



Short communication

Sorption enhanced reaction process for direct production of fuel-cell grade hydrogen by low temperature catalytic steam–methane reforming

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ABSTRACT

New experimental data are reported to demonstrate that a sorption enhanced reaction (SER) concept can be used to directly produce fuel-cell grade H₂ (<20 ppm CO) by carrying out the catalytic, endothermic, steam–methane reforming (SMR) reaction ($\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2$) in presence of a CO₂ selective chemisorbent such as K₂CO₃ promoted hydrotalcite at reaction temperatures of 520 and 550 °C, which are substantially lower than the conventional SMR reaction temperatures of 700–800 °C. The H₂ productivity of the sorption enhanced reactor can be large, and the conversion of CH₄ to H₂ can be very high circumventing the thermodynamic limitations of the SMR reaction due to the application of the Le Chatelier's principle in the SER concept. Mathematical simulations of a cyclic two-step SER concept showed that the H₂ productivity of the process (moles of essentially pure H₂ produced per kg of catalyst–chemisorbent admixture in the reactor per cycle) is much higher at a reaction temperature of 590 °C than that at 550 or 520 °C. On the other hand, the conversion of feed CH₄ to high purity H₂ product is relatively high (>99%) at all three temperatures. The conversion is much higher than that in a conventional catalyst-alone reactor at these temperatures, and it increases only moderately (<1%) as the reaction temperature is increased from 520 to 590 °C. These results are caused by complex interactions of four phenomena. They are (a) favorable thermodynamic equilibrium of the highly endothermic SMR reaction at the higher reaction temperature, (b) faster kinetics of SMR reaction at higher temperatures, (c) favorable removal of CO₂ from the reaction zone at lower temperatures, and (d) higher cyclic working capacity for CO₂ chemisorption at higher temperature.

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1. Introduction

A novel sorption enhanced reaction (SER) process concept was recently proposed for direct production of fuel-cell grade hydrogen by catalytic steam reforming of CH₄ at a temperature less than 600 °C [1–3]. The process simultaneously carries out the endothermic, equilibrium-controlled steam–methane reforming (SMR) reaction and removal of by-product CO₂ from the reaction zone inside a sorber-reactor packed with an admixture of a SMR catalyst and a CO₂ selective chemisorbent like K₂CO₃ promoted hydrotalcite. Thus, a fuel-cell grade H₂ product containing less than 30 ppm CO_x is directly produced from the reactor at feed gas pressure. The chemisorbent is periodically regenerated by counter-currently purging it with super-heated steam at the reaction temperature whereby the CO₂ is thermally desorbed. A CO₂ enriched waste gas (mixed with steam and dilute methane) is produced from the reactor during the regeneration step. Fig. 1 shows a cartoon of the over-all thermal swing SER–SMR process concept.

The two-step SER–SMR concept will require at least two parallel sorber-reactors for continuous operation [1–3]. A shell and tube configuration of the sorber-reactor design, where the tube side is packed with the catalyst–chemisorbent admixture and the shell-side is used to heat or cool the reactor by cross-flow of super-heated steam at appropriate conditions is a preferred design for the concept [2,3].

Fig. 2 is a schematic representation of the two cyclic steps of the process. They include:

- sorption enhanced reaction step by introducing the feed gas containing a mixture of CH₄ and steam at a pressure of 1–2 atm and at a temperature less than the reaction temperature, and
- regeneration step consisting of (i) counter-current reactor depressurization from the reaction pressure to a near ambient pressure level, (ii) counter-current steam purge at near ambient pressure and reaction temperature, and (iii) counter-current reactor pressurization from near ambient to reaction pressure with steam at reaction temperature.

