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Article

Hydrogen Production from Sorption Enhanced Biogas Steam Reforming Using Nickel-Based Catalysts

Janewit Phromprasit[1], Jonathan Powell[2], Amornchai Arpornwichanop[1], Alírio E. Rodrigues[3], and Suttichai Assabumrungrat[1,*]

1 Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
2 Newcastle University International – Singapore, School of Chemical Engineering and Advanced Materials, Faculty of Science, Agriculture and Engineering, Newcastle University, NE1 7RU, United Kingdom
3 Laboratory of Separation and Reaction Engineering, Associate Laboratory (LSRE) Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, s/n, 4200-465 Porto, Portugal

* E-mail: suttichai.a@chula.ac.th (Corresponding author)

Abstract. Hydrogen gas is a clean and sustainable fuel/energy carrier considered to be a possible alternative to fossil fuels. Sorption enhanced biogas steam reforming is a process which combines a CO_2 adsorption unit with a hydrogen production unit. In the CO_2 sorption section, CaO was selected as the adsorbent due to its high stoichiometric adsorption capacity. From the adsorption test, the highest adsorption capacity ($0.2849\ g_{CO2}/g_{CaO}$) was achieved at a temperature of 873 K. Four types of bed arrangement were investigated using a feed gas with a CH_4/CO_2 ratio of 1.5, an S/C ratio of 3, a temperature of 873 K and at atmospheric pressure. The results indicate that the Type II system (Catalyst physical mixed with sorbent system packed in fixed bed quartz reactor, 0.8 g of 12.5 wt.% Ni/Al_2O_3 mixed with 2 g of CaO) exhibits the highest improvement in CH_4 conversion with the introduction of CO_2 adsorption (93.0% and 81.7%, with and without CO_2 sorption, respectively) and high purity hydrogen was produced (97.0 % v/v and 62.3 % v/v, with and without CO_2 sorption respectively).

Keywords: Hydrogen production, sorption enhanced, biogas steam reforming, bed arrangements, nickel-based catalysts.

1. Introduction

Hydrogen can be produced from fossil fuels via one of several methods, such as methane decomposition (Eq. (1)) [1-2], steam reforming of methane (Eq. (2)) [2-8] and dry reforming of methane (Eq. (3)) [2, 9-12]. The steam reforming process is accompanied by a side reaction that is the water gas shift reaction (Eq. (4)). Methane decomposition and dry reforming of methane often involve the formation of coke, via reactions such as those shown in Eqs. (5) and (6), which deactivates the catalyst. Because of the endothermic nature of reforming reactions, the equilibrium reaction is run at a high temperature thus bringing about an increase in yield (equilibrium concentration) of the reforming products. Therefore, catalyst deactivation by carbon deposition and metal sintering become important issues [13].

Nowadays, due to its sustainable nature, biogas is of particular interest. It is produced by anaerobic digestion or fermentation of biodegradable materials such as green waste, manure and so on. It is combined with a reforming process for hydrogen production. Biogas steam reforming is a process which is a combination of methane steam reforming and dry methane reforming shown in Eqs. (2) and (3), respectively:

Methane decomposition:	$CH_4 \leftrightarrow 2H_2 + C$	$\Delta H_{298}^0 = +74.8$ kJ/mol	(1)
Steam methane reforming (SMR):	$CH_4 + H_2O \leftrightarrow 3H_2 + CO$	$\Delta H_{298}^0 = +206$ kJ/mol	(2)
Dry methane reforming (DMR):	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	$\Delta H_{298}^0 = +247$ kJ/mol	(3)
Water gas shift reaction (WGSR):	$CO + H_2O \leftrightarrow H_2 + CO_2$	$\Delta H_{298}^0 = -41.1$ kJ/mol	(4)
Coke formation reaction:	$2CO \leftrightarrow C + CO_2$	$\Delta H_{298}^0 = -172.6$ kJ/mol	(5)
	$CO + H_2 \leftrightarrow C + H_2O$	$\Delta H_{298}^0 = -152.8$ kJ/mol	(6)
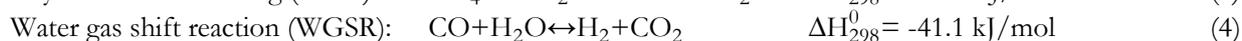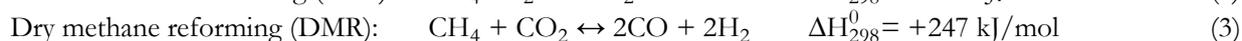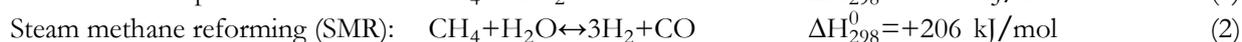
CO_2 sorption enhanced steam reforming has been investigated as a means of removing CO_2 from the hydrogen product stream, thus limiting green house gas emissions as well as to shift the equilibrium of the water gas shift reaction to the right, thus increasing the hydrogen production rate. Several CO_2 acceptors were studied [14] such as CaO, Li_2ZrO_3, $K-Li_2ZrO$, Na_2ZrO_3 and Li_4SiO_4 where K:Li:Zr is 0.2:2.2:1. The experimental adsorption capacity results indicated that the highest CO_2 sorption capacity was CaO (0.495 g_{CO_2}/g_{CaO} at 848 K. Moreover, hydrotalcite is a sorbent widely used as a CO_2 acceptor at high temperatures [15-17]. However, the CO_2 adsorption capacity of CaO and MG30-K (hydrotalcite with a Mg/Al ratios of 30/70 and impregnated with K_2CO_3 (20 wt.%)) have been compared by Chanburanasiri et al. [18]. The results indicated that MG30-K (0.0775 $g_{CO_2}/g_{adsorbent}$) exhibited lower CO_2 adsorption capacity than CaO (0.195 $g_{CO_2}/g_{adsorbent}$) at 673 K.

Sorption enhanced biogas steam reforming is a process that combines two unit operations (CO_2 sorption and hydrogen production) into one. For example, Martavaltzi and Lemonidou [19] investigated the combining of methane steam reforming with carbon dioxide capture using $CaO-Ca_{12}Al_{14}O_{33}$ as the sorbent, with a $CaO:Ca_{12}Al_{14}O_{33}$ mass ratio equal to 85:15. The experimental results indicated 93% conversion of methane at 923 K, 1 bar and with a steam to methane molar ratio of 3.4. Moreover, a gas composition with more than 92% hydrogen after 13 cycles was obtained in the outlet stream compared to the conventional steam reforming process where a composition of 77% hydrogen was obtained.

A Ni/CaO multifunctional catalyst used for hydrogen production via sorption enhanced steam methane reforming was investigated by Chanburanasiri et al. [18]. They found that 12.5 wt.% Ni/Al_2O_3+CaO exhibited the highest CH_4 conversion (89%) when compared with 12.5 wt.% Ni/CaO (86%) and 12.5 wt.% Ni/Al_2O_3 (84%, without adsorption effect). Moreover, 12.5 wt.% Ni/Al_2O_3+CaO gave a product gas stream with a higher concentration of H_2 (83%) when compared with the 12.5 wt.% Ni/CaO (82%), 12.5 wt.% Ni/MG30-K (75%) and 12.5 wt.% Ni/Al_2O_3 (72%). Where MG30-K is hydrotalcite (Mg/Al ratios of 30/70) that was impregnated with K_2CO_3 (20 wt.%). The same concept of hydrogen production has been applied to steam reforming of other feed stocks such as propane [20], glycerol [21], ethanol [22], methanol and *n*-butanol [23].

However, steam reforming of biogas containing a high content of CO_2 has not been widely investigated. Therefore, this study will focus on a suitable bed arrangement of catalyst and adsorbent, as well as effects of the operating parameters on the production of hydrogen via sorption enhanced biogas steam reformation. Of particular interest is the selection of catalyst-adsorbent bed arrangement necessary for handling the high content of CO_2 in the reaction system.

