

Improved Hydrogen Production by Sorption-Enhanced Steam Methane Reforming over Hydrotalcite- and Calcium-Based Hybrid Materials

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ABSTRACT: The sorption-enhanced reforming process (or SERP), which combines steam reforming and in situ carbon dioxide (CO_2) capture by adsorption, is a candidate technique for improved hydrogen (H_2) production. In the present work, the performance of hybrid materials comprising a Ni-based reforming catalyst and hydrotalcite- (Ni-HTc or HM1) or calcium-based sorbents (Ni-CaO/ Al_2O_3 or HM2) for sorption-enhanced steam methane reforming was compared. It was found that such lab-made hybrid materials exhibit superior adsorption characteristics and longer breakthrough times than powdered mixtures of commercial Ni/ Al_2O_3 catalyst and the respective sorbent (HTc or CaO). H_2 -rich gas (98.5 and 97.9%) was obtained using the investigated hybrid materials HM1 and HM2 for SERP. The influence of reaction variables such as temperature, steam/carbon ratio, and gas hourly space velocity on methane conversion and product gas composition was investigated. Stability tests for both the hybrid materials were performed for 20 cycles. Hydrotalcite-based hybrid material HM1 adsorbed up to 1.1 mol CO_2/kg sorbent at 673 K and was stable for 16 cycles. Conversely, the calcium-based hybrid material HM2 showed an adsorption capacity of 12.3 mol of CO_2/kg sorbent at 823 K and remained stable up to 11 cycles.

1. INTRODUCTION

There is, at present, great interest in the study of the sorption-enhanced reforming process (SERP), a candidate technique for producing pure H_2 via simultaneous reforming and adsorptive separation of CO_2 .^{1,2} SERP comprises reforming over a mixture of catalyst and chemisorbent at temperatures lower than those used in conventional steam reforming (SR). As a result, the energy requirement is low and catalyst sintering is reduced. Besides, the use of expensive materials for construction of the reactors is not essential. The chemisorbent selectively removes CO_2 formed during reaction, thereby favoring water–gas shift (WGS) and enhancing H_2 selectivity. The subsequent separation of CO_2 in a series of processing steps is eliminated. Further purification by methanation or preferential oxidation is eliminated, too, thereby reducing capital costs. The adsorbent is periodically regenerated (e.g., by pressure swing adsorption) and reused.

An ideal CO_2 sorbent should exhibit satisfactory adsorption characteristics, high cyclic stability, good mechanical strength, and suitable adsorption/desorption kinetics.³ Up to now, several types of adsorbents have been reported in the literature, e.g., mixed oxide materials such as calcium oxide (CaO), lithium metal oxides such as lithium zirconate (LZC), lithium orthosilicate (LOS), and hydrotalcite (HTc) materials. Among these, calcium-based sorbents like CaO exhibit the highest adsorption capacity, due to a strong chemical interaction with CO_2 that results in CaCO_3 formation. Major drawbacks of calcium-based sorbents are the rapid decrease in capacity during multicycle operation and the high regeneration energy requirement.^{4,5} For this reason, modified CaO-based sorbents were developed by either incorporating metal oxides in the structure or changing the Ca precursors.^{6–11} Recently, an energy-efficient combination of Ca and Cu/CuO chemical loop was proposed, in which the heat for the endothermic

decomposition of CaCO_3 was provided by the exothermic reduction of CuO with methane.¹²

Hydrotalcites are promising candidate sorbents used for CO_2 capture. They are renowned as layered double hydroxides belonging to the family of anionic clays. They comprise layers of magnesium and aluminum with interlayers consisting of carbonate ions and water molecules that are exchangeable.¹³ Magnesium, which is basic, facilitates the selective adsorption of acidic CO_2 . They offer two useful advantages, viz., the ease of regeneration and high cyclic stability for SERP.

To ensure fast adsorption/desorption kinetics and absence of diffusion limitations, hybrid materials comprising reforming catalyst and adsorbents which provide high rates of diffusion and improved access to active sites are promising. During the past decade, many such examples have been reported in the literature. For instance, Wu et al.¹⁴ produced H_2 (purity of 90%) using Ni-CaO- Al_2O_3 derived from HTc-like materials. Further, Cunha and co-workers^{15–17} synthesized highly stable Cu-based HTc materials for producing H_2 (purity of 90%) at $T < 873$ K. Martavaltzi and Lemonidou¹⁸ produced pure H_2 (90%) at 923 K using a hybrid CaO material stabilized by Ni- $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$. Kim et al.¹⁹ developed a catalyst-sorbent system such as CaO- $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ -Ni for producing pure H_2 (95%). Besides, the influence of varying Mg/Al ratio on the performance of hydrotalcites was also investigated.^{20,21} Synthesis of hybrid materials, which exhibit moderate to high adsorption capacity over a number of cycles and ease of regeneration, is crucial for improved H_2 production via SERP. In the present work, the performance of two lab-made hybrid materials comprising a Ni-based reforming catalyst and

Received: March 19, 2015

Revised: May 23, 2015

Published: May 25, 2015



hydrotalcite- (Ni-HTc or HM1) or calcium-based sorbents (Ni-CaO/Al₂O₃ or HM2) for sorption-enhanced steam methane reforming was compared. Further, these hybrid materials were weighed against powdered mixtures of the catalyst and the respective sorbent. To the best of our knowledge, no such assessment exists in the literature. The performance of our hybrid materials was very encouraging.

2. EXPERIMENTAL SECTION

2.1. Materials. Commercial Ni/Al₂O₃ catalyst (particle size 1200 nm) was purchased from Alfa Aesar Ltd. Powdered calcium oxide (size <160 nm) and hydrotalcite (<50 nm) were purchased from Sigma-Aldrich Pvt. Ltd., Mumbai. Magnesium nitrate, nickel nitrate, aluminum nitrate, sodium carbonate, and sodium hydroxide used during the synthesis of hybrid materials were also procured from Sigma-Aldrich Pvt. Ltd., Mumbai. Gases like air, H₂ and nitrogen (N₂) in cylinders (purity 99.995%) were acquired from Industrial Oxygen Company Ltd., Mumbai. Standard calibration gas mixtures containing CO, CO₂, and CH₄ were procured from Chemtron Laboratory Pvt. Ltd., Mumbai.

2.2. Hybrid Material Synthesis. Hybrid material Ni-HTc (HM1) was synthesized by the coprecipitation method previously reported in the literature.²² Nitrates of metal components such as nickel nitrate, magnesium nitrate, and aluminum nitrate were used in appropriate amounts. An Mg/Al ratio equal to 3 was selected so as to have a higher content of magnesium in the material, and hence, enhanced adsorption of CO₂. An aqueous solution of the metal nitrates was slowly added into a beaker containing an aqueous solution of sodium carbonate under continuous stirring at room temperature and a constant pH of 10. The pH of the solution was maintained using an aqueous solution of sodium hydroxide (2 M). The resulting suspension was then kept at room temperature for 24 h. The precipitate thus obtained was filtered and washed several times with deionized water to remove any traces of nitrates; this was further confirmed by the brown ring test. The resulting material was dried at 383 K overnight and ground to fine powder and calcined at 1073 K for 5 h in air. The material was then crushed and sieved to fine particles with 30–60 mesh size (0.3–0.6 mm).