The primary advantages of the concept, which are created by the utilization of the Le Chatelier's principles, are listed below:

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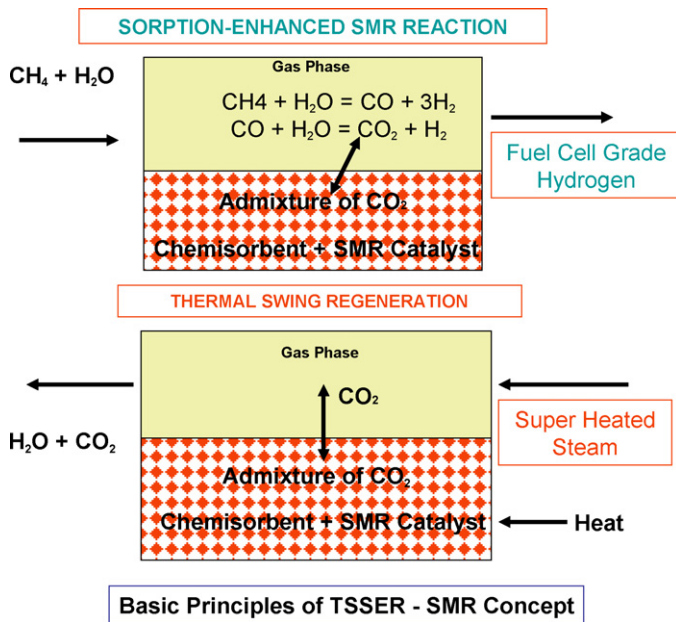


Fig. 1. Cartoon depicting the basic principles of SER-SMR concept.

- Direct production of fuel-cell grade H_2 at reactor pressure by circumventing the thermodynamic limitation of the SMR reaction while achieving a very high conversion of CH_4 to H_2 at a relatively lower temperature and substantially enhancing the rate of the forward SMR reaction.
- Direct supply of the heat of endothermic SMR reaction from the sensible heat stored in the reactor at the start of step (a).
- Indirect supply of the heat of thermal desorption of CO_2 during step (b).
- High cyclic CO_2 working capacity on the chemisorbent due to stringent thermal regeneration of the sorbent in step (b).
- Lower steam purge duty in regeneration step (b) per unit amount of H_2 produced during step (a).

The above-described process is deemed to be practically useful for supplying H_2 to fuel cells for residential or small-scale industrial power generation using pipeline natural gas [3,4].

A model simulation of the performance of the SMR-SER process using an admixture of a commercial SMR catalyst (Sud Chemie) and a sample of K_2CO_3 promoted hydrotalcite (Air Products, Inc.) showed that all of the above-mentioned advantages can be achieved by carrying out the SMR reaction at a temperature of $590^\circ C$ and periodically regenerating the chemisorbent by steam purge at that temperature [1,2]. Parametric studies of the effects of the process variables such as $CH_4:H_2O$ mole ratio in the reactor feed gas (CH_4 mole fraction in the feed = 0.05–0.32), feed gas temperature (350 – $490^\circ C$ introduced to a sorber-reactor maintained at a temperature of $590^\circ C$), reaction pressure (1.5–10 atm), and

catalyst to chemisorbent ratio in the sorber-reactor (1.5–30 wt% catalyst) on the process performance of the SMR-SER concept were also reported [2]. The purpose of the present communication is (a) to experimentally demonstrate the SMR-SER concept using the above-described catalyst-sorbent combination at two different temperatures (520 and $550^\circ C$), and (b) to investigate the possibility of using a lower reaction and regeneration temperature of 520 – $550^\circ C$ in the process. The key advantages of lower temperature operation ($<600^\circ C$) of the process are (a) use of less expensive cast steel as material of construction for the sorber-reactor, the heat exchangers, and other process hardware, and (b) increased CO_2 sorption capacity by the chemisorbent at the reaction temperature. The key disadvantages include (a) difficulty in overcoming the thermodynamic limitations (CH_4 to H_2 conversion) of the endothermic SMR reaction, which is a very strong function of temperature, at lower reaction temperatures, (b) reduction in the rate of the SMR reaction at lower temperatures, and (c) less efficient regeneration of the sorber by steam purge at lower temperatures due to strong sorption affinity of CO_2 on the chemisorbent, thereby causing reduction in the over-all H_2 productivity of the process. These relative merits and demerits can strongly influence the over-all performance and economics of the SER-SMR process.

