

Operational Window of Sorption Enhanced Steam Reforming of Methane over CaO–Ca₁₂Al₁₄O₃₃

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This study investigates the operational window of methane reforming in the presence of CO₂ sorbent CaO–Ca₁₂Al₁₄O₃₃ (85:15 wt). Atmospheric experiments were conducted, at constant steam to methane ratio and catalyst mass under various sorbent masses, total feed flows, and temperatures. When CaO–Ca₁₂Al₁₄O₃₃ is utilized at 650 °C, the equilibrium is shifted, for all the sorbent masses and the total flow rates studied, to higher hydrogen concentration (>93%) compared to conventional steam reforming (>77%). The methane conversion attained, at 650 °C, is 95%. A mathematical model was developed to describe the kinetics of the CaO–Ca₁₂Al₁₄O₃₃ carbonation. The predicted decrease in the carbonation rate due to the lowering in temperature (650 to 550 °C) agrees reasonably well with the observed 24% loss of methane conversion for the same temperature shift.

Introduction

Energy futurists believe that hydrogen production from renewable energy resources is the only long-term way to face the fossil fuel depletion.^{1–4} Moreover, they consider the global warming issue as the essential bridge to begin developing the hydrogen economy of the future. Today, however, these technologies are significantly more expensive than the conventional steam reforming from natural gas, even with the added costs of CO₂ capture and storage.⁵

Conventional steam reforming (SR) includes a multiple-step separation section and operates at severe conditions that lead to lower energy efficiency and higher CO₂ emissions. Therefore, a cost-effective and sustainable process for hydrogen production from fossil fuels is highly desirable. In recent years, there has been considerable interest to enhance the reactor performance by integrating a separation function within the reactor in order to exploit the fact that the reforming and shift reactions are equilibrium reactions.^{6–8} According to Le Chatelier's principle, in situ removal of one of the products (hydrogen or CO₂) will shift the equilibrium in favor of hydrogen yield. Two different process routes of this concept are currently under research. According to the first one, pure hydrogen can be extracted from the reactor by permselective membranes placed inside the reactor.⁸ In the other route called sorption enhanced reforming (SER), CO₂ sorption takes place in the reactor by utilizing a CO₂ solid acceptor mixed with the catalyst.

Both routes may lead to high fractions of hydrogen since the equilibrium limits of reforming and shift reactions are practically vanished. Therefore, the product purification steps are drastically reduced or even eliminated. High conversions of methane and CO can be targeted at lower temperatures reducing, thus, the energy and reactor material cost. Lower operating temperatures and CO concentration may limit the coking potential, permitting a lower steam to methane ratio. In addition to all these, SER also includes a heat integration potential. The highly exothermic

CO₂ sorption reaction can in situ supply the endothermic reforming reaction demands without considering the heat transfer barriers.

Florin and Harris,⁷ reviewed the potential CO₂ sorbents and argued that using CaO sorbents, for the in situ capture of CO₂, will be the most technically and economically viable option. CaO is capable of scavenging CO₂ to very low concentrations at moderate temperatures (450–700 °C) and at atmospheric pressure. Moreover, CaO is a low cost and abundant material because it can be derived from a range of naturally occurring precursors. However, it has been shown that calcium oxides are vulnerable to high temperatures in the reformer, therein showing fast reactivity loss. Abanades⁹ collected experimental data from different authors and concluded that the highest carbonation capacity of CaO is 14 mol/kg, decreases to 3.78 mol/kg after 20 cycles and keeps decreasing. Li et al.¹⁰ used CaO–Ca₁₂Al₁₄O₃₃ and succeeded a constant capacity of 5 mol/kg for 13 cycles. Our group further improved the performance of the CaO–Ca₁₂Al₁₄O₃₃ using CaO derived from calcined calcium acetate.¹¹ The new material with low tortuosity in its pore system results in a decreased resistance in CO₂ access to the active sites. Parametric analysis of the synthesis of the material revealed that the optimum weight ratio of CaO to Ca₁₂Al₁₄O₃₃ is 85:15. The sorption capacity achieved is 10 mol CO₂/kg of sorbent with a moderate loss after the first 5 cycles (ca. 15%).¹²

The superiority of combining steam reforming with in situ capture of CO₂, using CaO based sorbents, compared to conventional steam reforming has been revealed by thermodynamic study of the two processes.¹³ Figure 1 shows the equilibrium concentration of the gaseous components at the reactor outlet as a function of temperature. The operational conditions are labeled in Figure 1. The hydrogen concentration, in case of SER, for steam to methane ratio equal to 3 and in the temperature range of 450–650 °C, is predicted constant at values higher than 90%. On the other hand, the hydrogen equilibrium concentration, in the case of SR, can reach the maximum 77% at 650 °C. This higher quality hydrogen stream produced, in case of SER, results in higher hydrogen yield (94% instead of 84% in SR) even for 650 °C where methane conversion is similar for the two processes (95% for SR and

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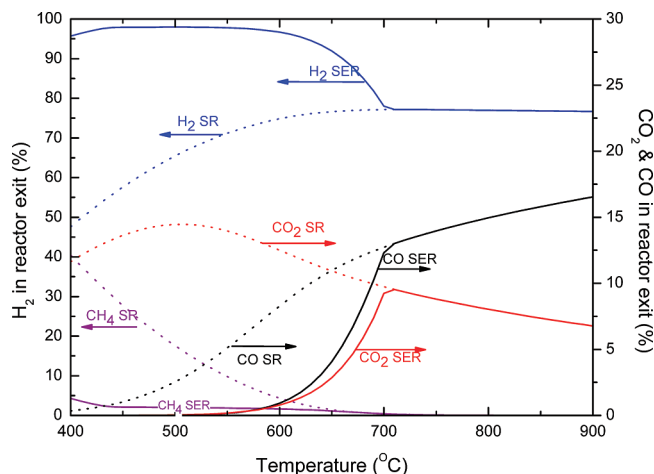


Figure 1. Effect of temperature on equilibrium reactor outlet composition of SR and SER (P : 1 atm, H_2O/CH_4 : 3 (molar ratio), CaO/CH_4 : 1 (molar ratio)).

