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Continuous Production of Hydrogen from Sorption-Enhanced Steam Methane Reforming in Two Parallel Fixed-Bed Reactors Operated in a Cyclic Manner

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Hydrogen with purity higher than 90% was produced continuously by sorption-enhanced steam methane reforming reactions in two parallel fixed-bed reactors operated in a cyclic manner. The process involved sorption-enhanced steam methane reforming reactions and a sorbent regeneration reaction. First, through addition of a CO₂ sorbent into a reforming reactor, the reactions of reforming, water–gas shift, and CO₂ sorption were combined, and more CH₄ was expected to convert H₂ in one reactor. Second, regeneration of the sorbent was carried out in the other reactor. The hydrogen production and sorbent regeneration processes were carried out simultaneously in the two fixed-bed reactors, operated in a cyclic manner by switching a methane/steam feed and an Ar-containing feed between the two reactors at a fixed feed switchover time. The critical value of the feed switchover time for achieving the production of higher concentrations of hydrogen was investigated and analyzed.

1. Introduction

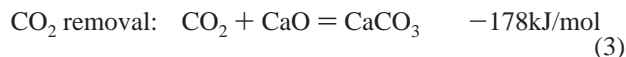
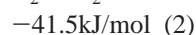
The hydrogen production process with addition of CO₂ sorbent into a conventional methane steam reforming reactor is called the sorption-enhanced reforming process (SERP). In the SERP, CO₂ can be removed in situ as soon as it is formed, and the reforming and water–gas shift reactions can proceed beyond the conventional thermodynamic limits, so that more methane will be converted to hydrogen. The SERP combines reaction and separation, and thus can result in process simplification, improved energy efficiency, and increased reactant conversion and product yield.^{1–11}

When a Ca-based sorbent is used to absorb CO₂, the important reactions in the SERP are

steam methane reforming (SMR):



water–gas shift (WGS): $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$



CaO must be regenerated after sorption



Many research works about the SERP and process development have been published, including the simultaneous reaction concept^{1–2} and reaction equilibrium,³ the water–gas shift reaction and carbon dioxide separation with calcium oxide in one reactor,⁴ the production of high-purity hydrogen in a single reactor,⁵ the durability of dolomite in multicycle SERP tests,⁶

a new hydrogen production by reaction-integrated novel gasification (HyPr-RING),⁷ a zero-emission fuel-cell vehicle system using the SERP,⁸ sorption-enhanced H₂ production reactions at low pressure,⁹ the SERP using an atmospheric-pressure bubbling fluidized-bed reactor,¹⁰ and the effect of Ca(OH)₂ formation on the SERP.¹¹

In all of the above investigations, the SERP and sorbent regeneration were carried out in a single reactor operated alternately in reaction and regeneration modes. No continuous high-purity hydrogen production tests were performed. For commercial application, both the SERP and sorbent regeneration need to be carried out continuously to produce a continuous H₂ stream. In this study, we investigated the continuous production of H₂ from the SERP with two fixed-bed reactors in two steps, reactions 1–3 followed by reaction 4. The two steps were carried out simultaneously and continuously in a cyclic manner in two fixed-bed reactors by switching methane/steam and argon feeds between the two reactors at a fixed feed switchover time.

2. Description of Experimental Rig and Conditions

The SERP and sorbent regeneration were carried out in two parallel fixed-bed reactors that were heated by electric furnaces; one of the reactors was used as the reformer, and the other was used as the regenerator. The two reactors had different feeds inlets and product gas outlets. A schematic diagram of the system of two parallel fixed-bed reactors is shown in Figure 1. Three three-way valves were connected to inlets of the two reactors in order to switch the two different gaseous feeds and water feed between the two reactors. Feeds were switched between the two reactors at a fixed interval of time (called the feed switchover time). The reaction temperature in both reactors was controlled and measured using thermocouples located in the catalyst/sorbent bed. During a reforming/regeneration cycle test, water was fed as a liquid using a high-pressure pump into