For the synthesis of hybrid material (HM2), i.e., Ni-CaO/Al₂O₃, the incipient wetness impregnation technique was adopted.²³ In this method, CaO and Al₂O₃ supports were impregnated with appropriate amounts of nickel nitrate hexahydrate. A Ca/Al ratio equal to 3 was selected. The mixture was continuously stirred to ensure proper impregnation. The resulting suspension was filtered, washed with deionized water repeatedly to remove the nitrates, dried overnight at 383 K, and finally calcined at 1173 K for 4 h. In both the hybrid materials, 10 wt % nickel loading was chosen.

2.3. Characterization of Hybrid Materials. After synthesis, both hybrid materials were characterized by using suitable techniques. Crystallinity and textural patterns were predicted from X-ray diffraction (XRD) data, which were recorded using a Rigaku—miniflex powder diffractometer with CuK (1.54 Å) radiation. The nitrogen adsorption–desorption technique (Micromeritics ASAP2010) was used to find the Brunauer–Emmet–Teller (BET) surface area, pore volume, and pore diameter by Barrett–Joyner–Halenda (BJH) and multipoint BET method. Scanning electron microscope (SEM) micrographs and energy dispersive X-ray spectroscopy (EDX) data were obtained by using a JEOL-JSM 6380 LA instrument.

2.4. Experimental Setup. A SS-316 tubular fixed-bed down-flow reactor (inner diameter 19 mm, outer diameter 25.4 mm length 50 mm), purchased from Chemito Technologies Pvt. Ltd., Mumbai, was used in all experiments. The setup was supplied with a control panel, temperature-controlled furnace, gas chromatograph (GC 8610) unit, and a data acquisition system (Proficy HMI/SCADA-ifax software). The temperature was controlled by using a temperature controller (West, Germany). A pressure transducer (0–100 bar) enabled the measurement of pressure with an uncertainty of ±0.1 bar.

2.5. Experimental Procedure. Five possible combinations of catalyst and sorbent were used. For the experiments on steam methane

reforming, a commercial Ni/Al₂O₃ catalyst (1.5 g) was packed between two beds of quartz wool. For the case when mixtures of powdered catalyst and sorbent were used (1.5 g each), the sorbent was packed first between a thin bed of quartz wool. Then, the catalyst was packed. A similar procedure was used for the hybrid materials (3 g).

The catalyst was reduced in the reactor under flowing H₂ (10 L/h) for 1 h. An HPLC pump was used to introduce steam at a predefined flow rate. CH₄ was supplied through a cylinder at a predefined flow rate. N₂ was used as the carrier gas during reaction. The steam–CH₄ mixture was vaporized and passed through the reactor. The ratio of the catalyst mass to the flow rate of methane was 6.3 g h/mol. All experiments were performed at 0.1 MPa pressure. The premix heater temperature was maintained at 523 K. Product gases were analyzed online using a gas chromatograph (GC) unit equipped with a TCD. Hayesep DB column was used for detecting H₂, CH₄, CO₂, and CO. Nitrogen was used as the carrier gas. Standard calibration gas mixtures were used to determine the product composition. The CO concentration in the product gases was below detection level, thereby suggesting that it was formed in trace amounts. This is a major advantage of SERP.

The conversion of CH₄ was defined as follows:

$$\text{CH}_4 \text{ conversion (\%)} = \frac{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{in}}} \times 100 \quad (1)$$

where [CH₄]_{in} and [CH₄]_{out} represent the inlet and outlet molar flow rate (mol/h) of CH₄. H₂ yield was defined as

$$\text{H}_2 \text{ yield (\%)} = \frac{[\text{H}_2]_{\text{out}}}{4 \times [\text{CH}_4]_{\text{in}}} \times 100 \quad (2)$$

where [H₂]_{out} represents the outlet molar flow rate (mol/h) of H₂. Gas hourly space velocity (GHSV) was defined as

$$\text{GHSV} = \text{outlet gas flow (mL/min)} / \text{weight of material (g)} \quad (3)$$

The adsorption capacity of the adsorbents was calculated by using the relation:

$$Q_{\text{ads}} = (F \cdot C_o \cdot t_b) / W \quad (4)$$

where F is the total molar flow of the feed gas (mol/min), C_o is the initial CO₂ concentration (mole %), W is the mass of the solid adsorbent loaded on the column (g), and t_b is the stoichiometric time in minutes, determined from the breakthrough curve.

3. RESULTS AND DISCUSSION

3.1. Characterization of Hybrid Materials. XRD patterns of the hybrid materials HM1 and HM2 before reduction are shown in Figure 1, panels a and b, respectively. For the case of HM1, the diffraction peaks at $2\theta = 43.1^\circ$, 62.65° , and 75.1° correspond to NiO. The peak observed at $2\theta = 37.1^\circ$ is typical of the HTc structure. Besides, a crystalline AlOOH phase is observed at $2\theta = 18.6^\circ$. These results were in line with a previous work.²⁴ For the case of HM2, peaks similar to those observed in HM1 correspond to NiO. Furthermore, the CaO peak at $2\theta = 33.2^\circ$ before reaction suggests that carbonation of CaO does not occur. The peak at $2\theta = 17.9^\circ$ indicates the presence of Ca(OH)₂ in the sample, possibly due to the reaction of CaO with steam. The formation of Ca(OH)₂ also occurred during reaction; this may affect the cyclic stability of the material because the reaction with steam results in lowering of S/C ratio and formation of coke. Diffraction peaks of calcium aluminate as stabilizer are seen at $2\theta = 29.3^\circ$ and 37.2° . This suggests interaction between calcium and aluminum precursors that is essential for increasing the cyclic stability of this hybrid material. Using the Scherrer formula, the phases and crystallite sizes of various peaks were calculated; these are represented in Table 1.