2. Experimental

2.1. Chemicals and Gases

Calcium oxide (CaO, Riedel-deHaën) was used as an adsorbent and support for the Ni catalyst. Commercial alumina (Al_2O_3, particle size of 0.05-0.15 mm, Fluka) was also used as a support for the Ni catalyst. A precursor of Ni solution was prepared from nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, Sigma Aldrich). Silicon carbide (SiC, particle size of 37-74 μm, Sigma Aldrich) was used as a bed diluent. Nitrogen gas (N_2, Thai Industrial Gas, TIG) ultra high purity grade (99.999%) used as a diluent gas when adsorption testing was performed, and when pre-treatment and reduction of the catalysts were carried out. Methane (99.999%) and carbon dioxide (99.999%) were used as the reactants simulating the use of biogas in the steam reforming process. Deionized water was used to produce the steam in the feed gas, injected into the reactor using a syringe pump.

2.2. Catalyst Preparation

Three catalysts were investigated for use in the sorption enhanced biogas steam reforming process, 12.5 wt.% Ni/Al_2O_3, 12.5 wt.% Ni/CaO and 5.4 wt.% Ni/CaO. This Ni composition was selected based on the results of previous work [18]. The incipient wetness impregnation method was used for loading Ni onto the supports (calcium oxide and alumina). The impregnated supports were then dried at 373 K overnight. The dried catalysts were calcined in air at 1073 K for 4 hours at a heating rate of 10 K/min.

2.3. Catalyst Characterization

X-ray diffraction (XRD) was used for catalyst characterization. The XRD patterns were obtained using a D8 Advance, Bruker AXS, equipped with a long fine focus ceramic Cu K_{α} X-ray source. The pattern was recorded in the range of $20° < 2\theta < 80°$ with incremental steps of 0.04°, and a scan speed of 0.5 s/step. The surface areas of the catalyst and adsorbent were obtained from N_2 adsorption and desorption BET isotherms using a Micromeritics Chemisorp 2750. The nitrogen adsorption desorption isotherms were measured at 77 K using 0.1 g of catalyst.

2.4. Adsorption Testing

Calcium oxide was selected as the CO_2 acceptor and was tested to measure its performance in terms of CO_2 adsorption. 2 g of calcium oxide was packed into a fixed bed quartz reactor (10 mm diameter and 500 mm length) and was supported by quartz wool. Figure 1 shows a schematic diagram of the experimental equipment used for the CO_2 sorption and the hydrogen production studies. Prior to the CO_2 sorption, the adsorbent was pre-treated to remove impurities such as $Ca(OH)_2$ and $CaCO_3$, by heating at a temperature of 1023 K in a N_2 atmosphere with a flow rate of 50 ml/min and at atmospheric pressure for 60 min. After that, the CO_2 sorption tests were carried out using 8% CO_2 in N_2 (total flow rate of 50 ml/min) fed into the fixed bed quartz reactor, at atmospheric pressure and at various temperatures (723, 773, 823 and 873 K) over the following catalysts, 12.5 wt.% Ni/Al_2O_3, 12.5 wt% Ni/CaO as well as pure CaO substrate. The gas products were trapped with the excess steam using an ice bath and were analyzed using a gas chromatograph (Shimadzu, GC-8A) equipped with two columns, a Molecular Sieve 5A to analyze H_2, CH_4, N_2 and CO and a Poraplot Q to analyze CO_2 at injection/detector temperature of 343 K and column temperature of 323 K.
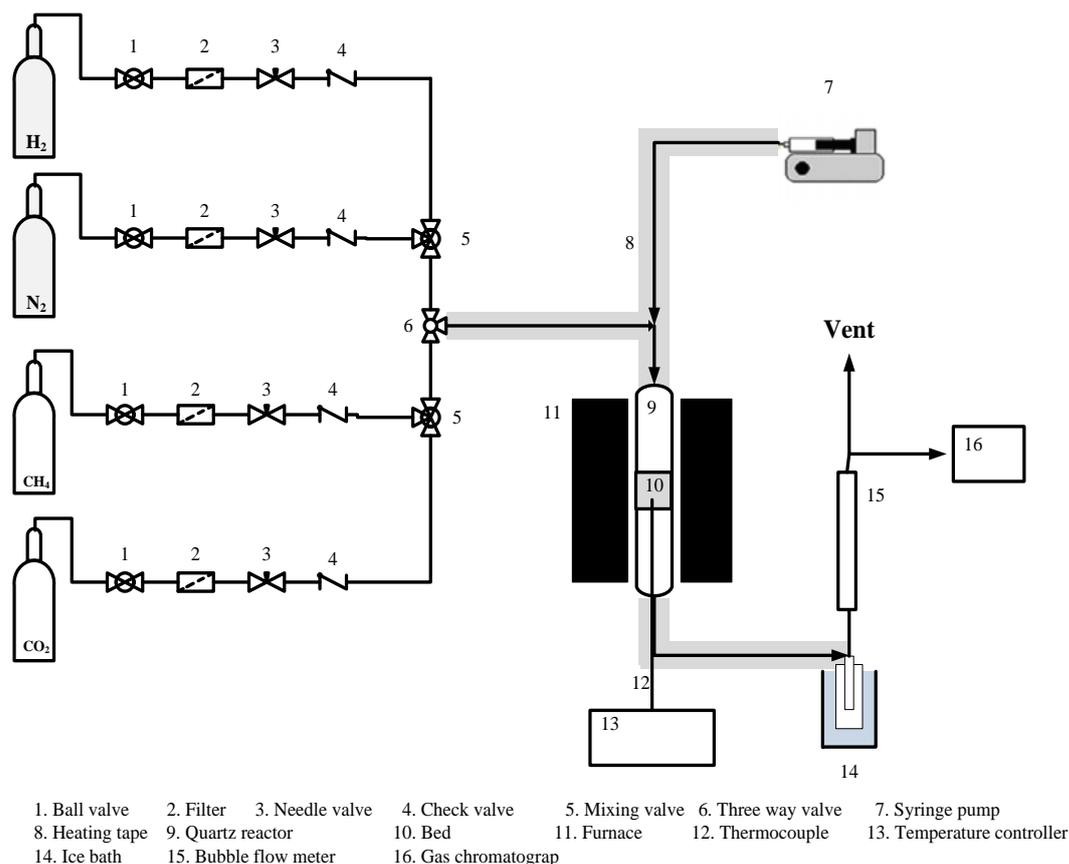
Fig. 1. Experimental equipments for hydrogen production via sorption enhanced biogas steam reforming study.

