

## Hydrogen Production via Steam Reforming of Methane with Simultaneous CO<sub>2</sub> Capture over CaO–Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>

Christina S. Martavaltzi,<sup>†,‡</sup> Eleftheria P. Pampaka,<sup>†</sup> Emmanuela S. Korkakaki,<sup>†</sup> and Angeliki A. Lemonidou<sup>\*,†,‡</sup>

<sup>†</sup>Department of Chemical Engineering, Aristotle University of Thessaloniki, P.O. Box 1517, University Campus, GR-54124 Thessaloniki, Greece, and <sup>‡</sup>Chemical Process Engineering Research Institute CPERI/CERTH, P.O. Box 361, sixth km Charilaou-Thermi road, 570 01 Thessaloniki, Greece

Received November 19, 2009. Revised Manuscript Received March 1, 2010

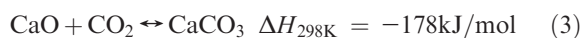
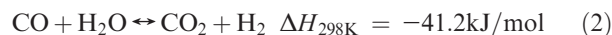
Two processes to produce hydrogen via steam reforming are compared in a laboratory fixed bed reactor: conventional steam reforming with a nickel-based catalyst and sorbent-enhanced steam reforming with a mixture of a nickel-based catalyst and CaO–Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> sorbent. A preliminary thermodynamic study was performed to determine the operating window of the sorption enhanced reforming at atmospheric pressure. Operating temperatures less than 650 °C are required to take advantage of the favorable thermodynamics due to the in situ capture of CO<sub>2</sub>, while maximum gain in methane conversion between the two process options is attained for a steam to methane molar ratio of around 3. Under these conditions, CaO–Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (85:15 wt) synthesized using calcium acetate as a CaO precursor acted as an effective CO<sub>2</sub> sorbent, reducing by 67% the amount of total CO<sub>2</sub> that would have been emitted in conventional steam reforming. Due to CO<sub>2</sub> capture, the methane steam reforming equilibrium shifted to higher hydrogen purities. Hydrogen concentrations higher than 92%, on a dry basis, were achieved at 650 °C, 1 atm of pressure, and a steam to methane molar ratio of 3.4, as opposed to 77% produced under the same conditions via the conventional steam reforming. The experimental reactor was operated batchwise and with cyclic alternation between reforming/sorption conditions and higher-temperature conditions to regenerate the sorbent. The performance of the material is deemed adequate as a moderate loss (ca. 15%) in sorption capacity after 13 consecutive cycles was observed.

### Introduction

The continuously increasing standard of living in developing and developed nations results in higher energy demands. On the other hand, the conventional energy supply via combustion of fossil fuels and subsequent emission of large volumes of carbon dioxide has led to one of the most serious global environmental problems. Therefore, there is a growing awareness that energy must be produced with significantly lower greenhouse gas emissions. Hydrogen is often referred to as a potential pollution-free energy carrier, but its advantages are unlikely to be realized, unless efficient means are found to produce hydrogen with reduced CO<sub>2</sub> emissions. Biomass, which is considered a CO<sub>2</sub> neutral energy source, can be used to produce hydrogen via different thermochemical routes (gasification, fast pyrolysis followed by steam reforming of the bio-oil produced, etc.).<sup>1–3</sup> However, high costs, along with the several technical problems that need to be solved, currently prohibit the industrial application of such biomass-based routes. It is very likely that the production of H<sub>2</sub> via steam reforming (SR) of natural gas will continue to be the dominant technology for the next few decades, despite the appreciable amount of CO<sub>2</sub> released during the operation of such units.

High-temperature operation of the SR reactor, catalyst deactivation due to coking, use of high-temperature metallurgy for the reactor construction, and complex design of the multicolumn pressure swing absorption (PSA) system raise significantly the cost of H<sub>2</sub> production.<sup>4–6</sup> Therefore, the development of new concepts for H<sub>2</sub> production via SR, with reduced capital cost and CO<sub>2</sub> emissions, is extremely desirable.

The continuous but complex multistep SR process can be replaced by a much simpler single-step process which employs a bed packed with an admixture of catalyst and sorbent for the selective removal of CO<sub>2</sub>. The latter is known as sorption-enhanced reforming (SER) in which the highly exothermic carbonation reaction of the sorbent is included in the reaction scheme. In the case of the use of calcium oxide as a carbon dioxide sorbent, the main reactions are the following:



The concept of sorption-enhanced steam reforming (SER) is based on Le Chatelier's principle, according to which the conversion of reactants to products and the rate of the forward reaction in an equilibrium controlled reaction can

\*Corresponding author phone: +30 2310 996273; fax: +30 2310 996184; e-mail: alemonidou@cheng.auth.gr.

(1) Huber, G. W.; Dumesic, J. A. *Today* **2006**, *111*, 119–132.

(2) Vagia, E. Ch.; Lemonidou, A. A. *Appl. Catal. A: General* **2008**, *351*, 111–121.

(3) Kechagiopoulos, P. N.; Voutetakis, S. S.; Lemonidou, A. A.; Vasalos, I. A. *Catal. Today* **2007**, *127*, 246–255.

(4) Johnsen, K.; Ryu, H. J.; Grace, J. R.; Lim, C. J. *Chem. Eng. Sci.* **2006**, *61*, 1191–1198.

(5) Wang, Y.; Rodrigues, A. E. *Fuel* **2005**, *84*, 1778–1789.

(6) Lee, D. K.; Baek, H.; Yoon, W. L. *Chem. Eng. Sci.* **2004**, *59*, 931–942.

be increased by selectively removing some of the reaction products from the reaction zone. As the sorbent is effectively consumed in reaction 3, the process is inherently dynamic in operation, requiring a regeneration step. In addition, the sorbent must maintain its activity through many cycles for the process to be economically viable.