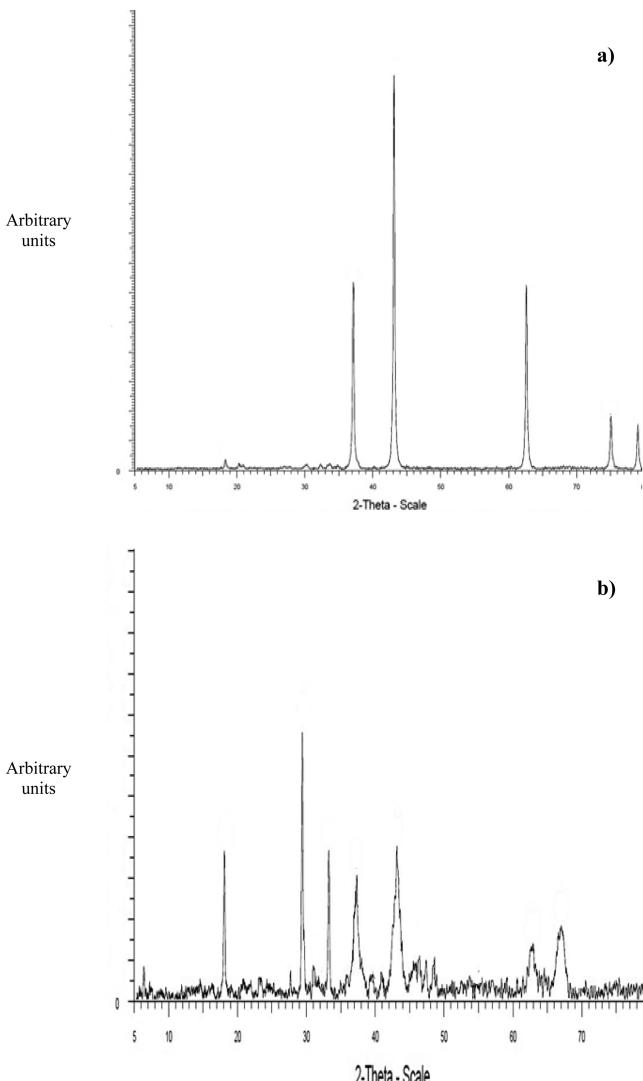


Figure 1. XRD patterns for (a) HM1 and (b) HM2.

Table 1. Crystallite Sizes of Hybrid Materials

hybrid material	phase	2θ position (°)	crystallite size, <i>d</i> (nm)
HM1	NiO	43.1	46.5
		62.65	34.9
		75.1	30.3
	HTc	37.1	52.9
		18.6	81.5
	NiO	43.1	46.5
HM2	NiO	62.65	34.9
		67.06	7
		29.3	79.8
	CaAl ₂ O ₄	37.2	12.5
		33.2	64.2
	CaO	17.9	121.1

Surface area, pore volume, and pore diameter are three key features that influence the adsorption capacity. These properties are represented in Table 2. The surface area of HM2 was found to be reasonably high. SEM images of the fresh hybrid materials (HM1 and HM2) are shown in Figure 2a,b. The highly porous sponge-like HTc structure of HM1 is evident in Figure 2a. In a previous work, it was reported that the addition

Table 2. Surface Area, Pore Volume, and Pore Diameter of the Hybrid Materials^a

hybrid material	surface area (m ² /g)		pore volume (cm ³ /g)		pore diameter (Å)	
	unused	after 20 cyclic tests	unused	after 20 cyclic tests	unused	after 20 cyclic tests
HM1	75.4	44	0.2	0.17	136.1	147
HM2	64.9	31.2	0.2	0.14	123	130

^aBefore and after cyclic testing.

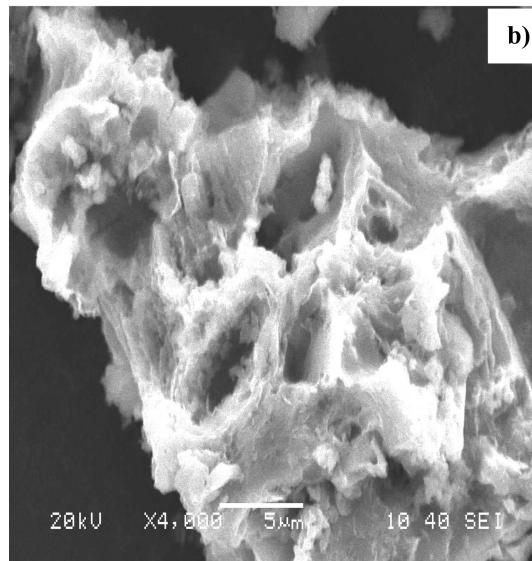
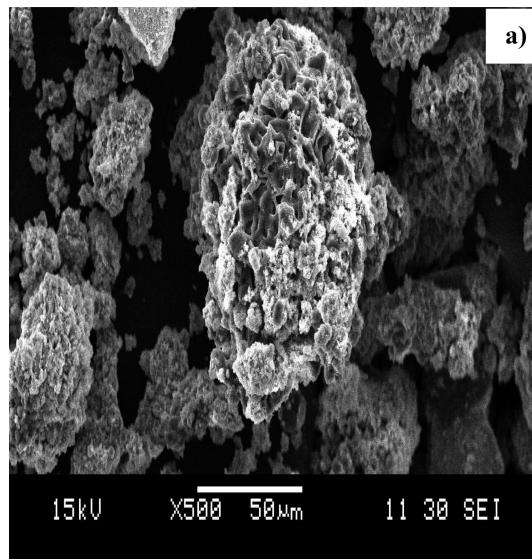


Figure 2. SEM images of (a) HM1 and (b) HM2.

of nickel does not alter the morphology, and small Ni crystallites are present inside the pores of the amorphous aluminum oxide support.²⁵ The macroporous structure of HM2 is seen in Figure 2b.

To report the composition of Ni, Mg, and Al in HM1 and Ni, Ca, and Al in HM2, EDX analysis was performed. Ratios of Mg (65.9 mass %)/Al (24.6 mass %) and Ca (61.2 mass %)/Al (28.5 mass %) were observed. Ni content in both the samples

was approximately 10%. A higher amount of Mg and Ca in the hybrid materials helps in increased adsorption of acidic CO₂.

3.2. Conventional Steam Reforming Using Ni/Al₂O₃.

Steam methane reforming was investigated using powdered Ni/Al₂O₃ catalyst. The influence of temperature on CH₄ conversion and H₂ yield was investigated in the 773–1073 K range. A rise in temperature expectedly facilitated H₂ production. As seen in Figure 3a, CH₄ conversion was

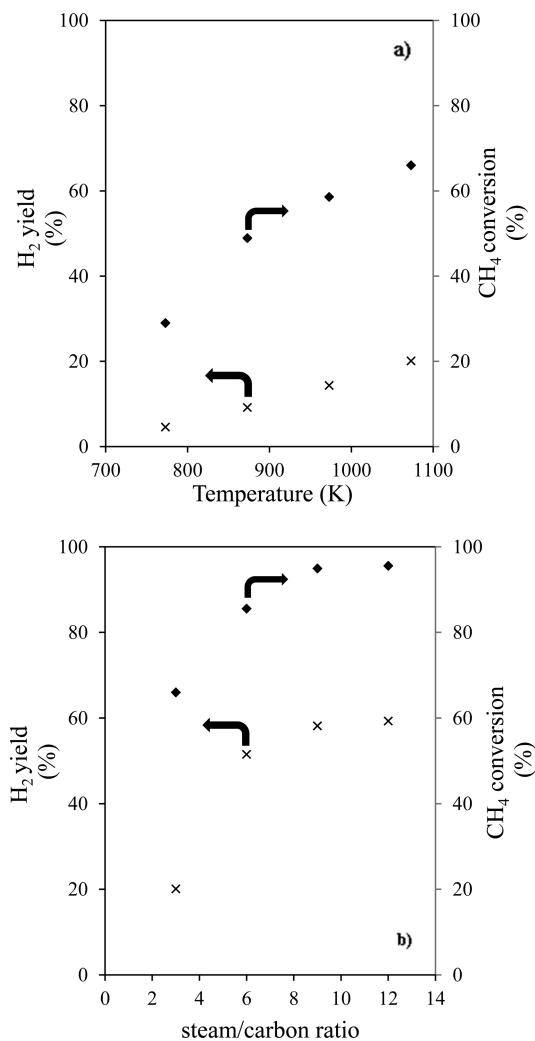


Figure 3. Effects of (a) temperature and (b) S/C ratios in the case of conventional steam methane reforming (reaction pressure = 0.1 MPa, GHSV = 3450 mL/(g h), time on stream = 4 h).