2.5. Sorption enhanced biogas steam reforming

Four types of bed arrangement were studied for hydrogen production via the sorption enhanced biogas steam reforming reaction as shown in Fig. 2. The type I systems (Type I (a) and (b)), containing 0.8 g of 12.5 wt.% Ni/Al_2O_3 and 12.5 wt.% Ni/CaO respectively, were mixed with 3.5 g of SiC diluent [11] (particle size of 37-74 μm) for the purpose of reducing the pressure drop across the bed by minimising the agglomeration/sintering between the $CaCO_3$ and CaO particles in the fixed bed quartz reactor (10 mm diameter and 500 mm length). The top and bottom of the catalyst bed for all the systems was supported by quartz wool. The second system (Type II), contained a mixture of 0.8 g of 12.5 wt.% Ni/Al_2O_3, 2 g of CaO and 1.5 g of SiC diluent. The third system (Type III) was divided in two sections where the top of bed was filled with 1 g of CaO mixed with 0.75 g of SiC, and the bottom of the bed was packed with 0.8 g of 12.5 wt.% Ni/Al_2O_3 mixed with 1 g of CaO and 0.75 g of SiC. The fourth system (Type IV), containing 2 g of CaO, was loaded with an equivalent amount of Ni as used in Type I, resulting in 5.4 wt.% Ni/CaO, mixed with 2 g of SiC and packed in to the reactor. After packing the adsorbent and catalyst into the reactor they were pre-treated at 1023 K for 60 min in a N_2 atmosphere, with a gas flow rate of 25 ml/min, and then they were reduced in a 50% H_2 in N_2 atmosphere (total flow rate of 50 ml/min) at 1023 K for 90 min. After the heat treatment and reduction steps, the sorption enhanced biogas steam reforming process was carried out with a CH_4 to CO_2 ratio of 1.5 [24], a steam to carbon ratio (S/C) of 3:1 where carbon referred to methane, at a temperature of 873 K and at atmospheric pressure. The product gases were trapped with the excess steam using an ice bath and analyzed using a thermal conductivity detector gas chromatograph (Shimadzu, GC-8A) equipped with two columns (Molecular Sieve 5A and Poraplot Q) to analyze H_2, CO, CO_2, N_2, and CH_4.
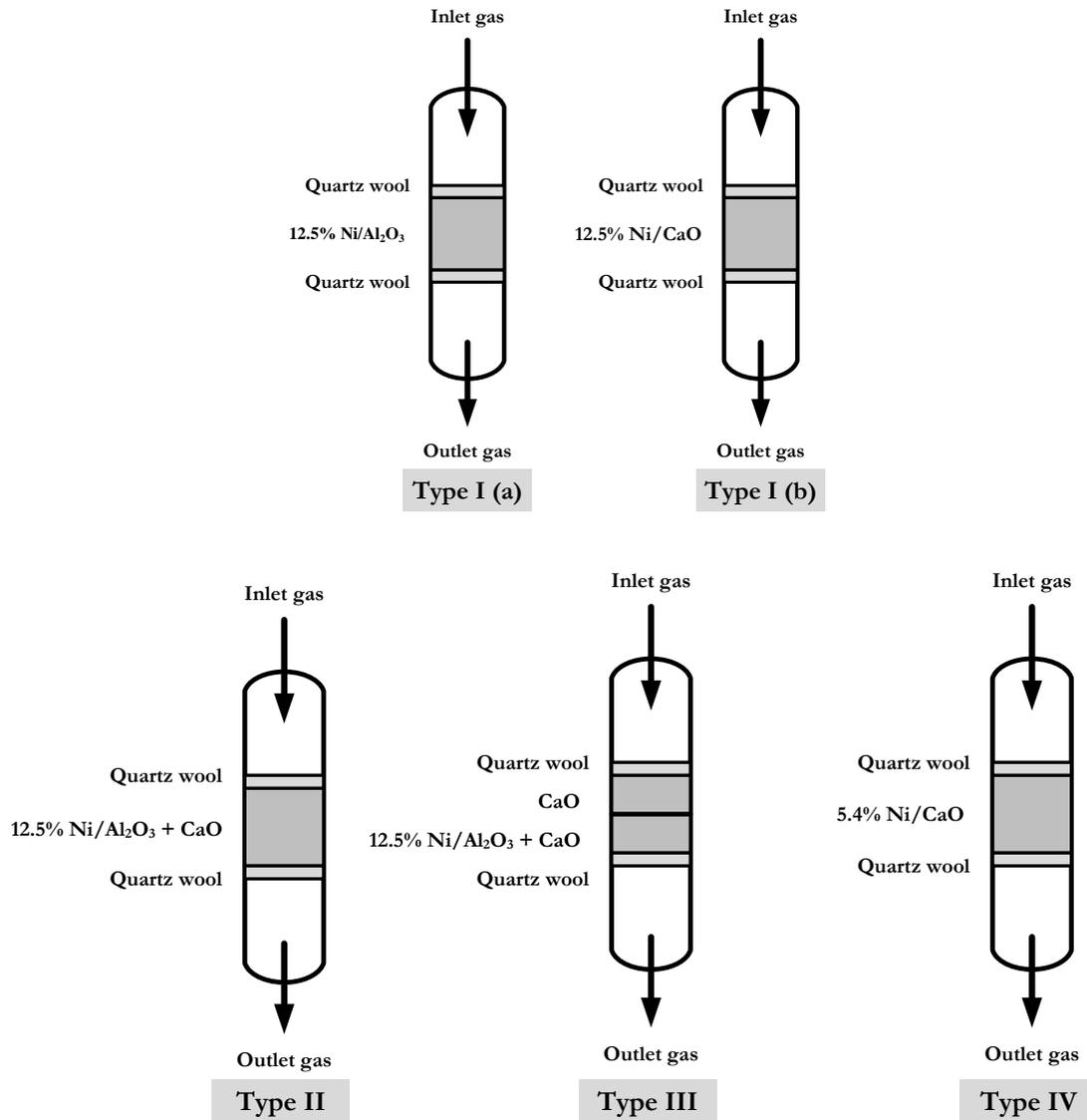
Fig. 2.   Types of bed arrangement for sorption enhanced biogas steam reforming experiments.

3. Results and Discussion

3.1. Thermodynamic Analysis

The reformer unit operation which in this case is used for hydrogen production via biogas steam reforming (Eqs. (2)-(4)), was simulated using the Aspen Plus program. Thermodynamic equilibrium was assumed using Gibbs free energy minimization. The NRTL Equation of State was used in the thermodynamic calculations. A methane to carbon dioxide ratio of 1.5 and a steam to carbon ratio of 3 were fed into a reformer. The inlet stream was heated to vaporise the liquid water to steam before feeding into the reformer at a temperature of 423 K.

The effect of temperature (673-1073 K) on the simulated biogas steam reforming reaction was investigated. The results indicated that the CH_4 conversion increased with increasing reaction temperature. Figure 3 shows that the CH_4 conversion above 873 K approached 100% and the hydrogen concentration reached the equilibrium value of 60%. This study has been investigated the effects of possible improvements to the sorption enhanced biogas steam reforming process to allow such CH_4 conversion levels and hydrogen partial pressures in the product stream to be achieved at lower temperatures. The motivation behind this is that the reactor wall materials required for high temperature operation are more expensive whilst the catalysts are more prone to deactivation due to the formation of coke as well as

sintering, which become significant at higher temperatures [13]. It was therefore found that the most suitable temperature for investigating sorption enhanced biogas steam reforming was below 873 K.
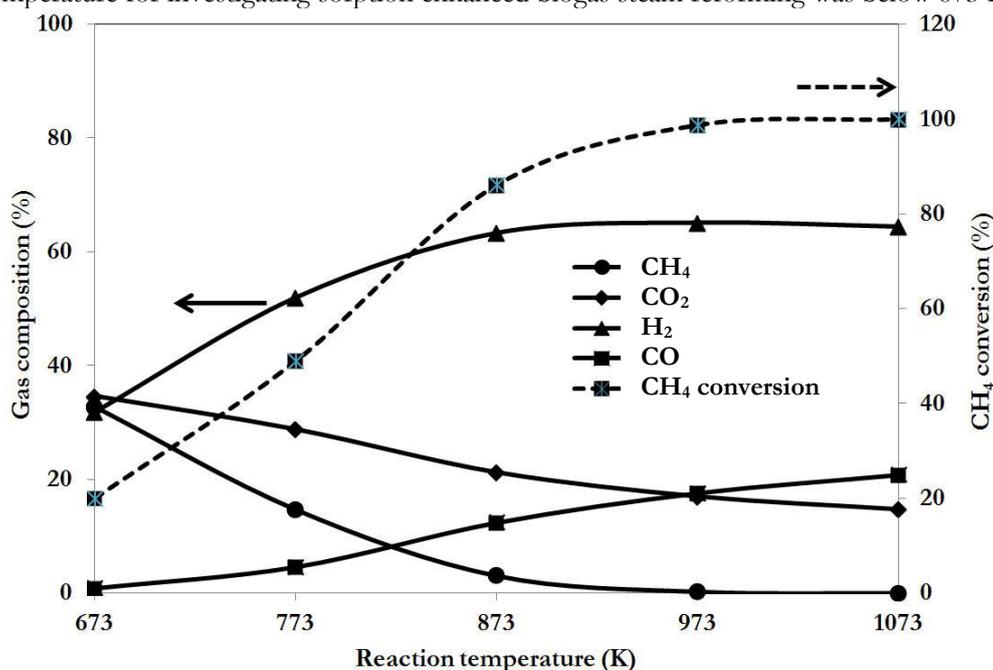
Fig. 3. Outlet gas compositions and CH_4 conversion at different temperatures (atmospheric pressure, CH_4/CO_2 of 1.5 and S/C of 3).