97% for SER). Moreover, when using a CO_2 acceptor, CO and CO_2 concentrations, at 650 °C, are drastically reduced from around 10 and 12% to around 4 and 3%, respectively.

Even though sorption enhanced reforming is not a new concept,¹⁴ there are only few experimental studies on the behavior of CaO based sorbents under different reforming conditions. Johnsen et al.¹⁵ used dolomite and a commercial reforming catalyst to produce equilibrium hydrogen concentration (98–99%) at 600 °C and 1 atm. Yi and Harrison¹⁶ also used dolomite to enhance steam reforming of methane. They performed SER experiments under various operational conditions to determine the preferable conditions for hydrogen production for PEM fuel cells. They reported that low temperature and/or high pressure are effective in reducing the CO concentration but with a sacrifice in H_2 concentration. Balasubramanian et al.¹⁷ used calcined $CaCO_3$ to study SER of methane under various temperatures, acceptor to catalyst ratio, feed gas flow rate, and other operational parameters. They concluded that the reaction conditions is a compromise between thermodynamic and kinetic limitations. Higher temperatures resulted in increased CH_4 conversion but decreased CO_2 removal. Li et al.¹⁸ used $CaO-Ca_{12}Al_{14}O_{33}$ (75:25 wt) with a standard Ni-based reforming catalyst in a continuous 400 min sorption-enhanced hydrogen production test employing two parallel fixed-bed reactors operated in a cyclic manner. Reaction conditions were 630 °C, 1 atm, and a steam over methane ratio equal to 5. The product gas contained about 95% H_2 and 2–4% CO_2 throughout the test.

The carbonation reaction kinetics is required to allow further understanding of the complex reaction system of sorption enhanced reforming. Several published studies deal with the mathematical description of the gas–solid carbonation reaction of CaO.^{19–21} In most of these studies, the grain model was successfully applied. Bhatia and Perlmutter¹⁹ noted that the reaction is initially rapid and chemically controlled and goes through a sudden transition to a much slower regime controlled by diffusion in the product $CaCO_3$ layer. They estimated that the activation energy of the diffusive controlled regime is 88.9 kJ/mol for temperatures below 415 °C and 179.2 kJ/mol for higher temperatures. Sun et al.²⁰ used the grain model to determine the rate-controlling steps. They calculated an activation energy of limestone and dolomite at the regime controlled by kinetics at 29 and 24 kJ/mol, respectively. They attributed the differences on the structural differences between the two sorbents. Dedman and Owen²¹ studied the carbonation conversion of CaO between 200

and 600 °C and calculated activation energy equal to 39.7 kJ/mol. Li and Cai²² developed a semiempirical apparent kinetic correlation for the carbonation conversion of $CaO-Ca_{12}Al_{14}O_{33}$. This expression is a function of temperature and CO_2 concentration and not of the total pressure.

The aim of the present work is to evaluate the performance of the $CaO-Ca_{12}Al_{14}O_{33}$ (85:15 wt) derived from calcium acetate,^{11,12} in sorption enhanced reforming of methane. To examine the suitability of the new material for SER, experiments under different operational conditions (temperature, sorbent loading, and gas flow rate) were conducted in a lab-scale unit. Moreover, a model that can describe the kinetic controlled regime of the sorption profile of $CaO-Ca_{12}Al_{14}O_{33}$ was developed.

Experimental Section

Chemicals, Sorbents, and Gases. Calcium acetate hydrate (Panreac, 99%) was used as the CaO precursor. Aluminum nitrate hydrate (Riedel-de Haen, 98%) was used for the synthesis of $CaO-Ca_{12}Al_{14}O_{33}$. Nitrogen (N50) was used as purge gas during the calcination period and as dilution gas during the carbonation period during thermogravimetric analysis (TGA). The concentration of carbon dioxide used for sorption tests was 15% (85% N_2). Methane N45, helium N50, and distilled water were used as feedstock at the laboratory-scale sorption enhanced reforming experiments.

Material Preparation–Characterization. The precursor material $(Ca(CH_3COO)_2 \cdot H_2O)$ was calcined (850 °C/1 h) in order to decompose to pure CaO in a box type furnace under air atmosphere. For the synthesis of $CaO-Ca_{12}Al_{14}O_{33}$, aluminum nitrate enneahydrate $(Al(NO_3)_3 \cdot 9H_2O)$ and CaO derived from calcination of calcium acetate was added to distilled water so that the weight ratios of $CaO:Ca_{12}Al_{14}O_{33}$ to be 85:15. Details on the synthesis procedure and on the characterization of the sorbent material can be found elsewhere.^{11,12}

The morphology of the as-synthesized sorbent was observed using a scanning electron microscope JEOL 6300.

Sorption Kinetics in TGA. An SDT Q600 (TA Instrument) thermal gravimetric analysis (TGA) instrument was employed for the carbonation experiments. SDT Q600 works in conjunction with a controller and associated software to make up a thermal analysis system. The weight sensitivity of the balance is 0.1 μ g.