2. Experimental demonstration of the SER-SMR concept

A single-column sorption apparatus was used to experimentally demonstrate the concept of sorption enhanced SMR reaction. The key components of the test unit included a sorption-reaction column [diameter = 1.73 cm, length, $L = 63.4$ cm] which was surrounded by three different heating tapes with feed back temperature controls. Other components of the apparatus included gas heating and cooling exchangers, flow measuring devices, and switch valves. A layer of insulation was wrapped around the column over the heating tapes. Several thermocouples were used to monitor the column temperatures at three different heights (mid point, gas entrance and exit ends). A more detailed description of the apparatus can be found elsewhere [5]. The tubular reactor was packed with an admixture of a commercial SMR catalyst (Ni/Al_2O_3 produced by Sud Chemie of Switzerland) and a CO_2 chemisorbent (K_2CO_3 promoted hydrotalcite donated by Air Products of USA). The ratios (wt%) of chemisorbent to catalyst were 2:1.

Prior to running any test, the catalyst-sorbent admixture was heated to $\sim 500^\circ C$ in argon. The catalyst was received in the oxidized form and it was reduced by heating it in a stream of a gas containing 10% $H_2 + Ar$ at a pressure of 1 atm and a temperature of $500^\circ C$ until the effluent gas from the sorber-reactor contained 10% H_2 . This procedure generally took ~ 6 h to complete. The reactor was then heated to and maintained at a constant temperature (520 or $550^\circ C$) using the heating tapes. The sorber-reactor was initially filled with argon at 101.3 kPa at the reaction temperature. A gaseous mixture consisting of 37.04 mol% H_2O , 7.41 mol% CH_4 and 55.56 mol% Ar ($H_2O:CH_4$ mole ratio = 5:1 on argon free basis) at ambient pressure was pre-heated to $490^\circ C$

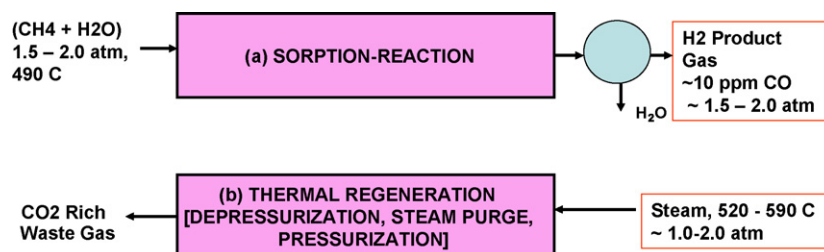


Fig. 2. Schematic representation of the two-bed SMR-SER process concept.

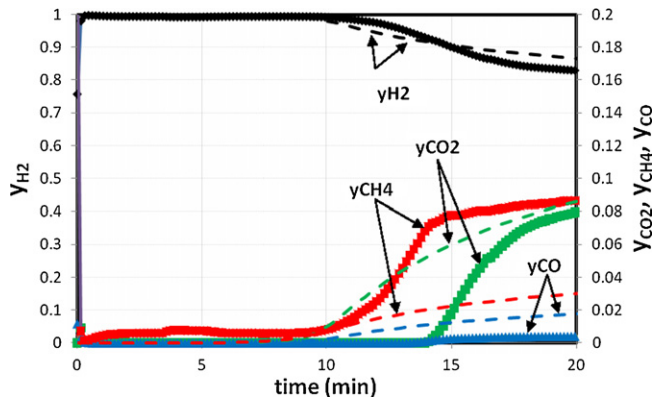


Fig. 3. Experimental demonstration of pure H₂ production by low temperature SER-SMR concept at 520 °C: solid lines, experiment; dashed lines, model calculation.

and passed through the packed-bed reactor. The total feed gas flow rate was 6.15 mmol cm⁻² of empty cross sectional area of the reactor/minute. The maximum temperature variation at any location along the length of the reactor during the sorption-reaction process was within ±2 °C. The mole fractions of CO₂, CO, CH₄ and H₂ in the reactor effluent gas were continuously analyzed using a quadrupole mass spectrometer made by Pfeiffer Vacuum.