Sorption enhanced reforming is a hybrid configuration which not only improves methane conversion and  $H_2$  selectivity but also decreases the complexity of the unit by enabling the in situ separation of  $CO_2$ . Moreover, the reaction enhancement may enable a lower operation temperature, which in turn may alleviate the problems associated with catalyst sintering, high process energy requirements, and poor energy integration within the plant environment.<sup>7,8</sup>

Studies on sorption-enhanced hydrogen production using calcium oxide have been published by several authors. Balasubramanian et al.<sup>9</sup> used a mechanical mixture of a calcium-based  $CO_2$  acceptor and a commercial steam reforming catalyst, producing >95%  $H_2$  at 650 °C and 15 atm of pressure using a ratio of solid mixture to methane equal to 0.45 g min  $cm^{-3}$  and a steam to methane molar ratio equal to 4. Johnsen et al.<sup>4</sup> used dolomite and a nickel based catalyst to produce 98%  $H_2$  at 600 °C and a 0.82 g min  $cm^{-3}$  ratio of solid mixture over methane. Yi and Harrison<sup>10</sup> used 24 g of uncalcined dolomite admixed with 1.5 g of commercial catalyst to produce 92%  $H_2$  at the low temperature of 460 °C under a methane flow of 150  $cm^3$ /min and a steam to methane ratio equal to 3. Li et al.<sup>11</sup> 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 involving two parallel fixed-bed reactors operated in a cyclic manner. Reaction conditions were 630 °C, 1 atm of pressure, and a steam to methane ratio equal to 5. The product gas contained about 95%  $H_2$  and 2–4%  $CO_2$  throughout the test.

The importance but also the main drawbacks of the utilization of  $CaO$ -based sorbents for  $CO_2$  capture are pointed out in the recently published review of Florin and Harris.<sup>12</sup>

Several research groups have been working on improving  $CaO$ -based sorbents.<sup>13–32</sup> Lu et al.<sup>15</sup> developed nanostructured  $CaO$  with a high surface area, thus, with high  $CO_2$  uptake efficiency. Calcium oxides are vulnerable to high temperatures in the carbonator and regenerator, therefore exhibiting quick activity loss. Abanades and Alvarez<sup>16</sup> reported that the absorption capacity for  $Ca$ -based sorbents decays as a function of the number of calcination–carbonation cycles. In another study, Abanades<sup>17</sup> collected experimental data from different authors and concluded that the initial highest carbonation capacity of  $CaO$  equal to 14 mol/kg decreases to 3.78 mol/kg after 20 cycles and keeps decreasing. Li et al.<sup>18,19</sup> used  $Ca_{12}Al_{14}O_{33}$  as a binder to improve the stability of  $CaO$ . Tests in a thermogravimetric instrument showed 41% adsorption capture after 50 carbonation–calcination cycles. Manovic and Anthony<sup>20,21</sup> also worked on the same direction using calcium aluminate cements to support  $CaO$  for high temperature applications. Our group further improved the performance of the  $CaO-Ca_{12}Al_{14}O_{33}$  system, using  $CaO$  derived from calcined calcium acetate.<sup>22</sup> This new material, with low tortuosity in its pore system, resulted in decreased resistance of the  $CO_2$  accessibility to the active sites. Parametric analysis of the synthesis of the material revealed that the optimum weight ratio of  $CaO$  to  $Ca_{12}Al_{14}O_{33}$  was 85:15.<sup>23</sup> The weight increase achieved was 10 mol of  $CO_2$ /kg of sorbent in the first 5 cycles with a moderate loss in capacity (15% after 45 sorption–desorption cycles).

This paper reports steam reforming experimental results from a laboratory-scale fixed bed reactor containing a commercial nickel-based reforming catalyst and those of a mixture of the same catalyst and the new  $CO_2$  sorbent  $CaO-Ca_{12}Al_{14}O_{33}$  (85:15 wt) derived from calcium acetate. The primary objective was to determine the potential of the utilization of the new material in sorption enhanced reforming at near 1 bar of pressure and 650 °C. In order to demonstrate the above, 13 consecutive reforming–regeneration cycles were conducted without separating the catalyst from the sorbent between cycles. The selection of the operating conditions was based on the results of preliminary thermodynamic analysis.

## Experimental Section

**Chemicals, Sorbent, Catalyst, and Gases.** Calcium acetate (Panreac, 99%) was used as  $CaO$  precursor, while aluminum nitrate hydrate (Riedel-de Haen, 98%) was used for the synthesis of the nanocomposite oxide  $CaO-Ca_{12}Al_{14}O_{33}$ . A commercial nickel based catalyst (18% NiO) from Süd-Chemie was employed as the reforming catalyst. Nitrogen (99.999%) was used as purge gas during the calcination period and as dilution gas during the carbonation period at TGA. Methane (99.995%), helium (99.999%), and distilled water were used as feedstock in the laboratory-scale sorption enhanced reforming experiments.

**Material Preparation.** The precursor material ( $Ca(CH_3COO)_2$ ) was calcined (850 °C/1 h) in order to decompose to pure  $CaO$  in a box type furnace under an air atmosphere. For the synthesis of