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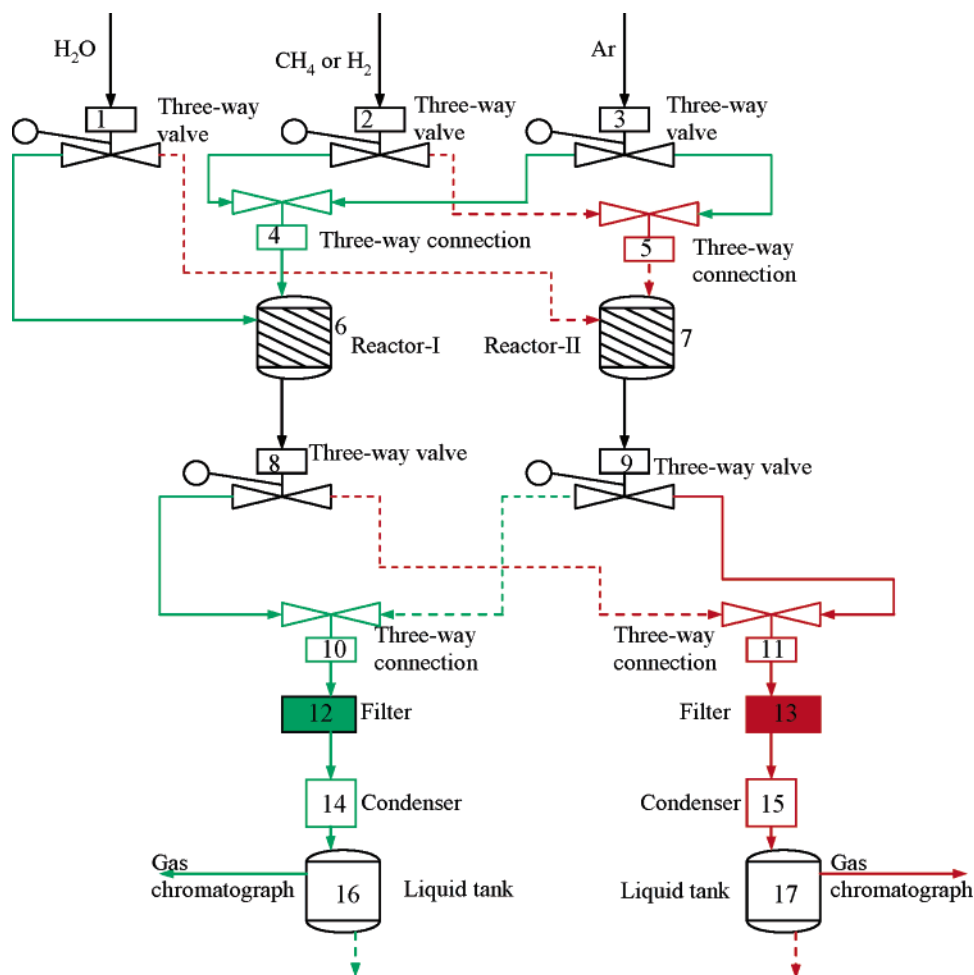


Figure 1. Parallel fixed-bed reactors operated in a cyclic manner.

reforming reactor I through three-way valve 1. CH₄ from a high-purity cylinder was also fed into reforming reactor I through three-way valve 2. The combined gas and water feeds entered near the top of reactor I and were preheated as they flowed downward into the preheater area in which quartz sand was packed. Then, the preheated gases flowed through the mixture of reforming catalyst and CO₂ sorbent and exited from the bottom of reactor I. The effluent gases from reactor I flowed into condenser 14 through three-way valve 8, and excess steam was removed in condenser 14. The product gases were analyzed using an AutoSystem XL gas chromatograph equipped with a thermal conductivity detector. The concentration of each component was determined as the normalized concentration in volume percent assuming the total amount of CH₄, H₂, CO, and CO₂ to be 100% after removal of water by condensation.

The sorbent regeneration reaction occurred simultaneously in reactor II. Ar from a high-purity cylinder was fed into regeneration reactor II through three-way valve 3. The temperature of reactor II was raised to 850 °C, where it was held for some time to make CaCO₃ decompose completely and reactivate the sorbent, and then the temperature of reactor II was reduced to the reforming temperature again. The regeneration gases from reactor II flowed into condenser 15 through three-way valve 9.