A small quantity of the material (15–20 mg) placed in an aluminum sample cup was initially heated at 850 °C in the presence of 100 cm^3/min pure N_2 for 10 min to remove possible humidity and CO_2 absorbed by the atmosphere. After completion of calcination, a predetermined carbonation temperature (500–550–600–650–690 °C) was approached while maintaining the flow of the inert gas. Following this, the flow with the desired CO_2 partial pressure (0.15 atm) was admitted to the measurement cell. Tests with variable CO_2 partial pressures (0.075–0.1–0.15 atm) were also conducted at 500–600–650 °C. The sorption duration was 30 min. The total flow was always higher than 100 cm^3/min to eliminate its effect on sorption capacity.

The results are presented as percent weight increase of the sorbent or as percent molar carbonation conversion X which is calculated based on the percent weight increase attained in TGA tests:

$$X(t), \% = \frac{1}{W_{CaO}} \text{ percent weight increase}(t) \frac{MW_{CaO}}{MW_{CO_2}}$$

Where W_{CaO} is the weight ratio of CaO in the $CaO-Ca_{12}Al_{14}O_{33}$ (85:15 wt) material and MW_i the molecular weight of component i .

Reforming Tests. The sorption enhanced steam reforming experiments were performed at atmospheric pressure in a laboratory unit equipped with a mass flow controlled system for the incoming gases, a fixed bed quartz reactor, and an online gas chromatograph. An HPLC pump (Gilson) was used for the admission of the distilled water to the reactor through a preheater. The fixed bed quartz reactor was equipped with a coaxial thermocouple for monitoring the temperature in the middle of solid bed. The external diameter of the reactor tube in the reaction zone is 18 mm. The reactor was heated electrically by a tubular furnace, with three independently controlled temperature zones. The hot gases exiting the reactor were cooled to condensate the unreacted steam. The gas phase products were analyzed with an online gas chromatograph (Agilent Technologies, 7890A) equipped with thermal conductivity detector. Two columns (Molecular Sieve and Poraplot) in series bypass configuration were used for the analysis of H_2 , CO , CO_2 , and CH_4 . The CO_2 concentration at the reactor exit was continuously monitored by a CO_2 analyzer (Horiba, VIA 510).

An admixture of a commercial nickel-based catalyst and $CaO-Ca_{12}Al_{14}O_{33}$, derived from calcium acetate, was used for the sorption enhanced steam reforming experiments. The catalyst was crushed and sieved to 100–180 μm . Before testing, the mixture of the solids was treated in H_2/He flow (30% in H_2) at 850 $^{\circ}C$ for 1 h so as to reduce the catalyst. This treatment at high temperature was also sufficient for ensuring the desorption of CO_2 and water possibly sorbed on $CaO-Ca_{12}Al_{14}O_{33}$ from the atmosphere. Approximately 1.5 g of the catalyst and 3–6 g of the sorbent was added to the reactor. The total inlet flow of methane and helium was 36–144 cm^3/min ($CH_4/He:1/2.3$), and the steam to methane molar ratio equal was to 3.4. Reforming reaction and CO_2 sorption (reforming period) were performed at 550–600–650 $^{\circ}C$. The sorbent regeneration was conducted at 850 $^{\circ}C$, in 100% He flow.

The results of SER experiments are presented as

Methane conversion

$$\text{methane conversion, \%} = \frac{\text{flow}_{CH_4, \text{in}} - \text{flow}_{CH_4, \text{out}}}{\text{flow}_{CH_4, \text{in}}} \times 100$$

Concentration of each gaseous component (% dry basis) at the reactor exit

$$\text{component}_i, \% = \frac{\text{flow}_{i, \text{out}}}{\text{flow}_{\text{total, out}} - \text{flow}_{He}} \times 100$$

Results and Discussion

Mathematical Model for the CO_2 Sorption on $CaO-Ca_{12}Al_{14}O_{33}$. As a typical gas–solid reaction producing a solid product, carbonation of CaO comprises of two regimes. The one with the highest rate, at the beginning of the carbonation reaction, which is kinetically controlled and the following, significantly slower, which is diffusion limited. The first regime describes the external surface reaction while in the diffusion controlled regime, the reaction between CO_2 and CaO is physically limited due to the increasing difficulty that CO_2 faces to permeate the carbonate layer and reach the unreacted CaO core.^{17,23–25}

In the present study, the carbonation conversion of $CaO-Ca_{12}Al_{14}O_{33}$ (85:15 wt) was tested in a TGA apparatus. The weight increase of $CaO-Ca_{12}Al_{14}O_{33}$ (85:15 wt) recorded in atmospheric experiments with constant CO_2 partial pressure (15% CO_2 in N_2) at various temperatures (500–690 $^{\circ}C$) is presented in Figure 2. The weight increase is an indirect

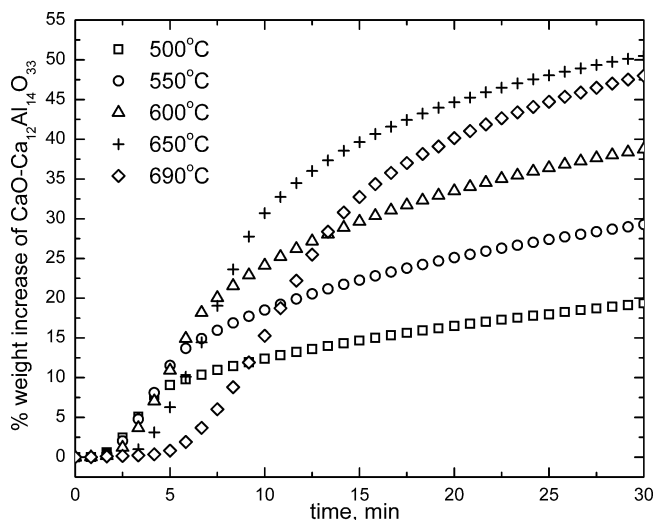


Figure 2. Effect of temperature on sorption capacity of $CaO-Ca_{12}Al_{14}O_{33}$ at constant CO_2 partial pressure (0.15 atm).