- (7) Ding, Y.; Alpay, E. *Chem. Eng. Sci.* **2000**, *55*, 3461–3474.
- (8) Harrison, D. P. *Ind. Eng. Chem. Res.* **2008**, *47*, 6486–6501.
- (9) Balasubramanian, B.; Ortiz, A. L.; Kaytakoglu, S.; Harrison, D. P. *Chem. Eng. Sci.* **1999**, *54*, 3543–3552.
- (10) Yi, K. B.; Harrison, D. P. *Ind. Eng. Chem. Res.* **2005**, *44*, 1665–1669.
- (11) Li, Z.-S.; Cai, N.-S.; Yang, J.-B. *Ind. Eng. Chem. Res.* **2006**, *45*, 8788–8793.
- (12) Florin, N. H.; Harris, A. T. *Energy Fuels* **2008**, *22*, 2734–2742.
- (13) Lu, H.; Smirniotis, P. G. *Ind. Eng. Chem. Res.* **2009**, *48*, 5454–5459.
- (14) Wang, M.; Lee, C.-G. *Energy Convers. Manage.* **2009**, *50*, 636–638.
- (15) Lu, H.; Smirniotis, P. G.; Ernst, F. O.; Pratsinis, S. E. *Chem. Eng. Sci.* **2009**, *64*, 1936–1943.
- (16) Abanades, J. C.; Alvarez, D. *Energy Fuels* **2003**, *17*, 308–315.
- (17) Abanades, J. C. *Chem. Eng. J.* **2002**, *90*, 303–306.
- (18) Li, Z.-S.; Cai, N.-S.; Huang, Y.-Y.; Han, H.-J. *Energy Fuels* **2005**, *19*, 1447–1452.
- (19) Li, Z.-S.; Cai, N.-S.; Huang, Y.-Y.; Han, H.-J. *Ind. Eng. Chem. Res.* **2006**, *45*, 1911–1917.
- (20) Manovic, V.; Anthony, E. J. *Environ. Sci. Technol.* **2009**, *43*, 7117–7122.
- (21) Manovic, V.; Anthony, E. J. *Energy Fuels* **2009**, *23*, 4797–4804.
- (22) Martavaltzi, C. S.; Lemonidou, A. A. *Microporous Mesoporous Mater.* **2008**, *110*, 119–127.
- (23) Martavaltzi, C. S.; Lemonidou, A. A. *Ind. Eng. Chem. Res.* **2008**, *47*, 9537–9543.
- (24) Gupta, H.; Fan, L.-S. *Ind. Eng. Chem. Res.* **2002**, *41*, 4035–4042.
- (25) Kuramoto, K.; Fujimoto, S.; Morita, A.; Shibano, S.; Suzuki, Y.; Hatano, H.; Shi-Ying, L.; Harada, M.; Takarada, T. *Ind. Eng. Chem. Res.* **2003**, *42*, 975–981.
- (26) Salvador, C.; Lu, D.; Anthony, E. J.; Abanades, J. C. *Chem. Eng. J.* **2003**, *96*, 187–195.

(27) Aihara, M.; Nagai, T.; Matsushita, J.; Negishi, Y.; Ohya, H. *App. Energy* **2001**, *69*, 225–238.

(28) Manovic, V.; Anthony, E. J. *Ind. Eng. Chem. Res.* **2009**, *48*, 8906–8912.

(29) Li, A.-S.; Cai, N.-S. *Energy Fuels* **2007**, *21*, 2909–2918.

(30) Hughes, R. W.; Lu, D.; Anthony, E. J.; Wu, Y. *Ind. Eng. Chem. Res.* **2004**, *43*, 5529–5539.

(31) Manovic, V.; Anthony, E. J. *Energy Fuels* **2008**, *22*, 1851–1857.

(32) Wu, S. F.; Li, Q. H.; Kim, J. N.; Yi, K. B. *Ind. Eng. Chem. Res.* **2008**, *47*, 180–184.

Table 1. Experimental Conditions

	temp., °C	CH <sub>4</sub> , cm <sup>3</sup> /min	H <sub>2</sub> O/CH <sub>4</sub> molar ratio	He, cm <sup>3</sup> /min	solid mass, g	S/C <sup>a</sup>
reforming period	650	11	3.4	25	4.5	2
regeneration period	850	0	0	100	4.5	2

<sup>a</sup>S/C: sorbent/catalyst (weight ratio).

CaO–Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, aluminum nitrate enneahydrate (Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O) and calcium oxide derived from calcination of calcium acetate were added in appropriate amounts to distilled water to achieve a weight ratio of CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> equal to 85:15. The suspension was stirred for 3 h at 70 °C and then dried at 120 °C overnight. To decompose the nitrates, the sample was calcined at 500 °C for 3 h in synthetic air. The sample was further treated by adding distilled water to break the aggregates formed at 500 °C and generate the hexagonally plated structure with uniform Ca/Al distribution.<sup>23</sup> The obtained kneaded paste was dried at 120 °C overnight and then calcined at 900 °C for 1.5 h to form the nanocomposite synthetic oxide.

**Sorbent Characterization.** The crystalline structure of the sorbent was characterized by X-ray diffraction (XRD) on a Siemens D500 diffractometer using Cu Kα radiation ( $\lambda$  = 1.5406 Å). Specific surface area and pore size distribution were measured on a Quantachrome Autosorb Automated Gas Sorption System. The measurements were performed using nitrogen physisorption and desorption isotherms at –196 °C. The sorbents were degassed at 250 °C overnight in the degassing port before the actual measurements.

**Material Testing.** An SDT Q600 (TA Instrument) thermal gravimetric analysis (TGA) instrument was employed for the carbonation and calcination experiments. A small quantity of the material placed in an aluminum sample cup was initially heated at 850 °C, in the presence of 100 cm<sup>3</sup>/min pure N<sub>2</sub>, for 10 min to remove possible humidity and CO<sub>2</sub> absorbed. The sample was then heated to the predetermined carbonation temperature (690 °C) under the flow of the inert gas. The selected CO<sub>2</sub> partial pressure was 0.15 atm in order to simulate the typical CO<sub>2</sub> volumetric concentration at the reformer reactor exit which does not surpass 15%. The sorption duration was 30 min. Desorption at 850 °C for 5 min under a 100 cm<sup>3</sup>/min pure N<sub>2</sub> flow followed.

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 the solid bed. Minor variations in the reactor temperature were observed during the reforming/sorption period. This is because the heat requirements for the endothermic reforming were almost balanced by the heat generated from the exothermic carbonation under the conditions studied. The external diameter of the reactor tube in the reaction zone was 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 condense the unreacted steam. The gas phase products were analyzed with an online gas chromatograph (Agilent Technologies, 7890A) equipped with TCD. The CO<sub>2</sub> concentration in the reactor exit was also monitored by a CO<sub>2</sub> analyzer (Horiba, VIA 510). An admixture of a commercial catalyst and CaO–Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, derived from calcium acetate, was used for sorption enhanced steam reforming experiments. The catalyst was crushed and sieved to 100–180 μm. Before testing, the material was reduced in a H<sub>2</sub>/He flow (30% in H<sub>2</sub>) at 850 °C for 1 h. This treatment at high temperature was also sufficient for ensuring the desorption of CO<sub>2</sub> and water possibly sorbed on CaO–Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> from the atmosphere. Approximately 1.5 g of the catalyst and 3 g of the sorbent (bed length: 6 cm), thoroughly mixed, were added to the reactor. The total

inlet flow of methane and helium was 36 cm<sup>3</sup>/min with a steam to methane molar ratio equal to 3.4. The reforming reaction and CO<sub>2</sub> sorption (reforming period) were conducted at 650 °C with a duration controlled by the sorption capacity. The sorbent regeneration was performed in a 100% He flow at 850 °C.<sup>11,33</sup> The operating conditions for cyclic stepwise sorption-enhanced steam methane reforming and sorbent regeneration reactions over CaO–Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> and a commercial catalyst are reported in Table 1.