Figs. 3 and 4 show the transient reactor effluent gas compositions of H₂, CO₂, CH₄ and CO in a dry and argon free basis as functions of time from these test runs at reactor temperatures of 520 and 550 °C, respectively. Most of these experiments were repeated several times to check their reproducibility.

It may be seen from Figs. 3 and 4 that the effluent gas from the sorber-reactor for both cases contains a stream of high purity H₂ (CO_x < 20 ppm) which is suitable for use in a H₂ fuel cell. Thereafter, CO, CH₄, and CO₂ simultaneously break through the sorber-reactor column and their mole fractions rapidly rise to different plateau levels which correspond to the thermodynamic reaction product concentrations of the SMR reaction (without the chemisorbent) at the reaction temperature. The average CH₄ mole fractions of the high purity H₂ product streams were, respectively, 1.05 and 0.35 mol% for reactor temperatures of 520 and 550 °C. The corresponding H₂ productivities were 0.152 and 0.175 mol kg⁻¹ of total solid in the reactor, and the conversions of feed CH₄ to pure H₂ product were, respectively, 96.2 and 98.6%.

These test results experimentally demonstrated that essentially CO_x free H₂ (on dry basis) can be directly produced by sorption enhanced SMR reaction at 520–550 °C using the promoted hydro-

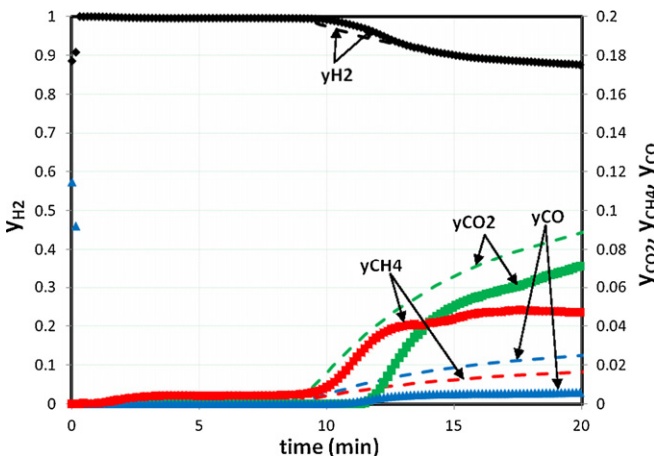


Fig. 4. Experimental demonstration of pure H₂ production by low temperature SER-SMR concept at 550 °C: solid lines, experiment; dashed lines, model calculation.

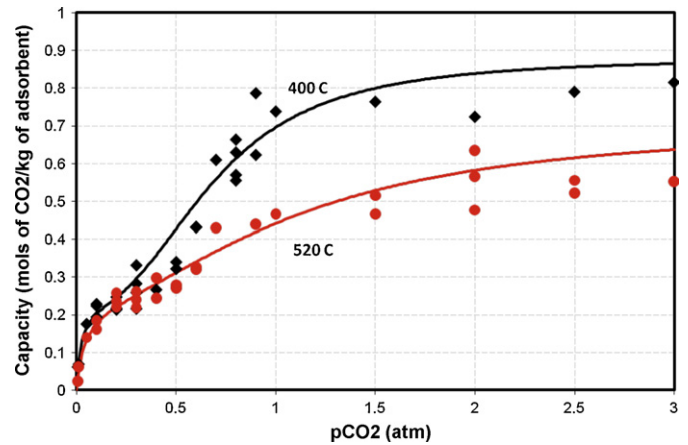


Fig. 5. CO₂ chemisorption isotherms on K₂CO₃ promoted hydrotalcite.

calcite as a CO₂ chemisorbent in conjunction with a commercial SMR catalyst. The data also show that a significantly higher H₂ productivity and conversion of CH₄ to H₂ can be achieved by operation of the SER-SMR concept at a temperature of 550 °C compared to those at 520 °C. This is due to much more favorable thermodynamics of the endothermic SMR reaction at the higher temperature even though the thermodynamic equilibrium sorption capacity of CO₂ on the K₂CO₃ promoted hydrotalcite (exothermic process) is lower at a higher temperature for a given CO₂ partial pressure in the gas phase. Fig. 5 shows the chemisorption isotherms for CO₂ on the promoted hydrotalcite at two temperatures. They were measured in our laboratory [6].