However, in this study CaO was selected as a CO_2 acceptor and was investigated as such over a range of temperatures (i.e. 723, 773, 823 and 873 K). Furthermore, two catalysts (12.5 wt.% Ni/Al_2O_3 and 12.5 wt.% Ni/CaO) were synthesized for this reaction by the incipient wetness impregnation method. XRD patterns were obtained for confirmation of catalyst and support composition. The XRD pattern of 12.5 wt.% Ni/Al_2O_3 indicated peaks of NiO and Al_2O_3, while 12.5 wt.% Ni/CaO indicated peaks of NiO, CaO, $Ca(OH)_2$ and $CaCO_3$ as shown in Fig. 4. BET surface area was measured for all fresh catalysts and supports, and the results are shown in Table 1. The surface area decreased with the presence of nickel metal most likely due to the nickel metal blocking pores in the support structure.
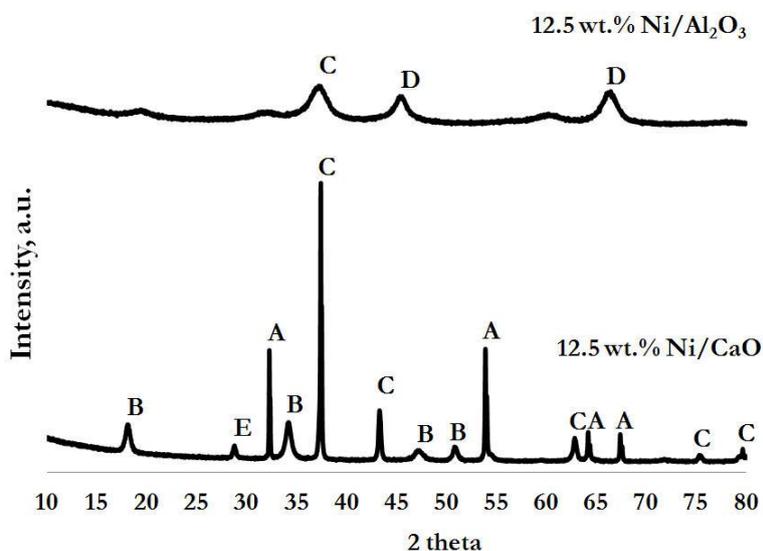
Fig. 4. XRD patterns of 12.5 wt.% Ni/Al_2O_3 and 12.5 wt.% Ni/CaO (A: CaO, B: $Ca(OH)_2$, C: NiO, D: Al_2O_3, and E: $CaCO_3$).

Table 1.   Surface area of fresh catalysts and supports.

Catalyst	BET surface area (m^2/g)
Al_2O_3	99.5
12.5 wt.% Ni/Al_2O_3	53.1
CaO	8.4
12.5 wt.% Ni/CaO	1.1
SiC	0.5

3.2. Adsorption Testing

Calcium oxide was selected for this study because of its high stoichiometric adsorption capacity when compared with Li_2ZrO_3, $K-Li_2ZrO_3$, Na_2ZrO_3 and Li_4SiO_4 [14]. The CO_2 sorption capacity was investigated over a range of temperatures, 723, 773, 823 and 873 K. The change in performance of the adsorbent was measured using the dimensionless term C/C_F and its variation with time, where C is the carbon dioxide concentration in the outlet stream and C_F is the carbon dioxide concentration in the inlet stream. Figure 5 shows the breakthrough curves for the CO_2 adsorption by CaO at different temperatures. They show that the breakthrough time increased with increasing adsorption temperature (24, 28, 36 and 50 min for temperatures of 723, 773, 823 and 873 K, respectively). Moreover, the C/C_F ratio at t < 30 min had a value of approximately 0 at the lower temperatures (723 and 773 K) indicating more effective adsorption of CO_2 in comparison to that at the higher temperatures (823 and 873 K) where the C/C_F ratio at t < 30 min was equal to 0.02 and 0.04, respectively. The adsorption capacities for each temperature are summarized in Table 2. The highest adsorption capacity observed was 0.2849 g_{CO2}/g_{CaO} at 873 K; which was therefore selected for the following adsorption test. The XRD patterns of fresh and used calcium oxide are shown in Fig. 6. They confirm that the calcium oxide reacted with the carbon dioxide (Eq. (7)), forming calcium carbonate ($CaCO_3$, peaks at 22.8 and 28.6).

Carbonation reaction: $CaO + CO_2 \rightarrow CaCO_3$ $\Delta H_{298}^0 = -179$ kJ/mol   (7)
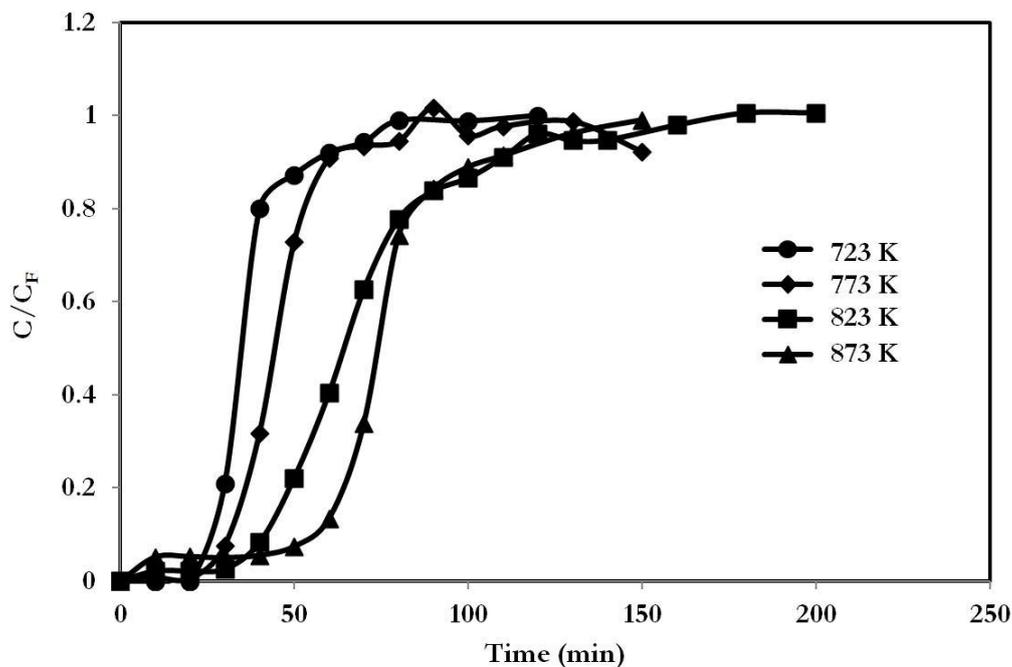
Fig. 5.   Breakthrough curves of CO_2 adsorption by CaO at different temperatures (T = 723, 773, 823 and 873 K), atmospheric pressure and using 8% CO_2 in N_2 as feed composition.

Table 2. CO_2 adsorption capacity of CaO at different temperatures.

Adsorption temperature (K)	Experimental adsorption capacity (g_{CO_2} / $g_{Adsorbant}$)
723	0.1427
773	0.1774
823	0.2503
873	0.2849
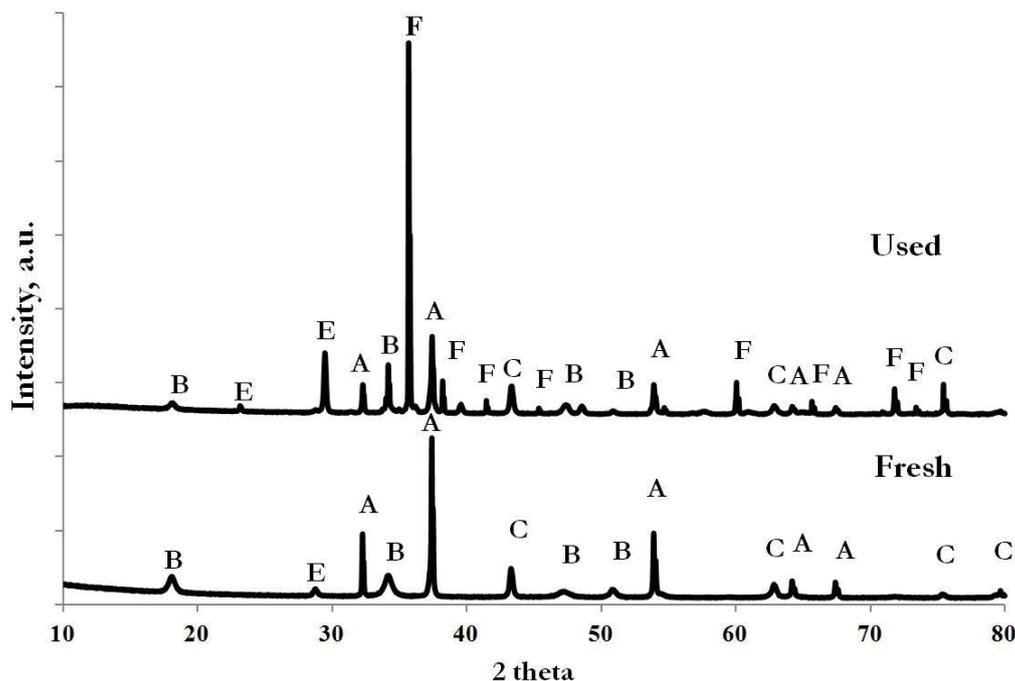
Fig. 6.   XRD patterns of fresh and used 12.5 wt.% Ni/CaO (A: CaO, B: Ca(OH)$_2$, C: NiO, D: Al$_2$O$_3$, E: CaCO$_3$ and F: SiC).