## Results and Discussion

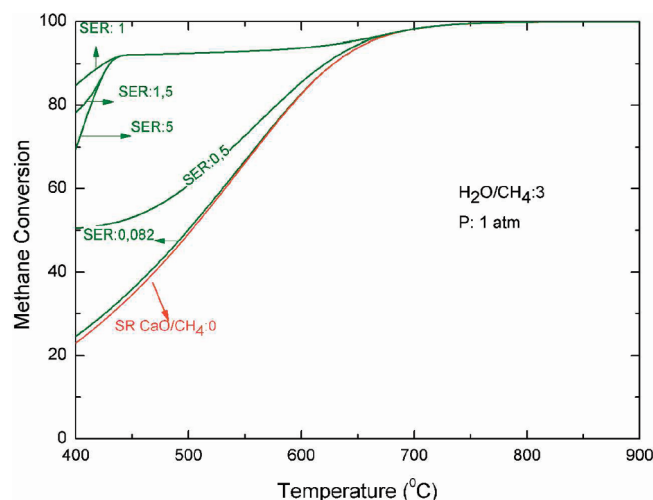
**Thermodynamic Analysis.** Thermodynamics clearly portray the potential advantages of combining reaction and separation for hydrogen production. A preliminary thermodynamic analysis was performed by calculating the equilibrium compositions which minimize the Gibbs free energy. The Aspen Plus 12.1 software was used for the calculations. This code requires specification of the system—at least the reactor—for the reaction calculations. The RGibbs reactor was selected for the calculations using the Peng–Robinson property method. The Aspen Plus code requires also the definition of the possible components in the equilibrium. Hydrogen, carbon dioxide, carbon monoxide, water, methane, calcium oxide, calcium hydroxide, and calcium carbonate were considered as equilibrium components. Carbon was also included in the products pool, but calculations showed that its concentration in the equilibrium stream was negligible. For the simplest hydrocarbon, methane, and with CaO as sorbent, the main reactions scheme can be described with reactions 1–3.

For the analysis, we assumed that the system of the three reactions is in equilibrium. Equilibrium compositions of methane steam reforming were calculated at atmospheric pressure using a steam to fuel a molar ratio of 1 to 5. The analysis was restricted to the 400–900 °C range. Below this range, the kinetics limit the reaction of methane steam reforming, while at  $T > 900$  °C, sintering effects of the materials dominate.

Figure 1 shows the effect of the sorbent to methane molar ratio on the equilibrium conversion of methane in the case of conventional steam reforming (SR) and sorption enhanced steam reforming (SER) as a function of temperature. In both SR and SER, temperature rise favors the endothermic reforming reaction, leading to higher methane conversions. An increase of sorbent has a positive effect on methane conversion, which attains a maximum value at a sorbent to methane molar ratio equal to 1. It should be noted that the above outcome does not take into account the CaO utilization perspective. The carbonation conversion of most of the CaO-based sorbents is limited due to diffusion related problems and decreases with the number of cycles, parameters that cannot be taken into account in a thermodynamic analysis. Therefore, for a specified sorbent and process, the determination of the optimum CaO to methane ratio can only be evaluated with a techno-economic study.

(33) Ortiz, A. L.; Harrison, D. P. *Ind. Eng. Chem. Res.* **2001**, *40*, 5102–5109.



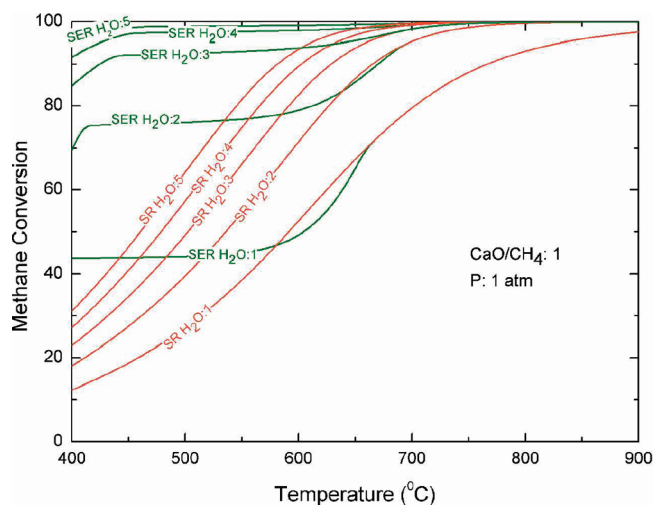


**Figure 1.** Effect of temperature and sorbent to methane molar ratio on the equilibrium conversion of methane in the case of SR and SER (molar  $H_2O/CH_4$ : 3, 1 atm).

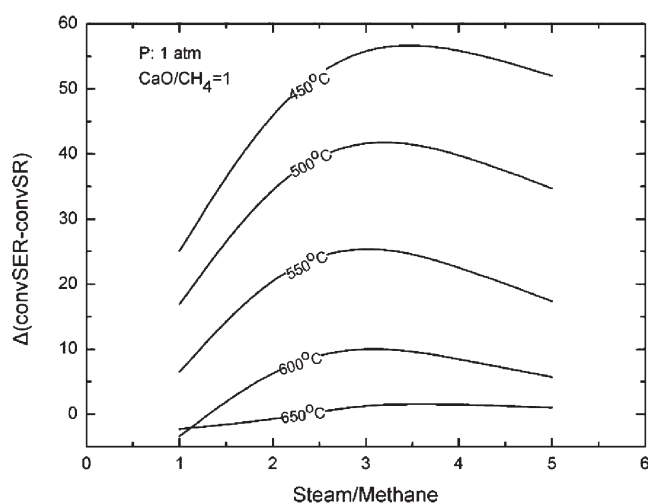
MacKenzie et al.<sup>34</sup> reported that the economics of flue gas  $CO_2$  capture using the calcium cycle are dominated by the cost of the utilized sorbent. The  $CaO/C$  ratio and the  $CaO$  deactivation rate are the key variables to improve the viability of the system. Reduction of these rates, possibly by development of new calcium-based sorbents, can lead to lower feedstock and operation costs as less material will be cycled and consequently wasted.