The solid lines in Fig. 5 represent the best fit of the isotherm data by an equilibrium model which accounts for simultaneous Langmuirian chemisorption of CO₂ on the sorbent surface and an additional complexation reaction between the gas and the sorbed CO₂ molecules [6]. The model was developed by us to describe reversible chemisorption of CO₂ on various sorbents [6,7]. According to this model the heats of chemisorption of CO₂ and the complexation reaction were, respectively, 5.02 and 10.07 kcal mol⁻¹ [6].

It should be mentioned here that the upper practical limit for the temperature of operation of the SER-SMR concept is <600 °C, which is governed by the thermal stability of the chemisorbent. The same temperature limit is also preferred by the process economics since much cheaper cast steel can be used as the material of construction of the equipments instead of expensive alloyed steel when the temperature is <600 °C. On the other hand, a lower temperature

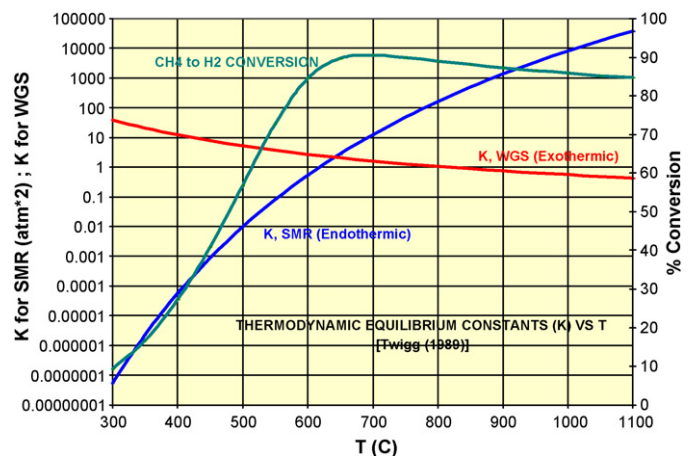


Fig. 6. Thermodynamic equilibrium constants and conversions for SMR reaction.

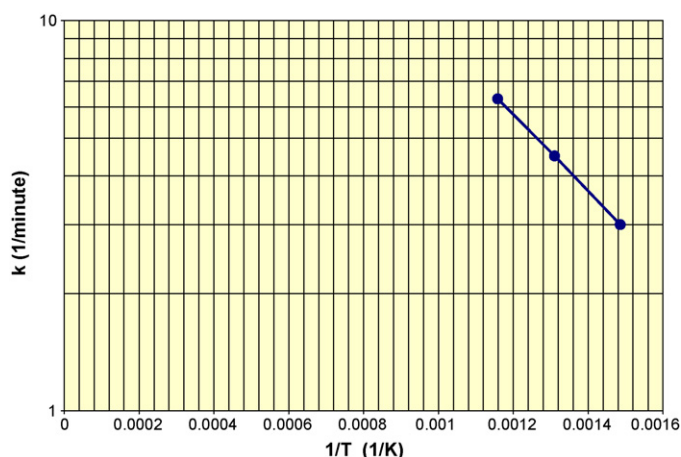


Fig. 7. Temperature dependence of CO₂ LDF mass transfer coefficients on potassium carbonate promoted hydrotalcite.

limit for the operation of the SER–SMR process may be ~400 °C. It is primarily governed by the thermodynamics of the SMR reaction.

The chemisorbent was found to be thermally stable at 600 °C under cyclic exposure to CO₂ [1]. We also did not observe any SMR catalyst poisoning due to the presence of the chemisorbent during our SER–SMR experiments.