The catalyst adsorbent systems used for sorption enhanced biogas steam reforming, 12.5 wt.% Ni/Al$_2$O$_3$, 12.5 wt.% Ni/CaO and CaO were tested for CO_2 sorption to determine and compare their adsorption capacities. Figure 7 shows that the breakthrough times (t_b) were 2, 30 and 50 min for 12.5 wt.% Ni/Al$_2$O$_3$, 12.5 wt.% Ni/CaO and CaO, respectively. For the 12.5 wt.% Ni/Al$_2$O$_3$ system, the rapid increase in the C/C_F ratio to a value of 1, in under 10 min and a break through time t_b less than 1 min, both indicate that there was little or no adsorption CO_2. The adsorption capacity of 12.5 wt.% Ni/CaO (0.173 g_{CO2}/g) was less than the adsorption capacity of CaO (0.285 g_{CO2}/g) because the mass of CaO in 12.5 wt.% Ni/CaO (1.75 g) was less than that of the pure CaO (2 g).
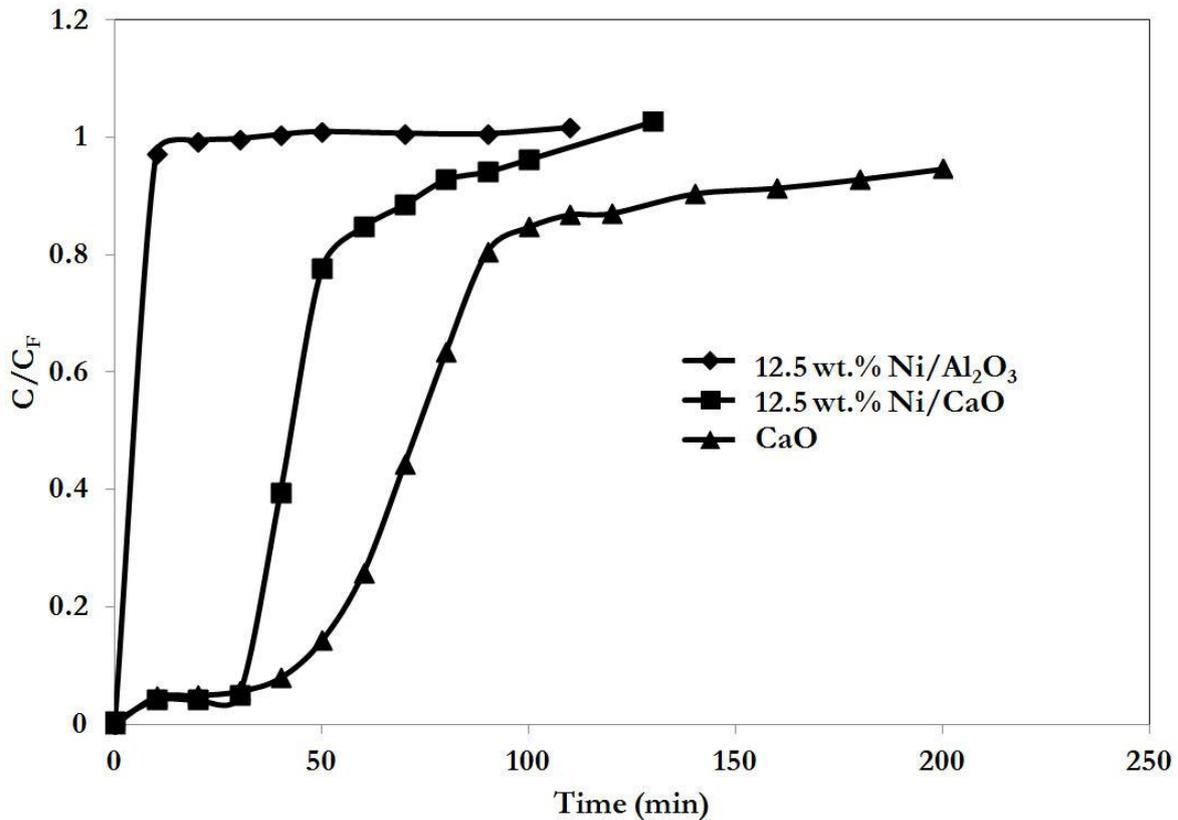
Fig. 7.   Breakthrough curves of CO_2 adsorption by CaO, 12.5 wt.% Ni/CaO and 12.5 wt.% Ni/Al$_2$O$_3$ at temperature of 873 K, atmospheric pressure and using 8% CO_2 in N_2 as feed composition.