Another interesting point of Figure 1 is that, at temperatures lower than 430 °C and for a sorbent to methane ratio greater than 1, the consumption of steam for the formation of  $Ca(OH)_2$  limits methane conversion. For temperatures higher than 430 °C and a sorbent to methane ratio equal to 1, more than 90% of the methane is converted, while for the same temperature range and in the absence of  $CaO$ , the conversion progressively increases from 30% up to 90%. In any  $CaO$  to  $CH_4$  ratio, for a steam to methane ratio equal to 3, under 1 atm of pressure, and temperatures above 680 °C, the  $CO_2$  capture reaction is no longer effective and the equilibrium methane concentration is the same for both processes.

The steam to methane molar ratio strongly affects methane conversion, for both SR and SER, as illustrated in Figure 2. The higher the ratio, the higher is the equilibrium methane conversion at a specific temperature. This effect is stronger in SER because higher steam concentrations lead to higher equilibrium  $CO_2$  partial pressures, enhancing sorption and sequentially methane conversion. However, for each temperature, there is a maximum steam to methane molar ratio, equal to 3, above which its effect on SER methane conversion is minimal. On the other hand, the effect of this ratio in SR methane conversion, in each temperature up to 600 °C, is substantial for all the investigated steam to methane molar ratios. In accordance with the above, Figure 3 demonstrates that the maximum advantage of SER over SR, with respect to methane conversion, can be attained with steam to methane molar ratios around 3 for temperatures up to 600 °C. It is well-known that the excess of steam not only favors the thermodynamics of the steam reforming reaction but also inhibits coke formation. However, higher steam



**Figure 2.** Effect of temperature and steam to methane molar ratio on the equilibrium conversion of methane in the case of SR and SER (molar  $CaO/CH_4$ : 1, 1 atm).



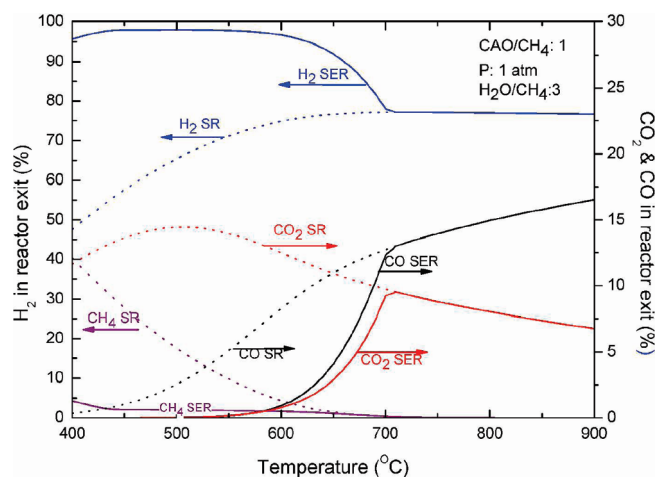
**Figure 3.** Variation in the  $CH_4$  conversion difference between SR and SER as a function of temperature and steam to methane molar ratio (molar  $CaO/CH_4$ : 1, 1 atm).

utilization induces a critical efficiency penalty due to higher energy demands for steam generation.<sup>35</sup> It is of high importance that in SER, for the various steam to methane molar ratios examined and for a broad temperature range, methane conversion remains almost constant because of the reverse effect of the exothermic sorption and water gas shift (WGS) reactions, as opposed to the endothermic reforming reaction (Figure 2). It is also remarkable that a steam to methane ratio equal to 1 is inadequate to cover the demands of the governing reforming reaction at temperatures higher than 600 °C. As a consequence, methane conversion drops at lower values than in SR.

Figure 4 compares the dry equilibrium composition at the reactor exit which results from reacting methane and steam in the presence (SER) and absence of  $CaO$  (SR), as a function of temperature. The formed mixtures consist of hydrogen, carbon monoxide, carbon dioxide, and unreacted methane.

(34) MacKenzie, A.; Granatstein, D. L.; Anthony, E. J.; Abanades, J. C. *Energy Fuels* 2007, 21, 920–926.

(35) Bartholomew, C. H.; Farrauto, R. J. *Fundamentals of Industrial Catalytic Processes*; John Wiley & Sons, Inc.: Hoboken, NJ, 2006; pp 268–270.

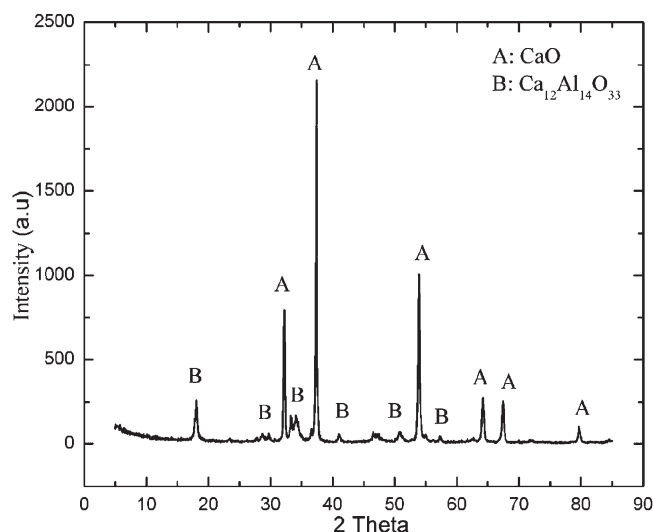


**Figure 4.** Effect of temperature on equilibrium reactor outlet composition of SR and SER.

In the conventional reforming process, the carbon monoxide content increases linearly with the temperature, as its formation depends on the endothermic steam reforming reaction. On the other hand, carbon dioxide concentration, which is determined by the exothermic water gas shift reaction, reaches a maximum of almost 15% near 500 °C. Hydrogen concentration depends on both reactions but is governed by the endothermic reforming reaction. As a result, it reaches a maximum of 77% at 650 °C and remains constant at higher temperatures. In the presence of the CO<sub>2</sub> sorbent, the equilibrium conversion of methane remains very high over the entire temperature range. Hydrogen purity is very high (98%) in the temperature range 450 to 550 °C and decreases at higher temperatures due to the exothermic nature of the carbonation reaction, which gradually diminishes for temperatures higher than 600 °C, finally ceasing at 710 °C. It is thus possible to produce high purity hydrogen at relatively low temperatures applying the SER process. Both carbon oxides are negligible for temperatures 400–600 °C due to the strong effect of the carbonation reaction of the CO<sub>2</sub> sorbent. For higher temperatures, up to 710 °C, their concentration increases, following afterward the course of conventional steam reforming.