After a fixed interval of time, the feeds were switched between reactor I and reactor II through three-way valves 1–3, and the product gases were also switched between the outlets of reactors I and II through three-way valves 8 and 9. At this stage, reactor I was used as the sorbent regeneration reactor, while reactor II was used as the reforming reactor.

The reforming catalyst was a standard Ni-based catalyst, NiO/Al₂O₃ (~20 wt % NiO), and CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) was chosen as the sorbent based on earlier results.^{12,13} Before the reactions were carried out, the catalyst in both reactors was reduced in a flow of H₂/Ar mixture (50 mol % hydrogen) at 600 °C for 2 h. Both catalyst and sorbent were crushed into powders with particle sizes in the range of 200–450 μm. Approximately 3–4 and 6–8 g of mixed sorbent and catalyst in a sorbent/catalyst mass ratio of 1–1.4 was added to reactors I and II, respectively. The sorbent regeneration was conducted in 100% Ar atmosphere. The equilibrium CO₂ pressure over CaCO₃ is a function of temperature, and 850 °C is sufficient to ensure adequate decomposition kinetics of CaCO₃. The reaction conditions for cyclic stepwise sorption-enhanced steam methane reforming and sorbent regeneration reactions over Ni-based catalyst and CaO/Ca₁₂Al₁₄O₃₃ sorbent in two parallel reactors are reported in Table 1.

3. Results and Discussion

Experimental results for the cyclic stepwise sorption-enhanced steam reforming of methane over Ni-based catalyst and CaO/Ca₁₂Al₁₄O₃₃ sorbent in two parallel reactors operated in a cyclic manner with a feed switchover time of 55–60 min are shown in Figure 2. The results indicate that a steady hydrogen stream with purity higher than 90% can be obtained in the process. The observed decreases in hydrogen concentration in Figure 2, which are due to a momentary change in flow rate, correspond to the switchover of feed methane/steam and feed argon between the two reactors. From Figure 2, it can be observed that the

Table 1. Experimental Conditions^a

parameter	temperature (°C)	pressure (atm)	CH ₄ flow rate (mL/min)	H ₂ O/CH ₄ ratio	Ar flow rate (mL/min)	solid mass (g)
Reactor I						
reforming period	630	1	6	5	0	3–4
regeneration period	850	1	0	0	230	
Reactor II						
reforming period	630	1	12	5	0	6–8
regeneration period	850	1	0	0	230	

^a Mass ratio of sorbent to catalyst between 1/1 and 1.4/1.

CO₂ concentrations during the reforming reaction period were in the range of 2–5%, which indicates that most of the CO₂ produced by the reforming and shift reactions are captured by CaO. Because of the detector's high sensitivity toward small changes in the gas flow rate, which results from the feed switchover between the two reactors, a decrease in H₂ concentration and an increase in CO₂ concentration in the chromatogram are observed. Nevertheless, the results of Figure 2 clearly show that high-purity H₂ can be produced continuously by carrying out the sorption-enhanced steam methane reforming process (reactions 1–3) and the sorbent regeneration process (reaction 4) simultaneously in two fixed-bed reactors operated in a cyclic manner.

After reforming, the CO₂ sorbent must be regenerated by CaCO₃ calcination for use in the next reforming cycle. If the sorbent is not regenerated completely by CaCO₃ decomposition, there will be an appreciable and continuous sorbent loss with increasing numbers of reforming/regeneration cycles, resulting in the decay of the CO₂ capture ability of the sorbent in the subsequent cycles. Therefore, a need for the complete decomposition of CaCO₃ within the interval of the feed switchover time is necessary to avoid sorbent activity loss. The CaCO₃ calcination reaction is endothermic and favored at higher temperature. Only if the equilibrium decomposition pressure of CaCO₃ is larger than the CO₂ partial pressure in the gas phase can the decomposition of CaCO₃ proceed thermodynamically. CaO regeneration from CaCO₃ decomposition is more difficult in the process of sorption-enhanced hydrogen production, especially for the direct production of H₂ simultaneously considering the maximum possible CO₂ sequestration, in which case more severe conditions of high concentrations of CO₂ and higher calcination temperatures in every cycle during regeneration must be used to produce a pure CO₂ stream.