indication of the carbonation conversion of the material. The effect of temperature on the carbonation is positive in the range of 500–650 $^{\circ}C$ as the overall kinetics is favored at higher temperatures. The results indicate the temperature 650 $^{\circ}C$ as the optimal, ensuring high reaction rates and the highest weight increase of the material, 50%, corresponding to almost 75% molar CaO carbonation conversion for 30 min treatment. Further increase in temperature leads to lower weight increase. At a temperature of 690 $^{\circ}C$, the overall amount of CO_2 sorbed (48%) is less than that at 650 $^{\circ}C$. The reason is that the reverse reaction, calcination, is progressively favored by thermodynamics due to the exothermicity of the forward carbonation reaction. The same trends were observed for the tests conducted with CO_2 partial pressure of 0.1 and 0.075 atm (not shown for brevity).

A closer look in Figure 2 reveals that there is an initial delay in CO_2 sorption. The explanation can be found in thermodynamics which determines that the sorption takes place only when the partial pressure of CO_2 , P_{e,CO_2} , is higher than its equilibrium value for constant temperature. The delay is a result of the progressive increase of CO_2 concentration in the space around the sample from zero to the equilibrium concentration. As also shown in Figure 2, higher temperatures induce longer delays in CO_2 sorption. This is in agreement with the CO_2 equilibrium partial pressure increase at higher temperatures (Figure 3).

Experiments at atmospheric pressure and temperatures 500–600–650 $^{\circ}C$ were also carried out to determine the effect of CO_2 partial pressure (0.075–0.1–0.15 atm) on the carbonation rate of $CaO-Ca_{12}Al_{14}O_{33}$. The CO_2 partial pressure range was selected based on realistic carbon dioxide concentration obtained in hydrogen production via methane steam reforming (see Figure 1). Figure 4 shows the weight increase of the sorbent, at 650 $^{\circ}C$, in progress with time for different CO_2 concentrations. It is observed that the slopes of the fast carbonation reaction period are strongly affected by the concentration of the gaseous reactant in agreement with previous studies for the same concentration ranges.^{20,26} Increasing CO_2 partial pressure from 7.5 to 15% has a positive effect on the chemical reaction rate leading to an increase in overall CaO conversion from 61 to 75%.

Sorption capacity, in early carbonation time which is crucial for industrial applications, is mostly determined by the kinetic controlled regime. Therefore, the prediction of the reaction conversion at the kinetic controlled regime is sufficient to allow insight into the optimum selection of the operating parameters of the sorption enhanced reaction which is the scope of this study.

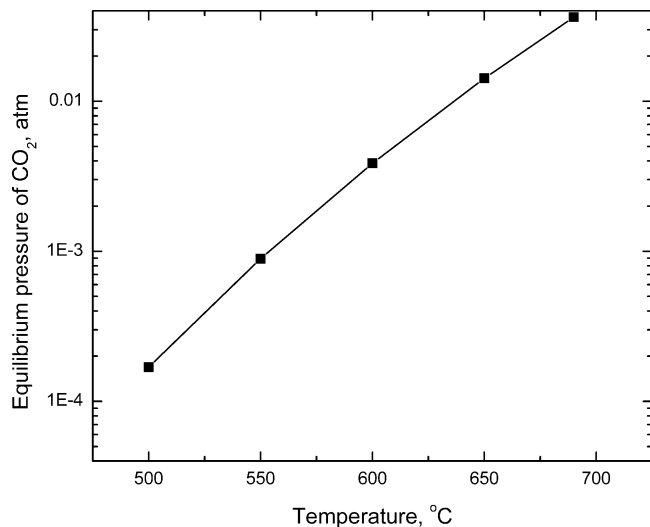


Figure 3. Effect of temperature on equilibrium pressure of CO₂.

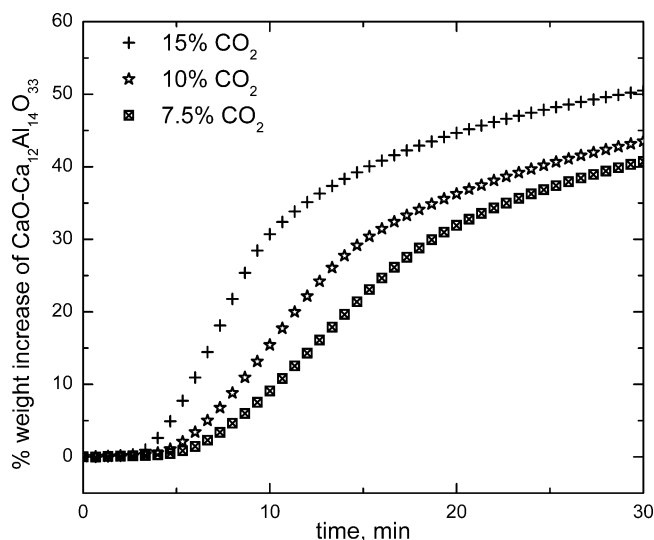
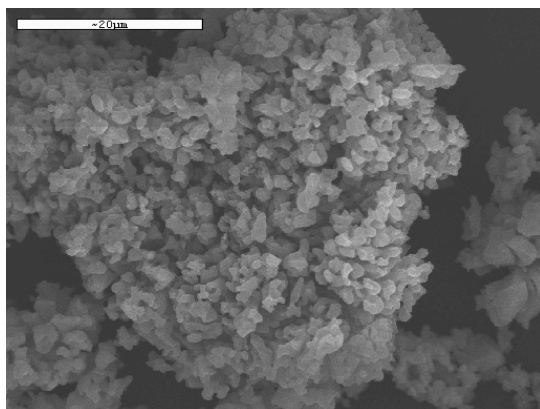


Figure 4. Effect of CO₂ concentration on sorption capacity of CaO–Ca₁₂Al₁₄O₃₃ at constant temperature (650 °C).