The present thermodynamic analysis reveals that for a steam to methane molar ratio equal to 3 the maximum advantage of SER over SR can be attained. Moreover, a CaO to methane ratio equal to 1 is the threshold to obtain maximum methane conversion. The study also demonstrates that the optimum temperature for SER lies in the range 450–600 °C. However, as previously mentioned, the selection of the temperature depends not only on thermodynamics but also on kinetics. The reforming kinetics are favored at high temperatures. In addition to that, the risk of carbon formation increases at low temperatures. Therefore, a temperature of 650 °C was selected for the SER experiments in this study. On the basis of the results of the SER thermodynamic analysis, under these conditions, more than 95% of methane can be potentially converted to produce high purity hydrogen (almost 93%), while according to the equilibrium of SR the hydrogen concentration cannot surpass 77%.

**Sorbent Characterization.** A polycrystalline nanocomposite oxide of Ca and Al, with a surface area and pore volume of 11.68 m<sup>2</sup>/g and 0.098 cm<sup>3</sup>/g, respectively, was successfully



**Figure 5.** X-ray diffractogram of the new material CaO–Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>.

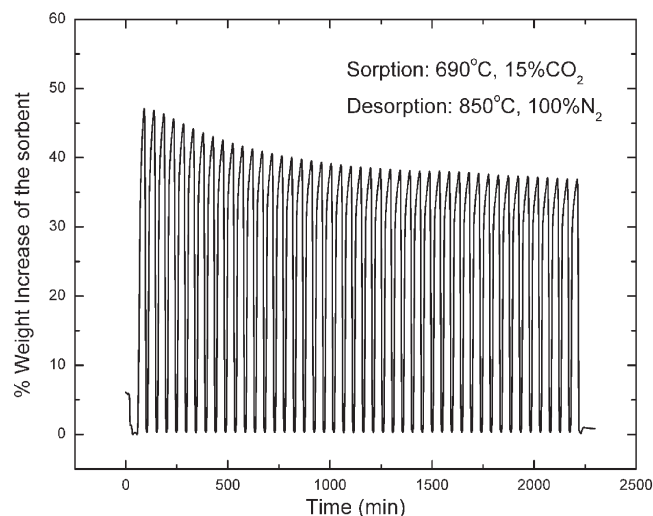
synthesized. Pore volume was calculated from the adsorption branch of the nitrogen isotherm.

The XRD pattern of the new sorbent material is presented in Figure 5. All characteristic peaks of CaO ( $2\theta = 32.2, 37.35, 53.85, 64.15, 67.3$ ) and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> ( $2\theta = 33.41, 41.21, 55.22, 57.52$ ) were clearly detected. The absence of any other Ca–Al mixed phases or hydrated mixed structures proved that the calcination conditions applied in the synthesis process (900 °C, 1.5 h) and the weight ratio of the metal precursors ensure the formation of the desired CaO–Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>.

**Sorption Capacity.** The CaO–Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (75:25 wt) sample proved to be an effective CO<sub>2</sub> sorbent with adequate cyclic stability.<sup>18–23</sup> The stability of CaO in repeated sorption–desorption cycles was attributed to the uniform dispersion of tolerant at high temperature Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> among CaO particles, which provides a stable framework inhibiting sintering of active CaO sites. A previous study of our group demonstrated that utilizing calcium acetate as a CaO precursor could lead to 65% improvement in the CO<sub>2</sub> uptake compared to CaO–Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> derived from other precursors.<sup>22</sup> Moreover, a CaO to Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> weight ratio equal to 85:15 proved superior to the 75:25 ratio.

The sorption capacity of the improved CaO–Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (85:15 wt) sorbent was tested in the TGA at 690 °C in 45 repetitive cycles of sorption–desorption using a flow of CO<sub>2</sub> in He (15% CO<sub>2</sub>). The variation in the weight of the sample is illustrated in Figure 6. The material initially captured almost 10 mol of CO<sub>2</sub> per kg, with a moderate loss in capacity (15%) after the fifth cycle. This loss can be characterized as negligible compared to other CaO sorbents which exhibit a far more drastic decrease of their fixing ability, as reviewed by Abanades.<sup>17</sup> It is important to note that, in the present study, in the TGA experiments, the desorption took place at 850 °C in the presence of pure N<sub>2</sub>, with conditions selected on the basis of the protocol followed for multicycle tests in the literature.<sup>11,13,25–29</sup> However, under realistic conditions, high CO<sub>2</sub> partial pressure and a temperature of about 950 °C during calcination are needed to produce a near pure CO<sub>2</sub> stream suitable for storage or use in an alternative chemical process.<sup>31</sup>

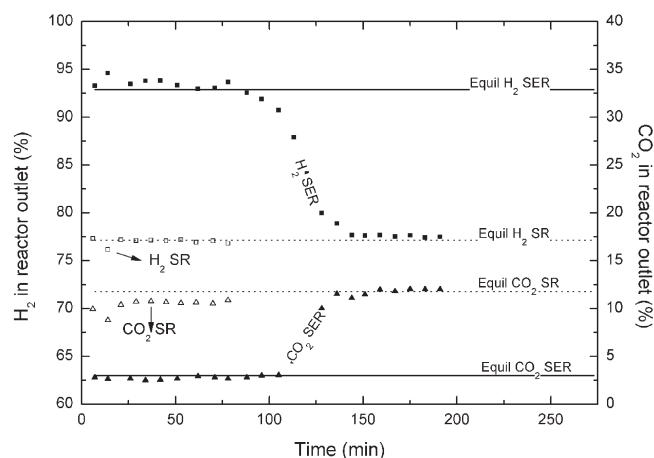
**Sorption Enhanced Reforming Experiments.** A reaction system of this type is inherently in an unsteady state because