3.3. Sorption Enhanced Biogas Steam Reforming Testing

Four types of bed arrangement were investigated including Type I (a) 12.5 wt.% Ni/Al$_2$O$_3$, Type I (b) 12.5 wt.% Ni/CaO, Type II 12.5 wt.% Ni/Al$_2$O$_3$+CaO, Type III CaO (top)+12.5 wt.% Ni/Al$_2$O$_3$+CaO (bottom), Type IV 5.4 wt.% Ni/CaO for hydrogen production via sorption enhanced biogas steam reforming. The reaction was carried out at a temperature of 873 K, with a CH$_4$/CO$_2$ ratio of 1.5, a S/C ratio of 3, a total flow rate of 50 ml/min and at atmospheric pressure. Results obtained for experiments without any CO_2 adsorption using the Type I (a) system, indicated that the hydrogen concentration and conversion reached steady state values after 15 minutes, with a hydrogen concentration of 60% and a conversion of 81.1 %, as shown in Fig. 8. However, previous work [18] investigating the use of a 12.5 wt.% Ni/CaO multifunctional catalyst in the sorption enhanced methane steam reforming process (low CO_2 partial pressures in the gas stream) shows high CH$_4$ conversion (approximately 80%) and high hydrogen concentrations (approximately 82% v/v) in the presence of CO_2 adsorption. Therefore in this work, a 12.5 wt.% Ni/CaO multifunctional catalyst was tested in the presence of a high CO_2 partial pressure in the feed, results for which are shown in Fig. 9. The results show a rapidly decreasing hydrogen concentration and CH$_4$ conversion with time for the Type I (b) catalyst (80.8% at 15 min and 42.6% at 300 min, and 77.8% at 15 min and 28.9% at 300 min for hydrogen concentration and CH$_4$ conversion, respectively) which indicates that catalyst deactivation is taking place. The cause of catalyst deactivation was the loss of active sites due to CaO reacting with CO_2 to form CaCO$_3$. Sultana et al. [25] reported that when CaO was formed to CaCO$_3$, the volume was increased from 16.9 ml/g of CaO to 36.1 ml/g of CaCO$_3$ significantly reduces the pore volume. This could result in complete or partial closure of pores. Causing significant limitation of CO_2 diffusion in the CaCO$_3$ layer, thus limiting the utilization of the inner core of the CaO.
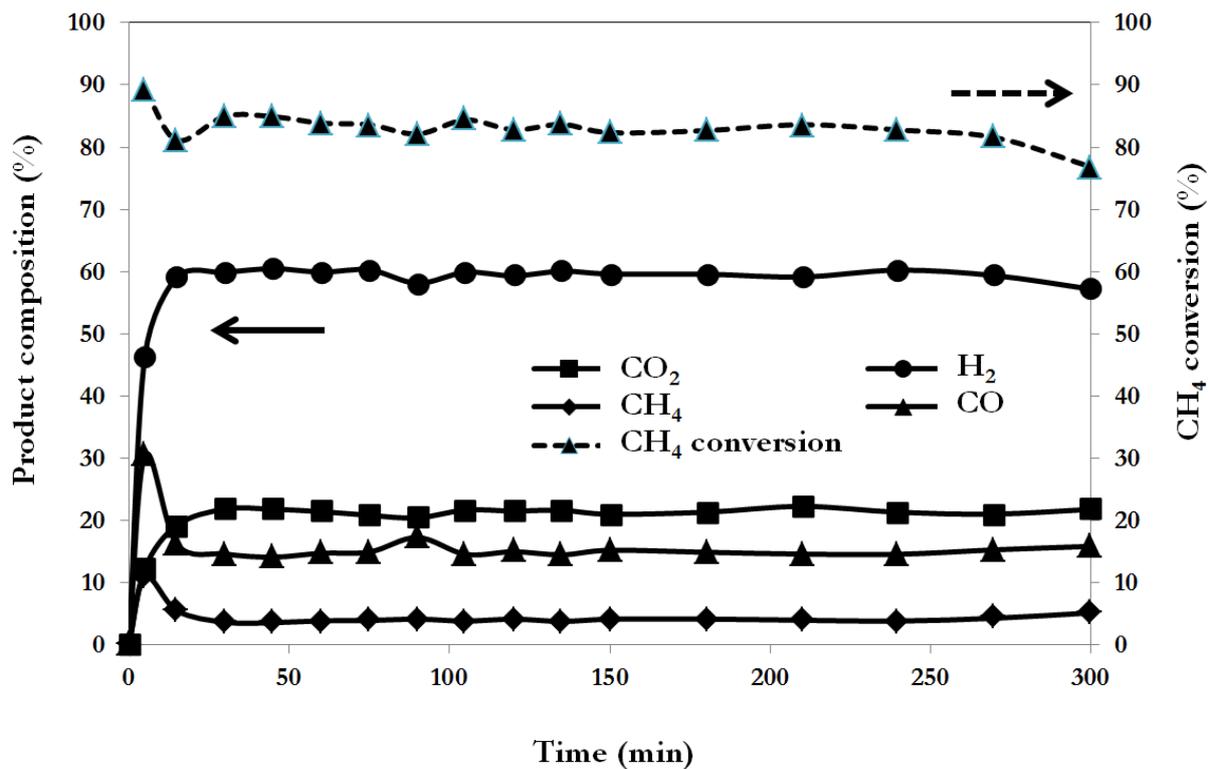
Fig. 8.   Gas product compositions (dry basis) and CH_4 conversion of Type I (a) for sorption enhanced biogas steam reforming at S/C of 3, CH_4/CO_2 of 1.5, reaction temperature of 873 K and atmospheric pressure.
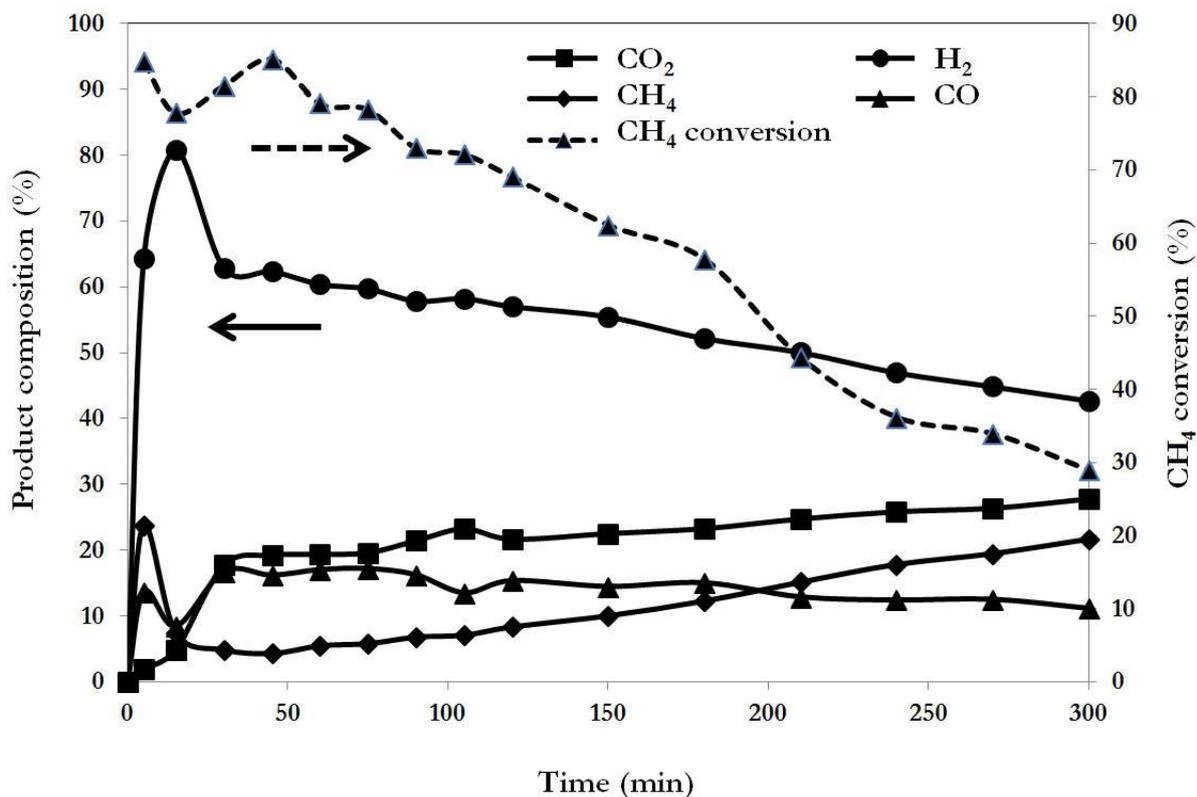
Fig. 9.   Gas product compositions (dry basis) and CH_4 conversion of Type I (b) for sorption enhanced biogas steam reforming at S/C of 3, CH_4/CO_2 of 1.5, reaction temperature of 873 K and atmospheric pressure.

The type II system (Fig. 10), is composed of 12.5 wt.% Ni/Al_2O_3 physically mixed with CaO and SiC. The results show that during the reaction time < 30 min, the CO_2 concentration in the product gas is almost zero and is accompanied by a high CH_4 conversion and H_2 concentration. During this same period the H_2 concentration and CH_4 conversion steadily increase. After this 30 min period the gas composition reaches a new steady state at 75 min with a CO_2 concentration of 20% and H_2 concentration of 60%, whilst the CH_4 conversion drops to a steady state value of 80%. The steady state hydrogen concentration and methane conversion of Type II were similar to those obtained for the Type I (a) system.
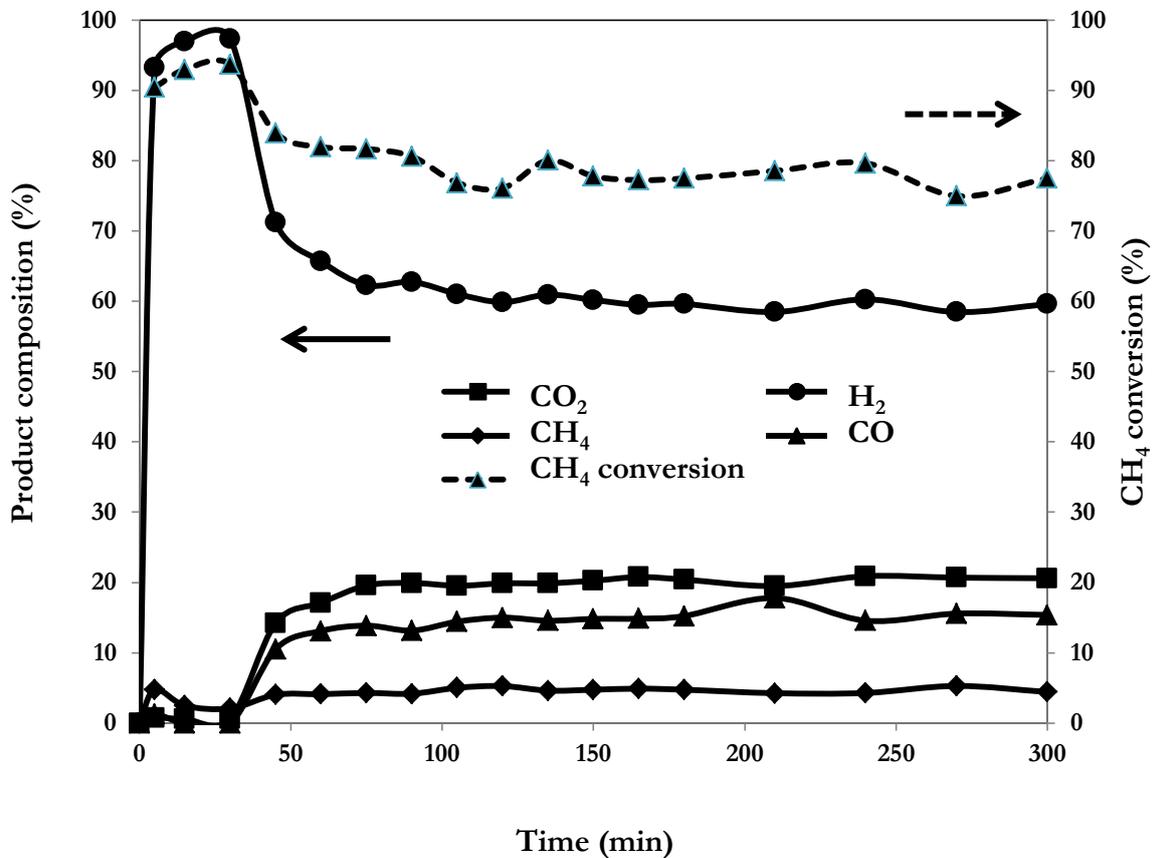
Fig. 10.   Gas product compositions (dry basis) and CH_4 conversion of Type II for the sorption enhanced biogas steam reforming at S/C of 3, CH_4/CO_2 of 1.5, reaction temperature of 873 K and atmospheric pressure.