maximized (66%) at 1073 K; the yield of H₂ was 20.1%. However, high reaction temperatures necessitate high energy costs. Also, H₂ purity is low, due to the presence of CO₂ in the product. As the steam/carbon (S/C) ratio increased from 3 to 12 mol/mol, both CH₄ conversion and H₂ yield significantly increased. These results are represented in Figure 3b. Employing higher S/C ratios for the reforming process is not uncommon.^{2,4} Clearly, catalyst deactivation due to coking is suppressed at high S/C ratios. However, it is worth noting that high steam requirement results in increased cost of H₂ production. To summarize, complete CH₄ conversion and high purity (>90%) of H₂ cannot be achieved in a single step because steam reforming reaction is limited by equilibrium. This limitation is overcome by SERP.

3.3. Sorption Enhanced Reforming of Methane. A series of experiments was done at T = 773 K and S/C = 9 mol/mol in two different ways. First, powdered Ni/Al₂O₃ and commercial HTc (or calcium oxide) were used together during experiments. The results are represented in Figure 4a (or Figure 4b). Since the reactor was operated in the down-flow mode, the packing of catalyst and sorbent was done such that the reactants were first contacted with the catalyst and then with the sorbent. Second, the efficacy of the lab-made hybrid materials HM1 and HM2 was tested. These results are represented in Figure 4c,d.

From our results, it is evident that H₂ yield in the presence of sorbents is higher than that obtained in the conventional steam reforming process. This is because CO₂ formed during the reaction is removed by adsorption. This results in a favorable shift in the equilibrium. SERP can be elucidated from Figure 4a–d. The process involves three basic steps. The first is a pre-breakthrough stage in which the adsorbent capacity is the highest and CO₂ formed during reaction is adsorbed on various sites. Surface area, porosity, and temperature are the key factors that influence the efficiency of the adsorbent. It is during this stage that H₂ purity is maximized. As the reaction progresses, the sites of the adsorbent are increasingly occupied, and new CO₂ molecules are unable to adsorb, thereby resulting in a decrease in the adsorption capacity of the adsorbent. This region is called the breakthrough stage; here, CO₂ concentration in the product gas rises, whereas the concentration of H₂ decreases. The breakthrough time of the adsorbent (*t_b*) is reached when CO₂ is detected in the outlet stream for the first time. During this stage, the saturation of the adsorbent occurs at a much faster rate than adsorption. Once the adsorbent is completely saturated and concentrations of H₂ and CO₂ reach their equilibrium values, no further changes occur. This stage is called the post-breakthrough stage; here, equilibrium is established. It is obvious from our results that equilibrium is reached within 2 h of time-on-stream; hence, further studies were performed using these equilibrium conditions.

It is worth noting that CH₄ conversion and H₂ yield using HM1 and HM2 were higher than those obtained using (catalyst + sorbent) mixtures (see Figure 4a–d), possibly due to the absence of diffusion limitations in hybrid materials. Moreover, hybrid materials exhibited superior adsorption characteristics and longer breakthrough times (see Table 3). Further, HM1 exhibited a lower breakthrough time (15 min) and adsorption capacity (0.9 mol CO₂/kg sorbent) than HM2 (35 min and 5.7 mol/kg). HM1 has a high content of Mg, which promotes CO₂ capture to a greater extent than Ca; however, HM2 has a high capacity due to strong chemisorption. From our study, it is evident that the investigated hybrid materials are promising candidate materials for improved H₂ production.

3.4. Effect of Temperature on Sorption Enhanced Reforming. The influence of temperature on the performance of HM1 and HM2 was studied in the 673–873 K range at 0.1 MPa pressure. The S/C ratio was 9, whereas GHSV was equal to 3600 mL/(g h). For the case of HM1, CH₄ conversion and H₂ yield decreased when temperature was increased. At T = 673 K, conversion (90%) and H₂ purity (96.6%) were maximized (see Figure 5a). The rise in temperature also results in lower breakthrough times and adsorption capacity. For this reason, maximum values (35 min and 1.1 mol/kg) were achieved at T = 673 K. We accomplished such high H₂ purity and sorption capacity at a temperature much lower than that reported in previous works.^{23,26} The basic molecular structure

