in the SER process [38]. At very high space velocities, the in situ separation of  $\text{CO}_2$  may not be efficient, causing the inhibition of the carbonation reaction [12]. According to the simulation study performed by Fernandez et al. for the SER process, a decrease in space velocity (estimated in terms of the mass hourly space velocity, MHSV, from around  $0.013 \text{ mol CH}_4 \text{ h}^{-1}(\text{g}_{\text{catalyst}} + \text{g}_{\text{sorbent}})^{-1}$  to  $0.052 \text{ mol CH}_4 \text{ h}^{-1}(\text{g}_{\text{catalyst}} + \text{g}_{\text{sorbent}})^{-1}$  in the reforming/carbonation step, at  $650 \text{ }^\circ\text{C}$ , 35 bar, steam-to-methane ratio of 5), produced an increase in  $\text{H}_2$  purity from 81 to 92% (d.b.) [39]. In agreement with these theoretical results, several experimental works have concluded that a decrease in MHSV leads to an increase in the  $\text{H}_2$  production [11,12,17,22,38]. Thus, the selection of the MHSV should ensure that equilibrium conditions are reached in the SER process, but also working with the largest possible supply of  $\text{CH}_4$  as possible in order to maximize  $\text{H}_2$  production and minimize the reactor size and the amount of catalyst required. However, most of the published experimental works developed in fixed beds have considered low MHSV (which implies lower  $\text{CH}_4$  inputs), and most of them were well below the MHSV commonly used in traditional steam reforming [6,11,13,14,22,26,38].

In addition, the space velocity is closely related to the sorbent-to-catalyst ratio (Z). On the one hand, the sorbent capture behavior is a relevant issue that will determine the quantity of sorbent needed. On the other hand, a deficient quantity of catalyst in the bed could give rise to low activity in the reforming reactions [25,39]. In any case, it is desirable to use the lowest amount of catalyst possible, due to its cost and also to reduce the thermal ballast in the bed [40]. When enough catalyst and sorbent are present to produce gas concentrations near to the SER equilibrium, a higher addition of sorbent will influence only the test duration [17]. Sorbent-to-catalyst proportions (Z) studied in several published works varied widely. Research performed using fixed beds have studied values of Z from very high catalyst proportions, such as  $Z = 0.3$  [28], up to high sorbent ratios ( $Z = 20$ ) [17], although most of the published works considered Z values from 1 to 4 [11–14,17,19,22]. In a previous work [6],  $Z = 1.6$ – $6.2$  were successfully studied in a fixed bed reactor (at an MHSV of around  $0.01 \text{ mol CH}_4 \text{ h}^{-1}(\text{g}_{\text{catalyst}} + \text{g}_{\text{sorbent}})^{-1}$ ). Equilibrium conditions were reached at every Z ratio tested, which indicated the possibility of operating the process with solid mixtures with lower catalyst concentration.

In this context, the adaptability of several mixtures composed of  $\text{NiO}/\text{NiAl}_2\text{O}_4$  (10%wt. NiO) and CaO-based sorbent are tested in the SER process under demanding and realistic conditions in order to know the operational limits of the synthesized solids and to assess their suitability in a commercial process. The effect of the sorbent-to-catalyst ratio (Z) (up to a high Z value, 11.7) at elevated MHSV (around  $0.04 \text{ mol CH}_4 \text{ h}^{-1}(\text{g}_{\text{catalyst}} + \text{g}_{\text{sorbent}})^{-1}$ ) has been studied. In addition, the cyclic behavior of these solids has been assessed using different calcination environments, including gas compositions representative of an industrial process. In particular, the influence on the reforming products of oxidizing streams in the calcination step comprising oxygen, steam and  $\text{CO}_2$  has been studied.

## 2. Experimental

### 2.1. Preparation and characterization of solids

The synthetic CaO-based sorbent was produced as follows. Calcined natural limestone (2 h at  $900 \text{ }^\circ\text{C}$ ), water and the appropriate amount of calcium aluminate cement (Electroland) were mixed in a beaker following the method described by Anthony et al.

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