Scheme 1. SEM Image of the As-Synthesized CaO–Ca₁₂Al₁₄O₃₃



Scanning electron microscopy, SEM, study of CaO–Ca₁₂Al₁₄O₃₃ (85:15) revealed that the CO₂ sorbent can be visualized as consisting of a number of small grains (Scheme 1). The macropores surrounding these grains facilitate the gas diffusion to the various grains. The aforementioned indicate that the grain model could be a good descriptive model for the mathematical description of CO₂ sorption on CaO–Ca₁₂Al₁₄O₃₃.

Moreover, the grain model has been used successfully, for the mathematical description of the carbonation reaction of other CaO–based sorbents, in earlier works.^{19,20,22} The general semiempirical equation describing the grain model is

$$\frac{dX}{dt} = k_s S(X) (1 - X)^m (C_{\text{CO}_2} - C_{e,\text{CO}_2})^n \quad (1)$$

Assuming spherical grains, the shape factor m is equal to $2/3$ ²⁸ and the carbonation rate, r , is represented by eq 2.

$$r = \frac{dX}{dt} = k_s S(X) (1 - X)^{2/3} (C_{\text{CO}_2} - C_{e,\text{CO}_2})^n \quad (2)$$

In this equation, r represents the reaction rate (min^{-1}), X the molar CaO conversion, k_s ($\text{mg}_{\text{CaO}} \text{mol}_{\text{CO}_2}^{-1} \text{min}^{-1}$) the surface reaction kinetic constant, C_{e,CO_2} (mol/m^3) the CO₂ equilibrium concentration, and n the reaction order. $S(X)$ is the denotation for the available surface area for reaction which is a function of the CaO conversion. The uniform distribution of the inactive Ca₁₂Al₁₄O₃₃ among the CaO particles provides a stable framework inhibiting sintering of CaO, thus ensuring the tolerance of the new material at high temperatures.^{10,11} Therefore, it can be assumed that the reduction of the surface area is only the result of the reaction progress and not of the agglomeration of CaO particles. In view of the above, the available surface area can be correlated with conversion by an equation of the form:²⁷

$$\frac{S(X) - S_p}{S_0 - S_p} = (1 - X)^\varphi \quad (3)$$

where φ (0.2) is an empirical constant for CaO–Ca₁₂Al₁₄O₃₃ and S_0 is the initial specific surface area of CaO–Ca₁₂Al₁₄O₃₃ (85:15 wt), equal to $11.68 \text{ m}^2/\text{g}$.^{12,13} S_p is the final available surface area of the material which is a function of the final conversion.

At low CaO conversion, when the surface area is S_0 , the logarithmic form of eq 2 becomes

$$\ln r_0 = \ln \left. \frac{dX}{dt} \right|_{t=0} = \ln(k_s S_0) + n \ln(C_{\text{CO}_2} - C_{e,\text{CO}_2}) \quad (4)$$

The slope of eq 4 gives the order of the carbonation reaction with respect to the CO₂ concentration. For the studied CO₂ partial pressure and temperature ranges, the order of the carbonation reaction of CaO–Ca₁₂Al₁₄O₃₃ (85:15) is very close to 1 in agreement with previous studies.^{19,20}

The kinetic constant for surface reaction, k_s ($\text{mg}_{\text{CaO}} \text{mol}_{\text{CO}_2}^{-1} \text{min}^{-1}$) is calculated, in each temperature, from eq 2 (for $n = 1$ and $X < 0.1$ where $S(X)$ is assumed equal to S_0) using the central finite difference numerical solution. The two parameters, activation energy E_a and pre-exponential factor k_{s0} can be obtained by fitting the Arrhenius eq 5 with experimental data (Figure 5).

$$k_s = k_{s0} \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

The activation energy, $E_a = 35.2 \pm 2.5 \text{ kJ/mol}$, derived from the slope of the line and the pre-exponential kinetic factor, $k_{s0} = 0.44 \text{ mg}_{\text{CaO}} \text{mol}_{\text{CO}_2}^{-1} \text{min}^{-1}$, from the reciprocal. The small difference of the calculated activation energy from those reported in the literature^{20,21} is ascribed to structural differences between the sorbents used (CaO–Ca₁₂Al₁₄O₃₃ in the present study vs dolomite or lime in the relevant literature).