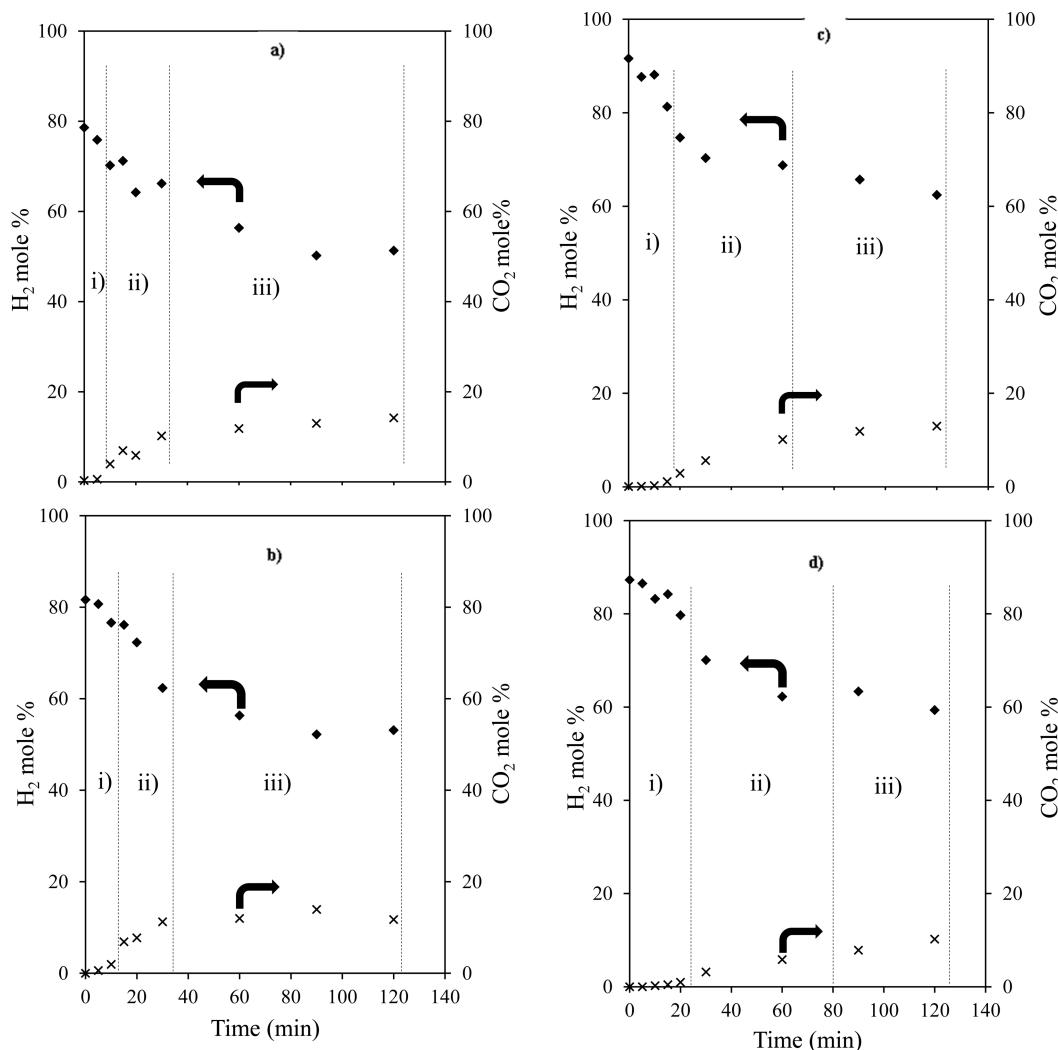


Figure 4. (a, b) Breakthrough curves for catalyst ($\text{Ni}/\text{Al}_2\text{O}_3$) and sorbent (HTc and CaO) used separately (reaction pressure = 0.1 MPa, temperature = 773 K, steam/carbon ratio = 9 mol/mol, time on stream = 2 h). (c, d) Breakthrough curves for HM1 and HM2 (reaction pressure = 0.1 MPa, temperature = 773 K, steam/carbon ratio = 9 mol/mol, GHSV = 3600 mL/(g h), time on stream = 2 h). (i – pre-breakthrough stage; ii – breakthrough stage; iii – post-breakthrough stage).

Table 3. Breakthrough Time and Adsorption Capacity of Various Combinations of Catalyst and Sorbent^a

catalyst	sorbent	breakthrough time, t_b (min)	Q_{ads} (mol CO ₂ /kg sorbent)
Ni/Al ₂ O ₃	CaO	10	2
Ni/Al ₂ O ₃	HTc	05	0.3
HM1		15	0.9
HM2		35	5.7

^aReaction conditions: reaction pressure = 0.1 MPa, temperature = 773 K, steam/carbon ratio = 9 mol/mol, GHSV = 3600 mL/(g h), time on stream = 2 h.

of HTc collapses at higher temperatures, due to loss of water of hydration. Besides, surface coverage is reduced, thereby resulting in reduced adsorption. Adsorption isotherms for HM1 in the 573–723 K range are shown in Figure 6; it is evident that chemisorption is predominant. This behavior is in line with a previous work.⁴ However, Hutson et al.²⁷ and Wu et al.²⁸ suggested that both physisorption and chemisorption are prevalent for HTc-based sorbents. Contrarily, CH₄ conversion and H₂ yield increased with an increase in temperature when

HM2 was used. CO₂ was strongly chemisorbed on CaO present in HM2, thus resulting in CaCO₃ formation. This process of chemisorption is favored at high temperatures. Because of the strong interaction, the breakthrough time and adsorption capacity increased with increasing temperature. For example, maximum values (50 min and 9.2 mol/kg) were achieved at $T = 823$ K. The results on H₂ purity are represented in Figure 5b. The dependency of sorption capacity of HM1 and HM2 on temperature is shown in Table 4.

3.5. Effect of S/C Ratio on Sorption Enhanced Reforming. The influence of S/C ratio on the performance of HM1 and HM2 was studied in the 3–9 mol/mol range at $P = 0.1$ MPa and GHSV = 3600 mL/(g h). While HM1 was tested at 673 K, HM2 was tested at 823 K. It was found that, even at low S/C ratios, both HM1 and HM2 promoted CH₄ conversion and H₂ yield. Besides, CO formed was negligible. Thus, SERP avoids the usage of excess steam and reduces energy costs. The activity of HM1 and HM2 is maintained even when less steam is provided. Optimum values of S/C were 6 and 5 mol/mol for HM1 and HM2, respectively. These results are represented in Figure 7a,b.

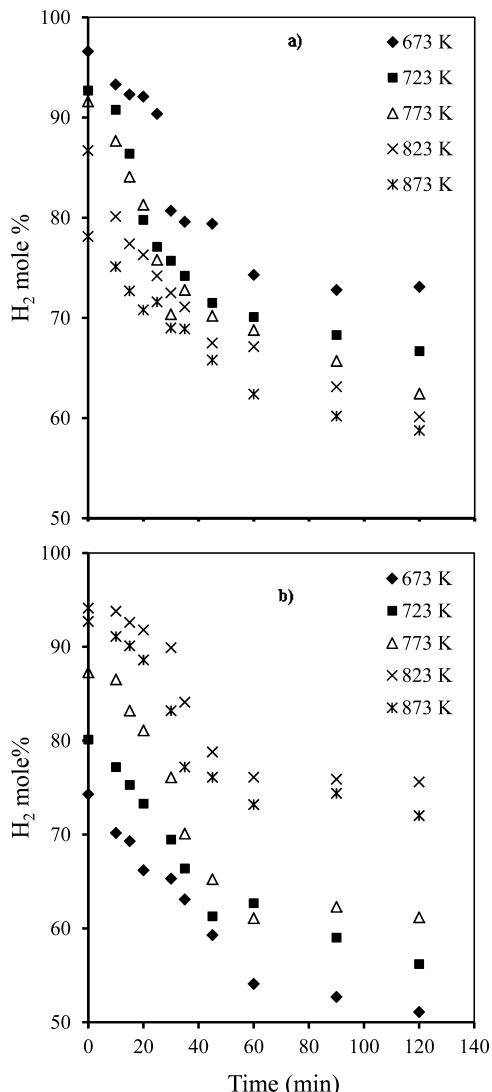


Figure 5. Effect of temperature on SER for (a) HM1 and (b) HM2 (reaction pressure = 0.1 MPa, steam/carbon ratio = 9 mol/mol, GHSV = 3600 mL/(g h), time on stream = 2 h).

3.6. Effect of GHSV on Sorption Enhanced Reforming. The effect of GHSV on SERP was investigated by varying the amounts of HM1 and HM2 in the 1.5–3 g range at $P = 0.1$ MPa. HM1 was tested at $T = 673$ K and S/C = 6 mol/mol, whereas HM2 was tested at $T = 823$ K and S/C = 5 mol/mol. These results are shown in Figure 8a,b. The rise in GHSV from 3600 to 7200 mL/(g h) resulted in decreased CH_4 conversion and H_2 yield. Thus, the higher the amount of hybrid material inside the reactor, the more the CO_2 adsorption capacity and H_2 yield.