The type III system (Fig. 11) has two sections of bed separated and supported by quartz wool. The results show a hydrogen concentration of 93.2% during the initial period when CO_2 adsorption takes place, but decreases as the breakthrough time is reached and reaches a steady state value of 64.4% when CO_2 adsorption is no longer taking place. Therefore with the incorporation of CO_2 adsorption the hydrogen concentration is approx. 30% higher, with no significant change in CH_4 conversion (84.7% with CO_2 sorption period and 82.6% without CO_2 sorption period). The low content of CaO in the bed results in little or no change in CH_4 conversion.
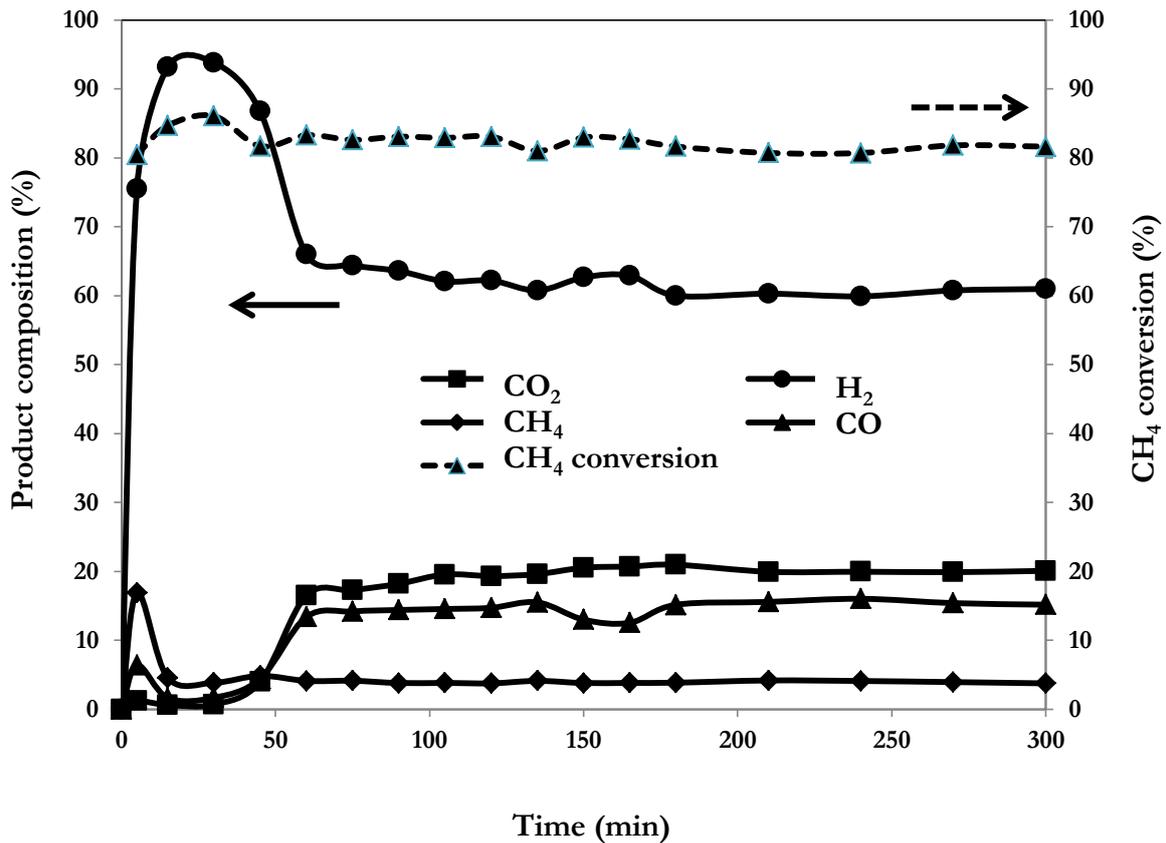
Fig. 11. Gas product compositions (dry basis) and CH_4 conversion of Type III for sorption enhanced biogas steam reforming at S/C of 3, CH_4/CO_2 of 1.5, reaction temperature of 873 K and atmospheric pressure.

In the Type IV reactor, the amount of CaO support was increased to 2 g whilst keeping the amount of Ni catalyst constant at a level equal to that used in the Type II reactor, resulting in 5.4 wt.% Ni/CaO. The test was performed, the results of which are shown in Fig. 12. The results show that the hydrogen concentration and CH_4 conversion decreased from 55.4% (5 min) to 6.1% (150 min) and 94.2% (5 min) to 22.7% (150 min), respectively. This behavior is due to the Type IV system experiencing deactivation of the catalyst as was the case for the Type I (b) system. As with the Type I (b) system this deactivation is due to loss of active sites due to partial or complete closure of pores. A summary of hydrogen concentration and CH_4 conversion results for all bed arrangement types are shown in Table 3. The most significant improvement in hydrogen concentration and CH_4 conversion with CO_2 adsorption was for the Type II system with improvements of 34.7% and 11.3%, respectively.
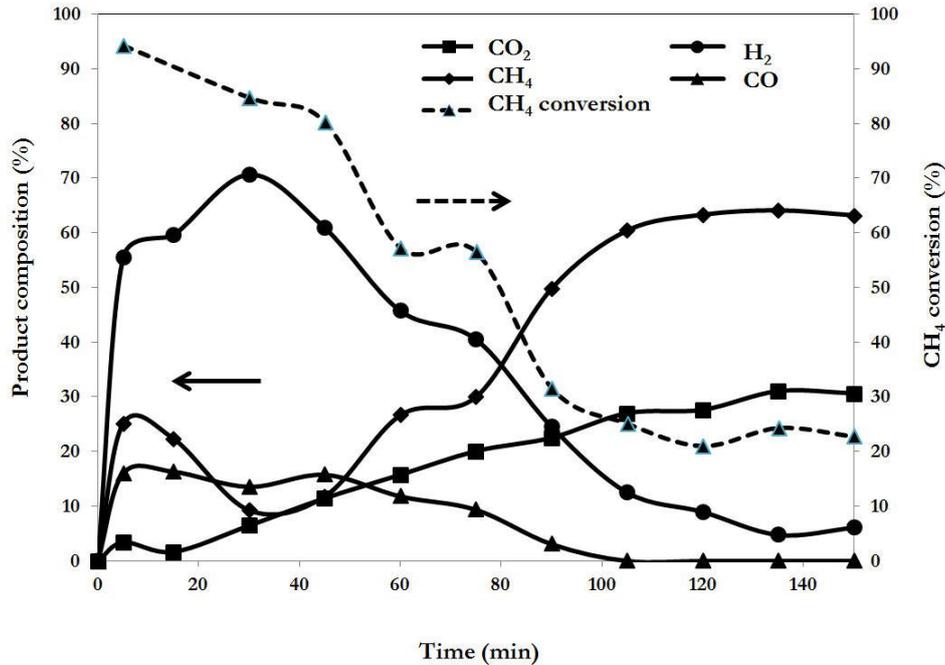
Fig. 12.   Gas product compositions (dry basis) and CH_4 conversion of Type IV for sorption enhanced biogas steam reforming at S/C of 3, CH_4/CO_2 of 1.5, reaction temperature of 873 K and atmospheric pressure.