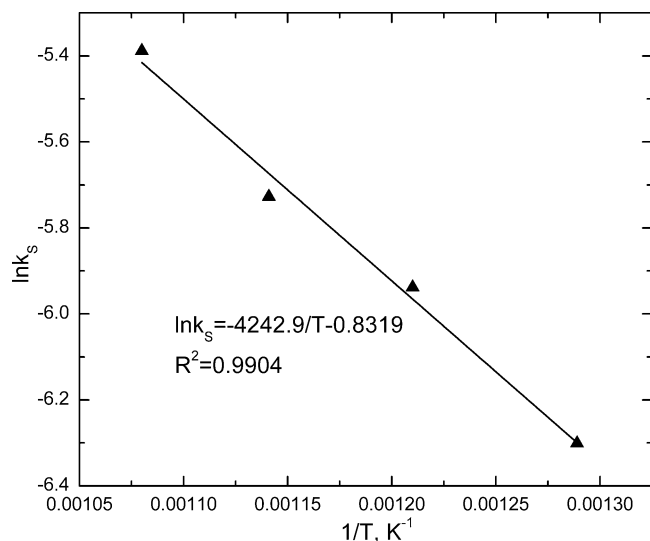


Figure 5. Logarithmic k_s versus reciprocal temperature in the chemical reaction controlled regime for $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (500–550–600–650 °C).

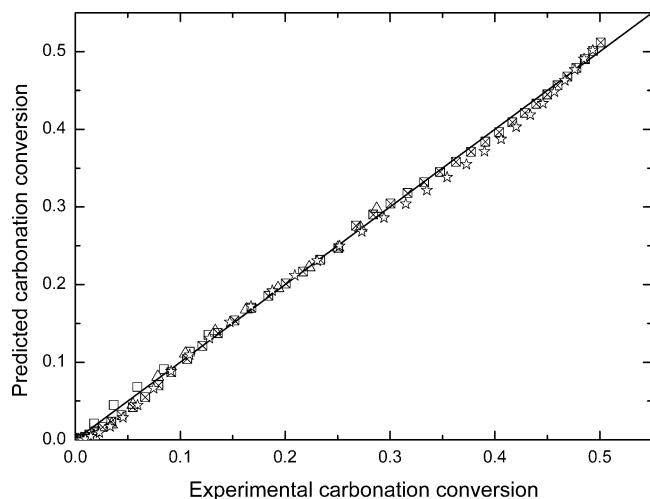


Figure 6. Comparison of experimental and predicted carbonation conversion for different temperatures (parity plot).

The conversions calculated by the proposed eq 2, when employing the parameters obtained for the kinetic regime, are presented, together with the experimental values, in Figure 6 (parity plot). The good convergence of the data of the parity plot show the adequacy of the grain model to predict the carbonation conversion of $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, at early stage, under the conditions studied.

Summarizing, the preliminary TGA based kinetic study of CO_2 sorption on $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ indicates that the optimum operational temperature among the studied, for maximum sorption capacity, is 650 °C. Moreover, the results of the model show that higher carbonation rates, which are beneficial for SER, are obtained when CO_2 partial pressure is equal to 0.15. This CO_2 partial pressure is possible, at 650 °C and 1 atm, only when steam to methane ratio is around 5.¹³ However, heat efficiency penalties arising for such high ratios, impose the use of lower steam to methane ratios. In the present study, sorption enhanced reforming experiments were conducted with steam to methane ratio around 3.4.

Sorption Enhanced Reforming Experiments. On account of the complete study of the new CO_2 sorbent, $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (85:15 wt), SER of methane was studied in a laboratory-scale unit under different operating conditions. The

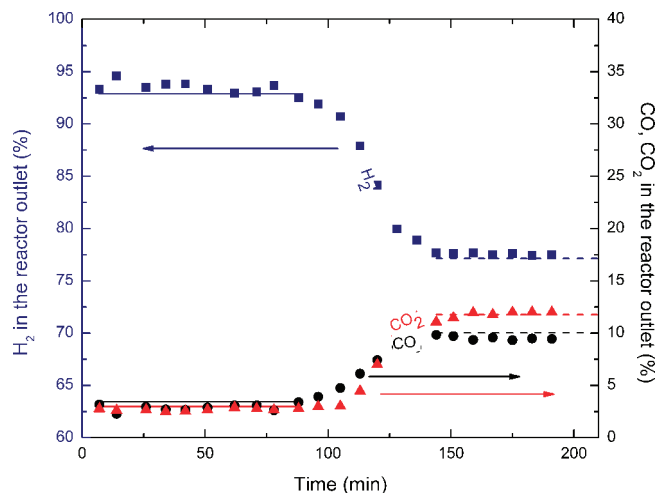


Figure 7. H_2 , CO, and CO_2 outlet concentrations (% dry basis) response curve in SER for sorbent and catalyst loadings equal to 3 g and 1.5 g, respectively. Reaction conditions: 1 atm, 650 °C, $\text{H}_2\text{O}/\text{CH}_4 = 3.4$.

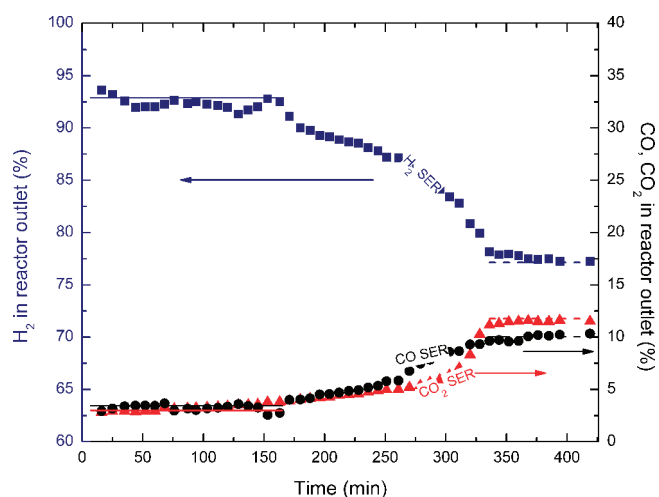


Figure 8. H_2 , CO, and CO_2 outlet concentrations (% dry basis) response curve in SER for sorbent and catalyst loadings equal to 6 g and 1.5 g, respectively. Reaction conditions: 1 atm, 650 °C, $\text{H}_2\text{O}/\text{CH}_4 = 3.4$.

reactions were studied over a temperature range of 550–650 °C, under 11–44 cm^3/min CH_4 in the feed, and for a sorbent to catalyst ratio varied between 2 and 4. The steam to methane ratio and the catalyst weight were kept constant at 3.4 and 1.5 g, respectively. The catalyst loading was selected so as to ensure equilibrium conversions of conventional SR under all the specified conditions. Figures 7 and 8 illustrate the concentration response curves of the gaseous components in the outlet of the reactor for two different sorbent loadings.