3.7. Regeneration and Cyclic Stability of Hybrid Materials. SERP can save energy and costs if it can produce high purity H_2 in the same amounts for a number of cycles. This depends on the regenerability of the added sorbents for in situ CO_2 capture. A series of experiments was done at optimum conditions for up to 20 cycles to test the stability of the individual sorbents, (catalyst + sorbent) mixtures and hybrid materials. For the case of CaO sorbent, the adsorption of CO_2 resulted in the formation of $CaCO_3$. The regeneration of CaO was carried out by increasing temperature up to 1173 K. At this temperature, the endothermic decomposition of $CaCO_3$ to

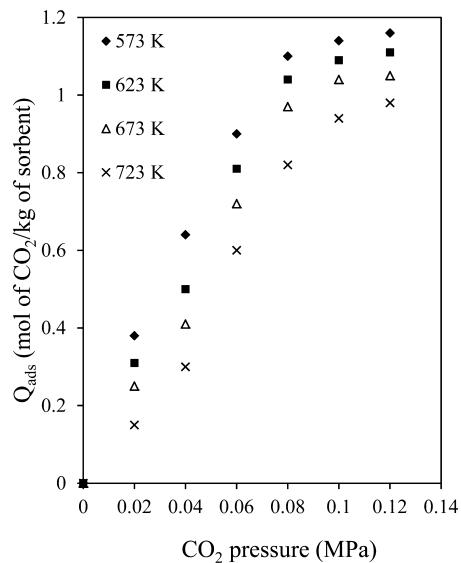


Figure 6. CO_2 adsorption isotherms for HM1 (reaction pressure = 0.1 MPa, steam/carbon ratio = 9 mol/mol, GHSV = 3600 mL/(g h), time on stream = 2 h).

Table 4. Adsorption Capacities of Hybrid Materials at Various Temperatures^a

temperature (K)	Q_{ads} (mol CO_2 /kg sorbent)	
	HM1	HM2
673	1.08	0.42
723	0.98	1.63
773	0.87	5.76
823	0.60	9.21
873	0.19	8.24

^aReaction conditions: reaction pressure = 0.1 MPa, steam/carbon ratio = 9 mol/mol, GHSV = 3600 mL/(g h), time on stream = 2 h.

CaO occurs, thereby releasing CO_2 . Using GC analysis, the complete regeneration of CO_2 was ascertained by its presence in the exit stream. For the case of HTc sorbent, regeneration was achieved by passing excess amounts of steam (1.5–2 times the flow rate of steam) at the reaction temperature for 20 min. The presence of steam assists in the regeneration of the basic HTc structure and avoids carbon deposition.

When (catalyst + sorbent) mixtures were used, H_2 content in the exit gas rapidly decreased after a few cycles. For mixtures of CaO and Ni/Al_2O_3 , the performance was identical just for two cycles. This was possibly due to sintering of the catalyst at the high regeneration temperature required for CaO .^{4,5} Contrarily, mixtures of HTc and Ni/Al_2O_3 were stable up to five cycles. However, HM1 and HM2 were stable for up to 16 and 11 cycles, respectively, and H_2 purity was high (>90%). These results are shown in Figure 9a,b. The cyclic stability of HM1 was higher than that of the materials developed by Cunha et al.¹⁶ and Wu et al.²⁴ Likewise, the cyclic performance of HM2 was superior to that of the material synthesized by Kim et al.¹⁹ Improved stability of hybrid materials can be attributed to effective metal–support interaction, better access to active sites and high dispersion.²⁹ Such stability reduces the cost of SERP. After 20 regeneration cycles, activity of both hybrid materials deteriorated, possibly due to the reduction in surface area caused by metal sintering (see Table 2). It should be noted that though the cyclic stability of HTc-based sorbents is higher than

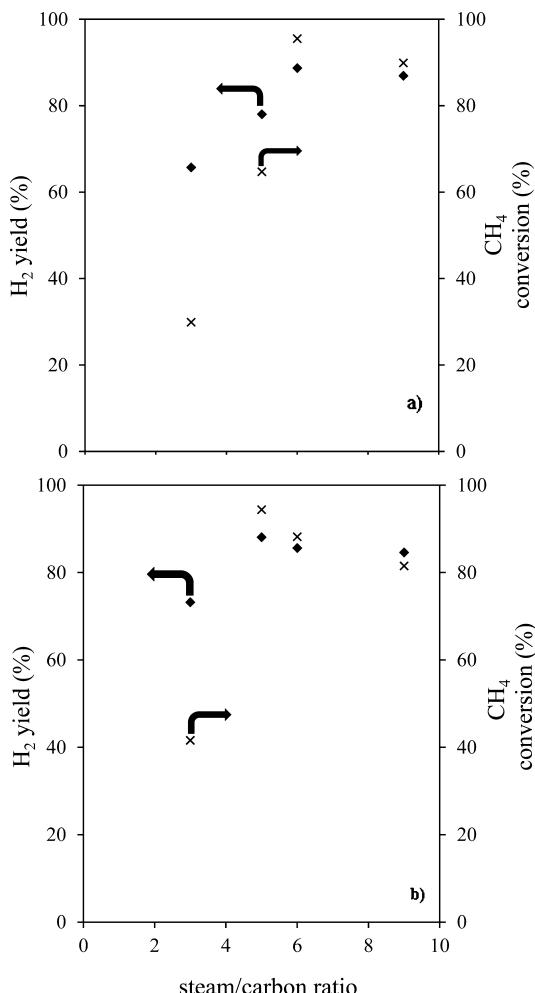


Figure 7. Effect of S/C ratios on SER for (a) HM1 and (b) HM2 (reaction pressure = 0.1 MPa, temperature = 673 K (HM1) and 823 K (HM2), GHSV = 3600 mL/(g h), time on stream = 2 h).

that of calcium-based sorbents, their adsorption capacity is very low.

3.8. Some General Remarks. Using calcium- and HTc-based sorbents as multifunctional materials for improved H₂ production is potentially attractive, although the two sorbents have contrasting adsorption capacities and regenerability characteristics. It was found that HM1 exhibited a maximum adsorption capacity of 1.1 mol CO₂/kg sorbent at its optimal conditions, viz. $T = 673\text{ K}$, $P = 0.1\text{ MPa}$, S/C = 6 mol/mol, $t_b = 45\text{ min}$, and GHSV = 3600 mL/(g h). The adsorption capacity of HM1 was higher than that reported in a previous work.³⁰ Further, HM1 showed better cyclic stability and lower regeneration energy requirement. HM1 is assumed to follow a multilayer adsorption isotherm (such as BET adsorption isotherm), where molecules getting adsorbed on the surface form a complex, and a single site can be occupied by several molecules of the adsorbate. Sorption capacity can be improved by suitably modifying the hydrotalcite structure (e.g., by increasing the interlayer spacing). HM2 exhibited a maximum adsorption capacity of 12.3 mol of CO₂/kg of sorbent at its optimal conditions, viz. $T = 823\text{ K}$, $P = 0.1\text{ MPa}$, S/C = 5 mol/mol, $t_b = 70\text{ min}$, and GHSV = 3600 mL/(g h). HM2 possessed very high adsorption capacity and longer breakthrough time. The stability of calcium-based sorbents significantly increased, due to the alumina-based support in the hybrid material. HM2