Table 3.   Summary of H_2 concentration and CH_4 conversion of different types of bed arrangement for sorption enhanced biogas steam reforming at 873 K.

Type of bed arrangement	H_2 concentration (%)		CH_4 conversion (%)	
	With CO_2 sorption	Without CO_2 sorption	With CO_2 sorption	Without CO_2 sorption
I (a)	-	60.0	-	81.1
I (b)	80.8	Deactivation	77.8	Deactivation
II	97.0	62.3	93.0	81.7
III	93.2	64.4	84.7	82.6

Although, the optimum temperature for obtaining the highest CO_2 sorption capacity was at 873 K, this is an undesirably high reaction temperature. Therefore, a lower temperature was tested at 773 K for the purpose of reducing the reactor wall material cost and energy consumption. The results show that an increase in hydrogen concentration of 35.2% can be achieved at 773 K by incorporating the CO_2 adsorption process, a concentration not significantly different from that obtained by the Type II system at 873 K which where an increase in hydrogen concentration of 34.7% was obtained, as shown by Fig. 13. However, the CH_4 conversion increased by 50.4% at 773 K, compared to that at 873 K which exhibited an increase in CH_4 conversion of only 11.3% as shown in Fig. 14. These results showed that at a lower reaction temperature (773 K) CH_4 conversions > 90% can be achieved when incorporating CO_2 sorption into the process, due to a shift in the equilibrium in the forward direction as a result of CO_2 removal from the gas stream, however the CH_4 conversion at 773 K without CO_2 sorption is still lower than at 873 K. It should be noted that the high CH_4 conversion for hydrogen production via the sorption enhanced biogas steam reforming process provides the opportunity to operate at lower temperatures thus reducing the energy demand and operating costs. However, CaO shows poor stability over multiple CO_2 sorption cycles therefore several researchers [26-29] have investigated the modification of CaO for improved stability and reductions in regeneration temperature. The improvement in stability of CaO for sorption enhanced biogas steam reforming provides a challenge for future work.
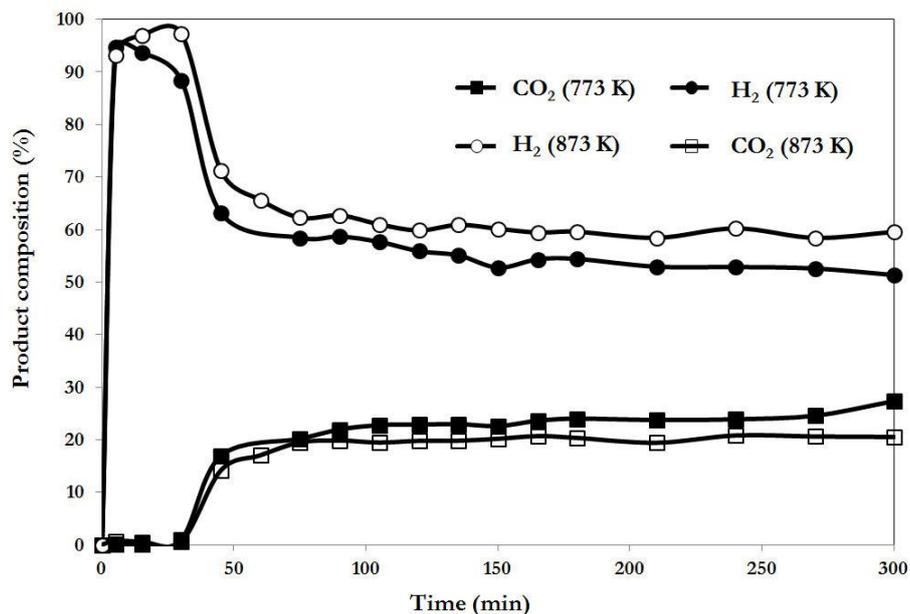
Fig. 13.   Effect of temperatures (773 and 873 K) of bed arrangement Type II by sorption enhanced biogas steam reforming at S/C of 3, CH_4/CO_2 of 1.5 and atmospheric pressure.
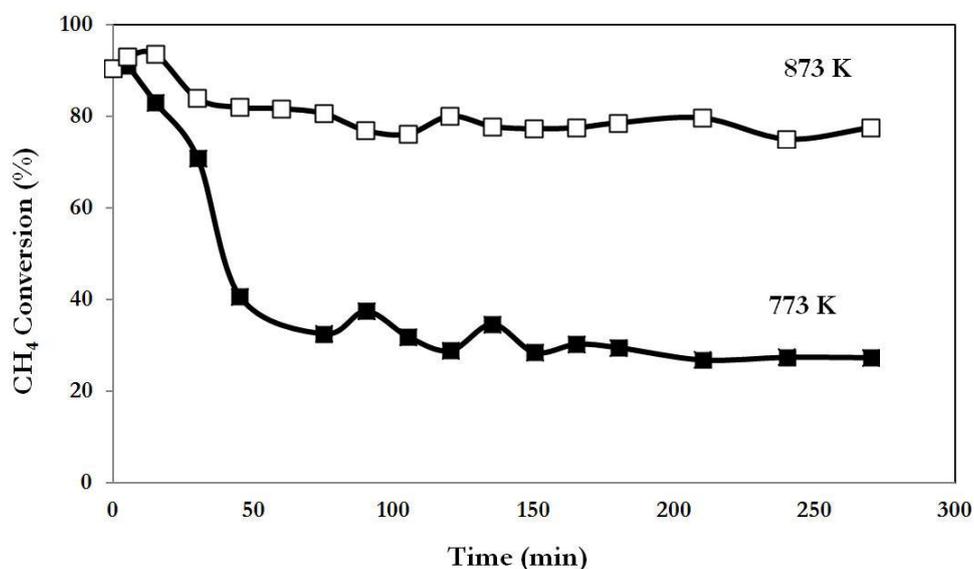
Fig. 14. CH_4 conversion of Type II for sorption enhanced biogas steam reforming at S/C of 3, CH_4/CO_2 of 1.5 and atmospheric pressure.

4. Conclusion

Calcium oxide was selected for CO_2 adsorption testing. Four adsorption temperatures (723-873 K) were tested and the results showed that the adsorption capacity increased with increasing adsorption temperature. The highest CO_2 sorption capacity was achieved at 873 K (0.2849 g_{CO2}/g_{CaO}). Four bed arrangement types were investigated for use in hydrogen production via the sorption enhanced biogas steam reforming process. The operating conditions were carried out at temperature of 873 K, with a CH_4/CO_2 ratio of 1.5, a S/C ratio of 3, a total flow rate of 50 ml/min and at atmospheric pressure. The Type I (a) system, 12.5 wt.% Ni/Al_2O_3, gave an outlet hydrogen concentration of 60.0% and a CH_4 conversion rate of 81.1%. The Type I (b) system 12.5 wt.% Ni/CaO, showed catalyst deactivation due to carbonation of calcium oxide at the surface layer. The best performing bed arrangement was the Type II system (12.5 wt.% Ni/Al_2O_3 physical mixed with CaO) which exhibited 34.7% improvement in the outlet hydrogen concentration and an 11.3% improvement in the CH_4 conversion at 873K as a result of the CO_2 adsorption process. Furthermore, when

the reaction was performed at a lower temperature (773 K), the hydrogen concentration was similarly enhanced to that at a temperature of 873 K (35.2% and 34.7%, respectively) but the CH_4 conversion was significantly enhanced by the CO_2 sorption, with a percentage increase in CH_4 conversion of 50.4% at 773 K compared to an increase in 11.3% at 873 K. The CH_4 conversion can be significantly improved with the incorporation of CO_2 sorption in the process with CH_4 conversion > 90% at lower temperatures (773 K).

Acknowledgement

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