In both figures, there are three discrete regimes, related to the progressive saturation of the sorbent. During the first period (prebreakthrough in the literature^{16,17}), the CO_2 separation proceeds with maximum efficiency shifting the reforming and water gas shift reactions. Hydrogen concentration is maximum (92–93%), while CO_2 and CO are minimum (2–3%), all approaching SER equilibrium predictions (solid lines). The prebreakthrough period is followed by the breakthrough period during which hydrogen concentration, in both studied cases, gradually decreases from 92–93% to 77–78%. The reason for this is that $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ is progressively saturated in CO_2 resulting in a decrease of the enhanced reforming extent. Therein, the concentration of the gases pass from the steady-state (prebreakthrough), through the unsteady-state period (breakthrough), to the steady-state period (postbreakthrough)

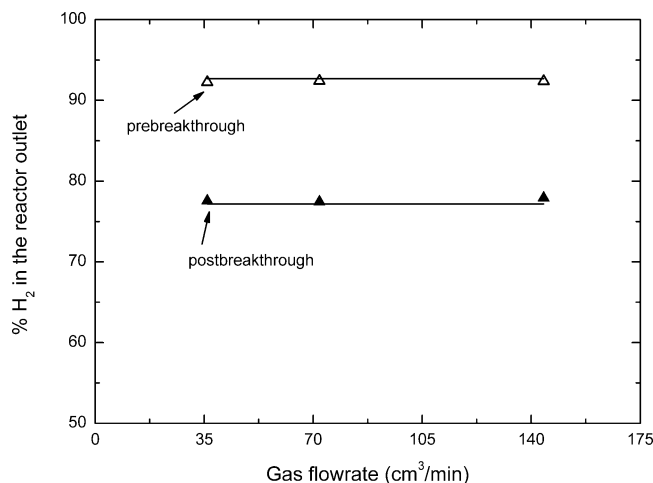


Figure 9. Prebreakthrough and postbreakthrough hydrogen concentration (dry basis) for different feed gas flow rate. Reaction conditions: 6 g sorbent, 1.5 g catalyst, 1 atm, 650 °C, $\text{H}_2\text{O}/\text{CH}_4 = 3.4$.

where the CO_2 separation is no longer effective. At this point, only the reforming and shift reactions are active and the experimental product gas concentrations conform with the conventional SR equilibrium (dashed lines). This explains why CO_2 and CO follow, opposite to hydrogen, an increasing course with CO_2 becoming more than 3 times higher (from 3% to almost 12%).

It is important to note that the duration of the prebreakthrough period is a function of the sorbent properties (sorption capacity and sorption kinetics) and operating conditions (sorbent mass, flow, temperature, pressure). For a fresh batch of the same material, the duration of the prebreakthrough period would increase only as a result of different operating conditions. In accordance with the above, the duration of the prebreakthrough period is almost twice (from 80 to 160 min) when increasing the sorbent mass from 3 to 6 g and keeping the other operating parameters constant (Figures 7 and 8).

The extension of the prebreakthrough duration, when utilizing higher sorbent mass, provides flexibility to increase the feed gas flow. Thus, the effect of the total feed gas flow rate variations (36–144 cm^3/min) was studied, running different experiments, at 650 °C, with the 6 g sorbent loading. The differences of the prebreakthrough and postbreakthrough outlet methane concentrations were low in agreement with the thermodynamic predictions (Figure 1). At 650 °C, the thermodynamics do not favor CO_2 sorption so to shift the methane conversions at values higher than those attained already in conventional steam reforming (95%). The experimental values obtained for SER methane conversion, for the three different flow rates, were varying from 93 to 96%. It is also important that variations in the feed gas flow rate did not impose any significant differences in postbreakthrough methane conversion implying that there was no any appreciable loss in catalyst activity to reduce the conversion either before or after the capacity of the sorbent was exhausted. Similarly to methane conversion, hydrogen concentration remained also unaffected, under different flow rates, both in prebreakthrough and postbreakthrough steady-state periods (Figure 9).

During prebreakthrough, the experimental hydrogen content was kept very close to the equilibrium value, 93%. Postbreakthrough hydrogen concentration slightly varied around 78% with the equilibrium being 77%. Thus, it is clear that the reaction rates, over the studied catalyst and sorbent were fast enough to establish equilibrium even at the maximum feed rate.