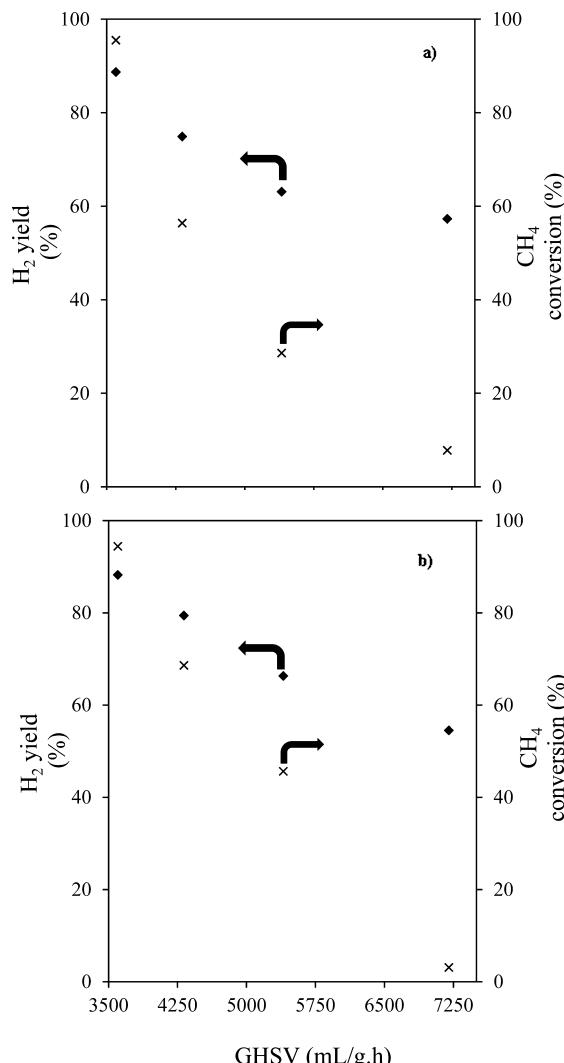


Figure 8. Effect of GHSV on SER for (a) HM1 and (b) HM2 (reaction pressure = 0.1 MPa, temperature = 673 K (HM1) and 823 K (HM2), steam/carbon ratio = 6 (HM1) and 5 mol/mol (HM2), time on stream = 2 h).

is assumed to follow a monolayer CO₂ adsorption (e.g., Langmuir isotherm). In this case, each adsorbate molecule occupies only a single site of the calcium-based adsorbent with no lateral interaction between the adsorbed CO₂ molecules.

In both cases, active nickel metal plays the role of an effective reforming catalyst. In our opinion, the usage of modified HTc-based multifunctional materials will prove highly beneficial for improved production of H₂ via SERP.

4. CONCLUSIONS

In the present work, a comparison between conventional steam methane reforming and sorption enhanced reforming process using two (catalyst + sorbent) mixtures and two multifunctional hybrid materials was presented. Both hybrid materials HM1 and HM2 were promising for the production of pure H₂ (with trace amounts of CO). Effects of reaction variables such as temperature, S/C ratios, and GHSV on the performance of HM1 and HM2 were investigated to determine the adsorption capacities and identify the optimum conditions. It was found that HM1 has low adsorption capacity and breakthrough time but high cyclic stability and ease of regeneration. Contrarily,

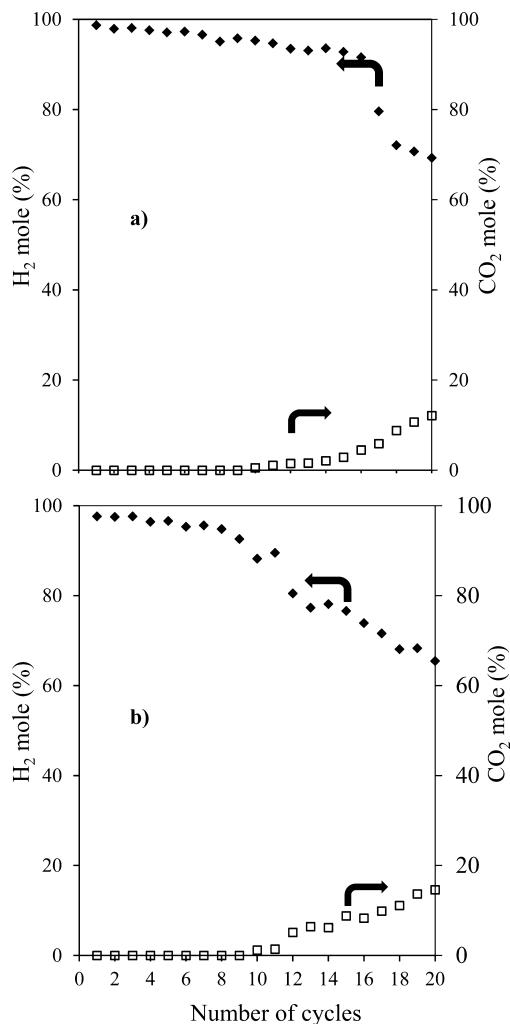


Figure 9. Cyclic stability studies for (a) HM1 and (b) HM2 (reaction pressure = 0.1 MPa, temperature = 673 K (HM1) and 823 K (HM2), steam/carbon ratio = 6 (HM1) and 5 mol/mol (HM2), GHSV = 3600 mL/(g h), time on stream = 2 h).

HM2 has high adsorption capacity and long breakthrough time, but the stringent regeneration temperature affects its stability. Employing multifunctional hybrid materials for H₂ production is potentially attractive for SERP.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

K.D.D. is thankful to DST-INSPIRE, Government of India, New Delhi, for providing financial assistance. P.D.V. is grateful to the TEQIP Phase II - Centre of Excellence for Process Intensification.