**Figure 6.** Cyclic sorption capacity of  $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  (85:15 wt) derived from calcium acetate (sorption: 690 °C, 30 min, 15%  $\text{CO}_2$ ; desorption: 850 °C, 5 min, 100%  $\text{N}_2$ ).

of the progressive saturation of the fixed amount of sorbent present in the reactor. The sorbent is progressively saturated, and its enhanced effect on the equilibrium gradually diminishes. A typical reactor response curve is characterized by three regimes. The first one, where the product composition is almost steady, is usually referred to as the prebreakthrough period.<sup>4,32</sup> During this period, the three reactions of the system—reforming, shift, and carbonation—are all active, and the concentration of the valuable  $\text{H}_2$  is at its maximum value while the undesired  $\text{CO}_2$  and  $\text{CO}$  attain their minimum values. The duration of this period is a function of the sorbent properties (sorption capacity and sorption kinetics), its mass, and the operating conditions. For a certain material and under the same conditions, the duration of the prebreakthrough period would decrease as the result of the deactivation of the sorption sites of the material. Prebreakthrough is followed by the breakthrough period, which begins when the leading edge of the surface carbonation reaction front reaches the exit of the fixed bed of the solid. At this point,  $\text{CO}_2$  removal becomes less effective, and as a result  $\text{CO}$  conversion in the shift reaction is limited. Under the same conditions, the duration of this period is affected by the diffusion of  $\text{CO}_2$  through the generated  $\text{CaCO}_3$  layer and by the available “space” in the interior of the material for the generation of the larger (compared to  $\text{CaO}$ ) specific volume  $\text{CaCO}_3$ .<sup>24</sup> Increase of the breakthrough time implies sorbent morphology degradation, thus deactivation. When the carbonation rate approaches zero, the postbreakthrough period is reached and the system behaves as it would in the absence of the  $\text{CO}_2$  sorbent. Only the reforming and shift reactions are active, and the product composition is determined by the kinetics and thermodynamics of these reactions.

As mentioned in the Experimental Section, a commercial steam reforming catalyst was used in the tests. The long-term efficiency of the catalyst was tested and confirmed under conditions far from those leading to equilibrium composition. Moreover, steam reforming experiments without a sorbent were carried out to test the activity of the commercial catalyst at 650 °C and a steam to methane molar ratio equal to 3.4 and were used as a reference for the experiments with a mixed bed of catalyst and sorbent. Figure 7 presents the

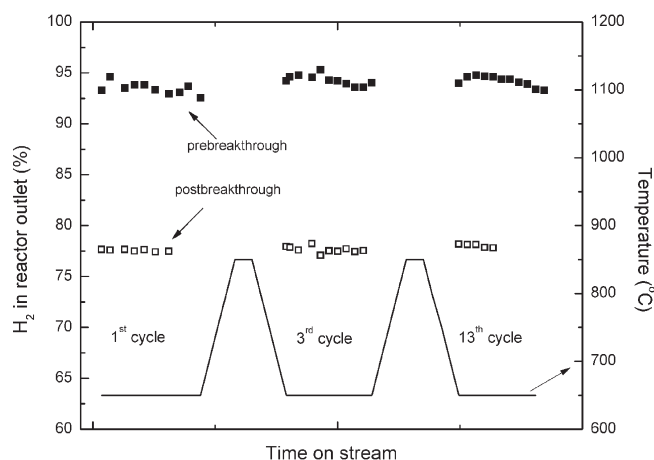


**Figure 7.** Outlet  $\text{H}_2$  and  $\text{CO}_2$  concentration (dry basis) response curve. Reaction conditions: 1 atm, 650 °C, molar  $\text{H}_2\text{O}/\text{CH}_4 = 3.4$ .

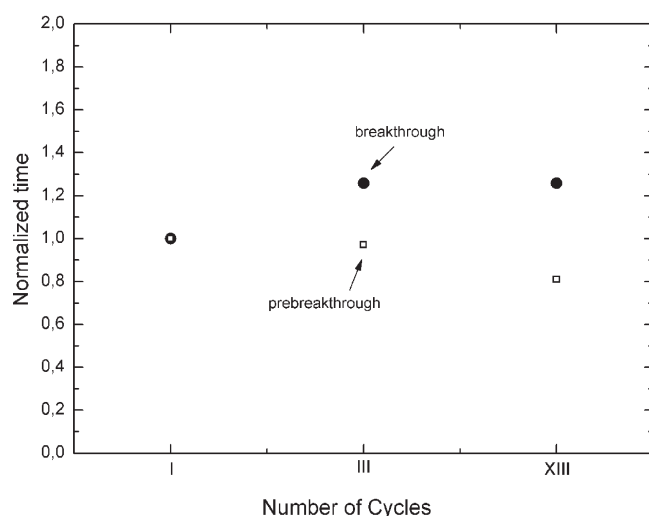
experimental results of SR (open symbols), SER (closed symbols), and the equilibrium concentrations (solid lines). The steam reforming results are close to the equilibrium values, indicating that the catalyst activity at the relevant conditions is high enough. The effluent gas composition indicates constant hydrogen concentration at near 77% and a  $\text{CO}_2$  concentration at 10–11% throughout the course of the experiment.

The new sorbent material  $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  (85:15) was then mixed with the reforming catalyst and introduced to the reactor. The reaction conditions are summarized in Table 1. The composition of the reactor exit stream in  $\text{H}_2$  and  $\text{CO}_2$  from the first sorption–desorption cycle of an experiment at 650 °C and a  $\text{H}_2\text{O}/\text{CH}_4$  feed ratio of 3.4 is illustrated in Figure 7, along with the corresponding results from the experiment without  $\text{CO}_2$  sorbent. The equilibrium values for the SER and SR system reactions are also included. A key feature of this figure is the close proximity of the experimental and equilibrium values in both the prebreakthrough and postbreakthrough periods. The effluent gas composition of the SER experiments follows a different trend than that of the SR. In the SER experiment, more than 93% of the methane was converted following the thermodynamic predictions. The low  $\text{CO}_2$  and  $\text{CO}$  contents (2–3% and 3–4%, respectively) observed in the prebreakthrough period prove the efficiency of the sorbent. Moreover, the high hydrogen concentration (>92%) demonstrates the enhancing effect of the sorbent on the conversion of methane to the desired product. As the sorbent started saturating, the hydrogen concentration decreased, whereas  $\text{CO}$  and  $\text{CO}_2$  increased, finally equilibrating to values almost equal to those of SR.