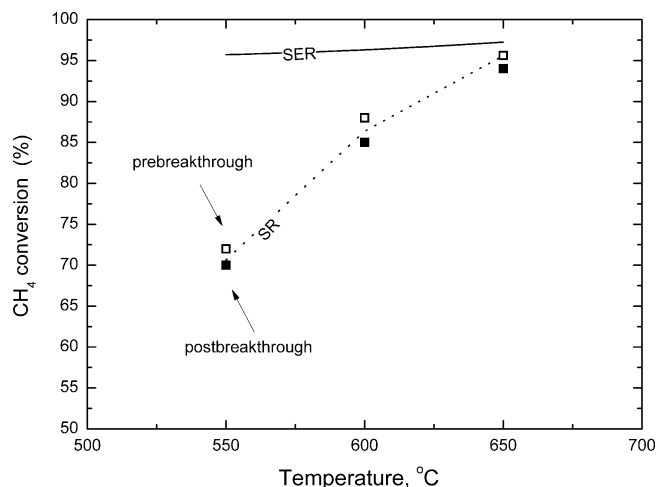


Figure 10. Prebreakthrough and postbreakthrough CH_4 conversion for different temperatures. Reaction conditions: 3 g sorbent, 1.5 g catalyst 1 atm, 650 °C, $\text{H}_2\text{O}/\text{CH}_4 = 3.4$.

Table 1. Effect of Temperature on SER Methane Conversion (Experimental) and on $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ Carbonation Rate (Model Predicted)

temperature, °C	experimental SER conversion, %	% reduction of SER conversion, %	predicted carbonation rate, min^{-1}	reduction of carbonation rate, %
650	95		0.049	
600	88	7.4	0.046	6.1
550	72	24	0.040	18.4

Results in the form of the experimental methane conversion during the prebreakthrough (open symbols) and postbreakthrough (closed symbols) periods as a function of the temperature are presented in Figure 10 where equilibrium of SER and SR are represented by solid and dotted lines, respectively, and experimental results, by symbols. The experiments were realized with 3 g sorbent loading and the lower flow rate. Thermodynamic calculations predict that methane conversion, in case of conventional steam reforming (SR), increases from 70 to 95% when increasing the temperature from 550 to 650 °C. On the contrary, methane conversion, in the case of sorption enhanced reforming (SER), is already high (95.7%) at 550 °C and further temperature increase to 650 °C results to only 1.5% conversion increase.¹³ The very close approach of the experimental postbreakthrough values (closed symbols) to the equilibrium line (dotted) shows that the activity and the total number of the active sites of the catalyst are adequate to reach conventional steam reforming (reforming and water gas shift reactions) equilibrium in the temperature range studied. However, the key feature of this figure is that the experimental methane conversion of prebreakthrough (open symbols) period approaches the sorption enhanced (reforming, water gas shift and carbonation reactions) equilibrium value (97%) only at 650 °C. For lower temperatures, methane conversion gradually falls short from SER equilibrium predictions resulting in 88% at 600 °C (instead of 96%) and 72% at 550 °C (instead of 95.7%). Most probably the kinetics of CO_2 fixing on $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, at temperatures lower than 650 °C, is slow to meet the equilibrium of carbonation reaction. As a consequence, the shift of the water gas shift and the steam reforming reaction from the SR equilibrium to the SER equilibrium is not possible. Indeed, the conversions attained for temperatures lower than 650 °C are very close to that of the SR equilibrium value. The aforementioned are in agreement with the results of the TGA kinetic study. In Table 1, the reduction of CO_2 sorption reaction rate with temperature, as predicted by

the kinetic model, is compared with the experimental values of methane conversion. The small difference among the thermodynamically predicted values of SER methane conversion (see solid line) in the temperature range studied from 550 to 650 °C (see Figure 10), allow us to consider as basis of the calculations the conversion at 650 °C. The results tabulated imply that methane conversion is related to CO₂ sorption rate. Decreasing the temperature by 100 °C, methane conversion during pre-breakthrough period decreases from 95% to 72% declining from SER equilibrium. Under the same temperature shift, the carbonation rate of CaO–Ca₁₂Al₁₄O₃₃ decreases by 18%.

Summarizing, it is concluded that CaO–Ca₁₂Al₁₄O₃₃ (85:15wt) is a promising CO₂ sorbent for high purity hydrogen production via sorption enhanced reforming. The operating temperature, for obtaining the maximum advantage of SER under the studied conditions, is 650 °C. When this is the case and for methane to steam ratio equal to 3.4 and total solid mass over total flow equal to 0.058gmin/cm³, a rich in hydrogen stream (>92%) is produced for 80 min. Moreover, our group conducted long-term experiments of CaO–Ca₁₂Al₁₄O₃₃ (85:15 wt), under the selected conditions. The material was tested for 13 consecutive cycles resulting in high (>92%) hydrogen concentration revealing its high potential for industrial applications.¹³

Conclusions

This study presents the evaluation of the CO₂ sorbent, CaO–Ca₁₂Al₁₄O₃₃ (85:15 wt), under different operational conditions of sorption enhanced steam reforming of methane. The presence of the solid sorbent, for all its loadings and total flow rates studied at 650 °C, shifts the equilibrium to higher hydrogen concentration (>93%) compared to conventional steam reforming (77%). At 650 °C, almost 95% of methane conversion is attained and the reformer exit stream contains only 2–3% of CO₂ and 3–4% of CO. For lower temperatures, the experimental conversion falls away from the equilibrium values of sorption enhanced reforming approaching those of steam reforming. The loss of the conversion by 24% can be ascribed to the lower sorption rate of the material. Evidence for this is provided by the mathematical model developed to describe the kinetics of the CO₂ sorption. The reduction in the carbonation (sorption) rate for the same temperature shift predicted by the model amounts to 18%. It is possible that the sorption kinetics of CaO–Ca₁₂Al₁₄O₃₃, at temperatures lower than 650 °C, is not fast enough to enhance the reforming reaction up to SER equilibrium state.

The grain model was successfully applied for the description of the kinetic regime of the CO₂ sorption by the CaO–Ca₁₂Al₁₄O₃₃ in the temperature range from 500 °C to 650°. The estimated value of the activation energy amounts to 35.2 ± 2.5 kJ/mol.

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