NOMENCLATURE

C_o = initial CO₂ concentration, mole %

F = molar flow rate of feed gas, mol/min

P = pressure, MPa

Q_{ads} = adsorption capacity, mol CO₂/kg of sorbent
 t_b = breakthrough time, min
 W = mass of sorbent, g

REFERENCES

- Ding, Y.; Alpay, E. Adsorption-enhanced steam-CH₄ reforming. *Chem. Eng. Sci.* **2000**, *55*, 3929–3940.
- Mayorga, S. G.; Hufton, J. R.; Sircar, S.; Gaffney, T. R. *Sorption Enhanced Reaction Process for Production of Hydrogen*; Phase I Final Report, DOE/GO/10059-T1, 1997.
- Ding, Y.; Alpay, E. Equilibrium and kinetics of CO₂ adsorption on HTc adsorbent. *Chem. Eng. Sci.* **2000**, *55*, 3461–3474.
- Hufton, J. R.; Mayorga, S.; Sircar, S. Sorption-enhanced reaction process for H₂ production. *AIChE J.* **1999**, *45*, 248–256.
- Inui, T.; Okugawa, Y.; Yasuda, M. Relationship between properties of various zeolites and their CO₂-adsorption behaviors in pressure swing adsorption operation. *Ind. Eng. Chem. Res.* **1988**, *27*, 1103–1109.
- Radfarnia, H. R.; Illiuta, M. C. Development of Al-stabilized CaO-Nickel hybrid sorbent-catalyst for sorption enhanced steam methane reforming. *Chem. Eng. Sci.* **2014**, *109*, 212–219.
- Liu, W.; Low, N. W.; Feng, B.; Wang, G.; da costa, J. C. D. Calcium precursors for the production of CaO sorbents for multi-cycle CO₂ capture. *Environ. Sci. Technol.* **2010**, *44*, 841–847.
- Li, L.; King, D. L.; Nie, Z.; Li, X. S.; Howard, C. MgAl₂O₄ spinel-stabilized calcium oxide absorbents with improved durability for high-temperature CO₂ capture. *Energy Fuels* **2010**, *24*, 3698–3703.
- Martavaltzi, C. S.; Lemonidou, A. A. Development of new CaO based sorbent materials for CO₂ removal at high temperature. *Microporous Mesoporous Mater.* **2008**, *110*, 119–127.
- Lu, H.; Reddy, E. P.; Smirniotis, P. G. Calcium oxide based sorbents for capture of CO₂ at high temperatures. *Ind. Eng. Chem. Res.* **2006**, *45*, 3944–3949.
- Li, Z. S.; Cai, N. S.; Huang, Y. Y.; Han, H. J. Synthesis, experimental studies and analysis of a new calcium-based CO₂ sorbent. *Energy Fuels* **2005**, *19*, 1447–1452.
- Abanades, J. C.; Murillo, R.; Fernandez, J. R.; Grasa, G.; Martinez, I. New CO₂ capture process for hydrogen production combining Ca and Cu chemical loops. *Environ. Sci. Technol.* **2010**, *44*, 6901–6904.
- Ding, Y.; Alpay, E. High temperature recovery of CO₂ from flue gases using HTc adsorbent. *Process Safety Environ.* **2001**, *79*, 45–51.
- Wu, G.; Zhang, C.; Li, S.; Huang, Z.; Yan, S.; Wang, S.; Ma, X.; Gong, J. Sorption enhanced steam reforming of ethanol on Ni-CaO-Al₂O₃ multifunctional catalysts derived from HTc-like compounds. *Energy Environ. Sci.* **2012**, *5*, 8942–8949.
- Cunha, A. F.; Wu, Y. J.; Santos, J. C.; Rodrigues, A. E. Steam reforming of ethanol on copper catalysts derived from HTc-like materials. *Ind. Eng. Chem. Res.* **2012**, *51*, 13132–13143.
- Cunha, A. F.; Wu, Y. J.; Diaz Alvarado, F. A.; Santos, J. C.; Vaidya, P. D.; Rodrigues, A. E. Steam reforming of ethanol on a Ni/Al₂O₃ catalyst coupled with a HTc-like sorbent in a multilayer pattern for CO₂ uptake. *Can. J. Chem. Eng.* **2012**, *90*, 1514–1526.
- Cunha, A. F.; Wu, Y. J.; Santos, J. C.; Rodrigues, A. E. Sorption enhanced steam reforming of ethanol on HTc-like compounds impregnated with active copper. *Chem. Eng. Res. Des.* **2013**, *91*, 581–592.
- Martavaltzi, C. S.; Lemonidou, A. A. Hydrogen production via sorption enhanced reforming of methane: Development of novel hybrid material-reforming catalyst and CO₂ sorbent. *Chem. Eng. Sci.* **2010**, *65*, 4134–4140.
- Kim, J. N.; Ko, C. H.; Yi, K. B. Sorption enhanced hydrogen production using one-body CaO-Ca₁₂Al₁₄O₃₃-Ni composite as catalytic absorbent. *Int. J. Hydrogen Energy* **2013**, *38*, 6072–6078.
- Hutson, N. D.; Attwood, B. C. High temperature adsorption of CO₂ on various hydrotalcite-like compounds. *Adsorption* **2008**, *14*, 781–789.

- (21) Moreira, R. F. P. M.; Soares, J. L.; Casarin, G. L.; Rodrigues, A. E. Adsorption of CO₂ on hydrotalcite-like compounds in a fixed bed. *Sep. Sci. Technol.* **2006**, *41*, 341–357.
- (22) Li, D.; Wang, L.; Koike, M.; Nakagawa, Y.; Tomishige, K. Steam reforming of tar from pyrolysis of biomass over Ni/Mg/Al catalysts prepared from HTc-like precursors. *Appl. Catal. B: Environ.* **2011**, *102*, S28–S38.
- (23) Chanburanasiri, N.; Ribeiro, A. N.; Rodrigues, A. E.; Arpornwichanop, A.; Laosiripojana, N.; Praserthdam, P.; Assabumrungrat, S. Hydrogen production via sorption enhanced steam methane reforming process using Ni/CaO multifunctional catalyst. *Ind. Eng. Chem. Res.* **2011**, *50*, 13662–13671.
- (24) Wu, Y. J.; Li, P.; Yu, J. G.; Cunha, A. F.; Rodrigues, A. E. Sorption-enhanced steam reforming of ethanol on NiMgAl multifunctional materials: Experimental and numerical investigation. *Chem. Eng. J.* **2013**, *231*, 36–48.
- (25) Cavani, F.; Trifiro, F.; Vaccari, A. HTc type anionic clays: Preparation, properties and applications. *Catal. Today.* **1991**, *11*, 173–301.
- (26) Wu, Y. J.; Li, P.; Yu, J. G.; Cunha, A. F.; Rodrigues, A. E. High-purity hydrogen production by sorption-enhanced steam reforming of ethanol: A cyclic operation simulation study. *Ind. Eng. Chem. Res.* **2014**, *53*, 8515–8527.
- (27) Hutson, N. D.; Speakman, S. A.; Payzant, E. A. Structural effects on the high temperature adsorption of CO₂ on a synthetic hydrotalcite. *Chem. Mater.* **2004**, *16*, 4135–4143.
- (28) Wu, Y. J.; Li, P.; Yu, J. G.; Cunha, A. F.; Rodrigues, A. E. K-Promoted hydrotalcites for CO₂ capture in sorption enhanced reactions. *Chem. Eng. Technol.* **2013**, *36*, 567–574.
- (29) Alzamora, L. E.; Ross, J. R. H.; Kruissink, E. C.; van Riejen, L. L. Coprecipitated nickel–alumina catalysts for methanation at high temperature. Part 2. Variation of total and metallic areas as a function of sample composition and method of pretreatment. *J. Chem. Soc. Faraday Trans.* **1981**, *77*, 665–681.
- (30) Harrison, P. Sorption–enhanced hydrogen production: A review. *Ind. Eng. Chem. Res.* **2008**, *47*, 6486–6501.