The hydrogen concentration during the prebreakthrough period of the first, third, and 13th cycles is shown in Figure 8. The minor differences in the profiles between the first and the 13th cycles point indirectly to the adequate stability of the sorbent and the catalyst under the examined conditions. The durations of the prebreakthrough and breakthrough periods provide an indication of the stability of the sorbent. Figure 9 presents the normalized prebreakthrough and breakthrough times for the first, third, and 13th cycles. The normalized time is defined as the ratio of the time of cycle  $i$  to the time of the first cycle. A clear reduction of the prebreakthrough period and an evident increase of the breakthrough period can be observed. The reduction in the prebreakthrough period is most probably a result of the decrease of the



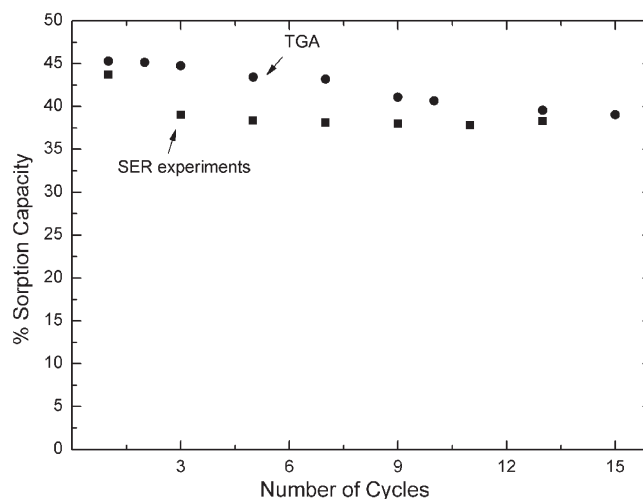
**Figure 8.** Prebreakthrough and postbreakthrough hydrogen concentration (dry basis) for the 1st, 3rd, and 13th reforming–regeneration cycles in SER. Reaction conditions: 1 atm, 650 °C, molar  $\text{H}_2\text{O}/\text{CH}_4 = 3.4$ .



**Figure 9.** Normalized prebreakthrough and breakthrough times for the 1st, 3rd, and 13th reforming–regeneration cycles in SER. Reaction conditions: 1 atm, 650 °C,  $\text{H}_2\text{O}/\text{CH}_4 = 3.4$ .

external surface sorption sites of the material. On the other hand, the slight increase in the breakthrough duration, as shown in Figure 9, indicates not a loss but a transformation of some of the external surface sites to less accessible ones. Overall, after a certain number of cycles, only part of the sites was permanently lost, resulting in a moderate loss of  $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  sorption capacity (15%). The stability of  $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  (75:25) in methane sorption enhanced reforming has been also demonstrated in the literature.<sup>11</sup> However, direct comparison with the present results is not possible due to the differences in the material composition and operating conditions.

The  $\text{CO}_2$  capture effectiveness of the new material under real reaction conditions was also determined on the basis of rough calculations of the mass of the  $\text{CO}_2$  desorbed during the regeneration in each cycle. These calculations, based on the integration of the desorption curves of the  $\text{CO}_2$  analyzer, showed that 3 g of the material captured approximately 1.3 and 1.15 g of  $\text{CO}_2$  at the first and fifth cycles, respectively. These values account for a 44% and a 38% sorption capacity, as shown in Figure 10, where the SER experimental



**Figure 10.** Comparison of SER and TGA sorption capacity of  $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  (85:15wt) for multicycle testing.

results are presented together with the TGA results. It should be stressed that this figure should not be used for direct comparison of the sorption capacity in TGA and SER experiments, as the operating conditions are not similar. It however provides a qualitative indication of the trend in stability. Two areas with different slopes can be seen for both the TGA and the SER curves. The SER capacity decreased for the first 5 cycles while attaining an almost flat profile for the remaining cycles in agreement with the TGA capacity curve.

The amount of  $\text{CO}_2$  emitted during the prebreakthrough period of the first cycle of the SER experiments is 67% less than the amount of total  $\text{CO}_2$  that would have been emitted in conventional steam reforming. Therefore, the application of the SER process not only increases the hydrogen purity but also reduces the number of necessary downstream processing steps.

## Conclusions

Previously reported results showed that high purity hydrogen can be produced in a single processing step via the sorption-enhanced steam-methane reforming using  $\text{CaO}$  as a  $\text{CO}_2$  sorbent. However, the decrease in sorbent conversion detected in most of the multicycle studies limits the economic viability of sorption enhanced reforming.

This study demonstrates that  $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  (85:15 wt) synthesized using calcium acetate as a  $\text{CaO}$  precursor may be effectively used as a  $\text{CO}_2$  sorbent. More than 93% of the methane is converted at the low temperature of 650 °C and 1 bar of pressure with a steam to methane molar ratio equal to 3.4. The high hydrogen purity, >92%, of the reforming outlet stream compared to the 77% hydrogen concentration in the case of the conventional steam reforming reveals the high importance of the sorbents' presence. At the same time, with the use of  $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ , the necessity of downstream purification steps decreases due to the low  $\text{CO}$  and  $\text{CO}_2$  contents (2–3% and 3–4%) at the reformer exit. Multicycle tests show a moderate decrease in the  $\text{CaO}-\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  sorption capacity, providing incentive for further improvement and evaluation under more realistic process conditions.

**Acknowledgment.** The authors are grateful to Ms. Evangelia Tousiaki for her help in the synthesis of the materials, Mr. Dimitris Sergiadis for his help in thermodynamic analysis, and Dr. Lori Nalbandian and Dr. Eleni Heracleous for the fruitful discussions.