The thermodynamic equilibrium constant of the SMR reaction and the net equilibrium conversion of CH₄ to H₂ by the endothermic SMR reaction ($\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2$, $\Delta H_R = 39.3 \text{ kcal mol}^{-1}$) can be low when the temperature is below 400 °C as shown in Fig. 6 [1,9]. Consequently, the amount of pure H₂ product and the conversion of CH₄ to H₂ by the SER–SMR concept will also be low at temperatures below 400 °C even though the CO₂ sorption capacity on the chemisorbent may be relatively high.

The kinetics of CO₂ chemisorption can also limit the lower acceptable temperature for practical operation of the SER–SMR concept. It has been shown that the linear driving force (LDF) model can adequately describe the kinetics and column dynamics of sorption and desorption of CO₂ on the promoted hydrotalcite [2,6]. Fig. 7 shows the temperature dependence (exponential) of the LDF mass transfer coefficient (k , min⁻¹) for CO₂ on the promoted hydrotalcite. These data were also measured in our laboratory [2,6]. The activation energy for the kinetics of CO₂ sorption–desorption on the promoted hydrotalcite was found to be ~4.503 kcal mol⁻¹.

Thus, there can be ~3.5-fold decrease in the CO₂ mass transfer coefficient if the reaction temperature is reduced from 550 to 300 °C. However, the thermodynamic limitations on the extent of the SMR reaction at lower temperatures may be much more pronounced than that imposed by slower CO₂ chemisorption kinetics at reduced temperatures in the range of 300–400 °C.

3. Model simulation of SER–SMR process concept

The performance of the two-step SER–SMR process concept was mathematically simulated using a ‘CSTR in series’ model which accounted for the mass and energy balances inside a shell and tube sorber-reactor undergoing the SER process for production of fuel-cell grade H₂ by SMR. The K₂CO₃ promoted hydrotalcite was used as the CO₂ chemisorbent in the process. The ratio of catalyst to chemisorbent was 10:90. A detailed description of the model and the method of solution can be found elsewhere [1]. The model used the CO₂ chemisorption isotherms and kinetic parameters of Figs. 5 and 7, respectively, in conjunction with the thermodynamic and kinetic characteristics of the SMR reaction described in Fig. 6 and the kinetic model published by Xu and Froment for SMR [8], respectively. The model was initially used to predict the perfor-

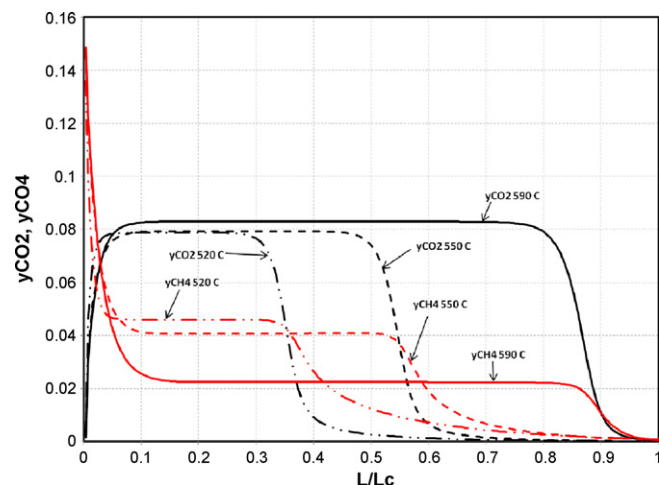


Fig. 8. Gas phase mole fractions (dry basis) inside the sorber-reactor at the end of step (a) of the SER concept for three different reaction temperatures.

mance of the sorption–reaction step of the process only. The dashed lines in Figs. 3 and 4 describe the simulation results. They demonstrate that the model calculations trace the experimental results fairly closely. This proves that the model parameters describing the CO₂ chemisorption equilibrium and kinetics on the promoted hydrotalcite and the kinetics of the catalytic SMR reaction used in the model are valid to simulate the SER–SMR process performance.

The simulation of the SER–SMR process assumed that the feed gas to the sorber-reactor (tubes having an ID of 2.54 cm and a length of 250 cm) was pre-heated to 450 °C and three different temperatures (520, 550, and 590 °C) were used as reaction temperatures. The sorber-reactor tubes were heated to these temperatures at the end of step (b) of the process. The molar ratio of H₂O:CH₄ in the sorber-reactor feed gas was 5:1 and the gas pressure was 1.5 atm. The feed gas was pre-heated to a temperature of 450 °C before introducing it to the reactor in order to carry out the SER process. The durations of the sorption–reaction and the regeneration steps of the process were 10 min each and the average mole fraction of CO in the H₂ product from step (a) of the process was ~10 ppm. Table 1 summarizes the simulation results.

It may be seen from Table 1 that the fuel-cell grade H₂ productivity is increased substantially as the reaction temperature is increased. For example, H₂ productivities were, respectively, 1.9 and 2.8 times larger when the reaction temperatures were 550 and 590 °C compared to that at 520 °C. On the other hand, the increase in the absolute conversion of CH₄ to H₂ during step (a) of the SER process was less than one percentage point when the reaction temperature was increased from 520 to 590 °C. The conversions were very high (>99%) in all three cases. Furthermore, they were much higher than that could be achieved by a catalyst-alone reactor at the corresponding temperatures (see Fig. 6).

The net cyclic CO₂ working capacities of the sorber-reactor [total integrated moles of CO₂ per unit amount of the solid in the sorber-reactor at the end of step (a) of the process minus that at the end of the step (b) of the process] for production of fuel-cell grade H₂ [~10 ppm CO on average in the H₂ effluent gas during step (a) of the process] were simulated to be, respectively, 0.052, 0.097 and 0.146 mol kg⁻¹ at reaction temperatures of 520, 550, and 590 °C. Thus, there was nearly a threefold increase in the cyclic CO₂ working capacity of the SER process when the reaction temperature was raised from 520 to 590 °C.

Fig. 8 shows the simulated gas phase mole fractions of CO₂ and CH₄ inside the sorber-reactor of length L_c at reaction temperatures of 520, 550 and 590 °C as a function of dimensionless distance (L/L_c) from the feed gas end at the end of step (a) of the SER process. The

Table 1
Simulated performances of the SER–SMR sorber–reactor.

Reactor feed		Reactor temperature (°C)	H ₂ product purity (ppm)	H ₂ productivity (mol kg ⁻¹ of total solid)	Feed CH ₄ to product H ₂ conversion (%)	Steam purge duty for regeneration in step (b) (mol mol ⁻¹ of H ₂ product)
CH ₄ :H ₂ O	Pressure (bar)					
1:5	1.5	590	CO = 10 CO ₂ = 13 CH ₄ = 60	0.440	99.8%	7.2
1:5	1.5	550	CO = 10 CO ₂ = 23 CH ₄ = 129	0.296	99.5%	8.2
1:5	1.5	520	CO = 10 CO ₂ = 31 CH ₄ = 480	0.157	99.1%	13.3

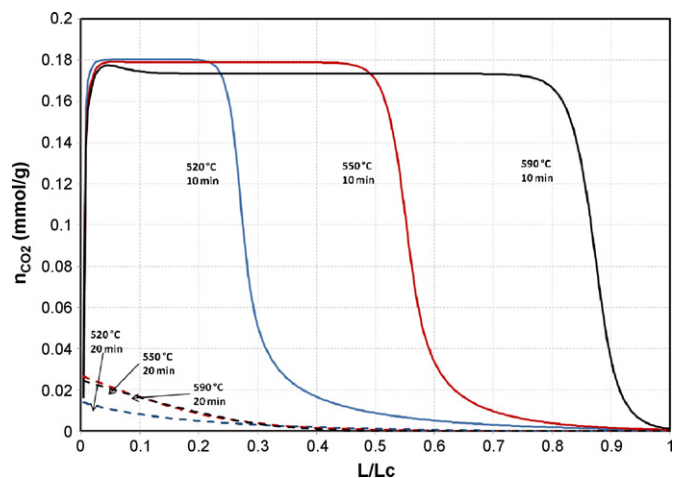


Fig. 9. Column CO₂ loading profiles for two-step SER–SMR process for H₂ production: solid lines, end of step (a); dashed lines, end of step (b).

solid lines in Fig. 9 show the corresponding simulated CO₂ loading profiles (n_{CO_2} , mol kg⁻¹ of total solid) inside the sorber–reactor as a function of dimensionless distance (L/L_c) from the feed gas end of the sorber–reactor. The dashed lines in Fig. 9 show the simulated CO₂ loading profiles inside the sorber–reactor at the end of step (b) of the process at the same regeneration temperatures.

Figs. 8 and 9 show that the length of the reaction mass transfer zone (RMTZ) for production and sorption of CO₂ inside the sorber–reactor is relatively small at the end of step (a) of the process when the reaction temperature is 590 °C. Thus, a relatively larger amount of fuel-cell grade H₂ is produced during step (a) of the process at that temperature before CO_x breaks through the reactor product-end. On the other hand, the length of the RMTZ increases due to stretching of the leading edge of that zone as the reaction temperature is reduced, which decreases the productivity of fuel-cell grade H₂ during step (a) of the process. In particular, the leading edge of the RMTZ is stretched enormously when the reaction temperature is 520 °C causing much earlier breakthrough of CO_x from the sorber–reactor and hence, drastically lowering the cyclic CO₂ capacity of the reactor to produce fuel-cell grade H₂.

The dashed lines in Fig. 9 show that CO₂ is completely removed from more than half of the sorber–reactor at the product-end by counter-current steam purge at reaction temperature during step (b) of the process in order to produce a fuel-cell grade H₂ during step (a) of the process. A very small amount of residual CO₂ is left inside the sorber–reactor [~4% of CO₂ present at the start of step (b)] at the end of step (b) for each case of simulation. The residual CO₂ was pushed back towards the feed-end of the sorber–reactor during step (b).

These results were caused by complex interactions of four physical phenomena: (a) favorable thermodynamics of endothermic SMR reaction at the higher reaction temperatures, (b) slower kinetics of SMR reaction at lower temperatures, (c) favorable removal of

CO₂ from the reaction zone by selective chemisorption at lower temperature operations, and (d) higher net CO₂ cyclic working capacity of the chemisorbent at the higher regeneration temperature. In particular, two points must be emphasized: (a) the stretching of the leading edge of the RMTZ at lower temperatures (<550 °C) was caused by the relatively slower kinetics of SMR reaction because the kinetics of chemisorption of CO₂ on the promoted hydrotalcite was very fast even at a temperature of 400 °C [1,6], and (b) the sorption enhanced reaction concept was capable of circumventing the severe thermodynamic limitations imposed by the endothermic SMR reaction even at a temperature of 520 °C, and thereby allowing direct production of fuel-cell grade H₂ with high CH₄ to H₂ conversion at that temperature.

Operation of the concept at lower temperature, however, reduces the net H₂ productivity by the concept. The amount of steam purge used in step (b) was lowest for regeneration at 590 °C, and it progressively increased as the reaction temperature was decreased. However, direct production of fuel-cell grade H₂ with high conversion of CH₄ to H₂ was possible at a lower temperature range of 520–590 °C.

4. Summary

It is experimentally demonstrated that the concept of SER for SMR can be used to directly produce fuel-cell grade H₂ (~10 ppm CO) with very high CH₄ to H₂ conversion (>99%) using an admixture of a commercial SMR catalyst and a CO₂ chemisorbent such as K₂CO₃ promoted hydrotalcite at reaction temperatures of 520–590 °C. Thus, the SER concept permits to carry out the SMR reaction at a much lower temperature than the conventional reaction temperature of 700–900 °C without sacrificing the reactor performance. It also eliminates the subsequent H₂ purification step by a conventional pressure swing adsorption process.

The model simulation of a cyclic two-step thermal swing SER process was carried out at temperatures of 520, 550 and 590 °C. The reaction and regeneration temperature of 590 °C yielded a larger H₂ productivity by the cyclic process due to (a) relatively faster kinetics of SMR reaction and (b) higher CO₂ working capacity by the process.

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