In this study, it was calculated that the mass of CaCO₃ after the reforming period was ~0.8 and ~1.6 g inside reactors I and II, respectively. The regeneration gas atmosphere was 100% Ar, and the calcination temperature of 850 °C was sufficient to ensure adequate CaCO₃ decomposition kinetics.

In the process of continuous hydrogen production from the SERP, some compounds might be formed through the interaction of the Al₂O₃ support with Ni from the catalyst, but XRD analysis of the mixture of the sorbent and reforming catalyst following multicycle tests showed no evidence of the formation of mixed metal oxide compounds such as NiAl₂O₄.

The influence of the feed switchover time on process performance is presented in Figure 3. In the first seven reforming/sorbent regeneration cycles, as shown in Figure 3, feed switchover time was about to 55–60 min, and the experimental results indicate that the capture ability of the sorbent began to decline after 40 min during reforming period, resulting in the decrease of the hydrogen concentration and the increase of the CO₂ concentration in the subsequent reaction stages. From cycle 7 to cycle 12, the feed switchover time was reduced to 40 min. From Figure 3, it can be seen that the H₂ concentration always remained higher than 90% and a continuous stream of hydrogen could also be obtained. The results clearly show that there is a critical value for the feed switchover time, which was about 45 min for the CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) sorbent under the specified reaction conditions in Figure 3. However, the critical value of the feed switchover time might vary with the reaction conditions for the same sorbent and it might also differ for different sorbents.

The observed lower H₂ concentration and, consequently, the higher CO₂ concentration, as shown in Figure 3 for the long switchover time (55–60 min), were due to the decreasing CO₂ removal efficiency of sorbent. The response from a typical sorption-enhanced H₂ production reaction test can be divided into three regions: prebreakthrough, breakthrough, and post-breakthrough.^{5,6,10} For commercial application, the continuous production of H₂ is required, and both the sorption-enhanced steam methane reforming and sorbent regeneration reactions need to be carried out continuously. Feeds must be switched in a cyclic manner between the two parallel fixed-bed reactors at a fixed interval of feed switchover time. In this study, the critical feed switchover time was defined as the duration of the prebreakthrough period. To understand the critical feed switchover time in the process of two parallel fixed-bed reactors, a thermodynamic calculation of sorption-enhanced steam methane reforming based on CaO sorbent was carried out to analyze the effects of some parameters on the critical feed switchover time.

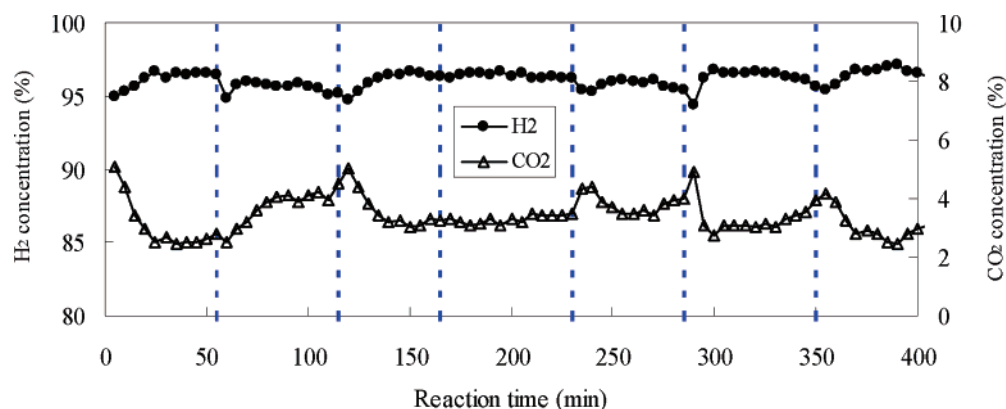


Figure 2. Evolution of H₂ and CO₂ concentrations (dry basis) with time in two fixed-bed reactors. (Dashed lines indicate switching of the reactors. The total solid masses in reactors I and II were ~4 and ~8 g, respectively, and the mass ratio of sorbent to catalyst was 1.4.)

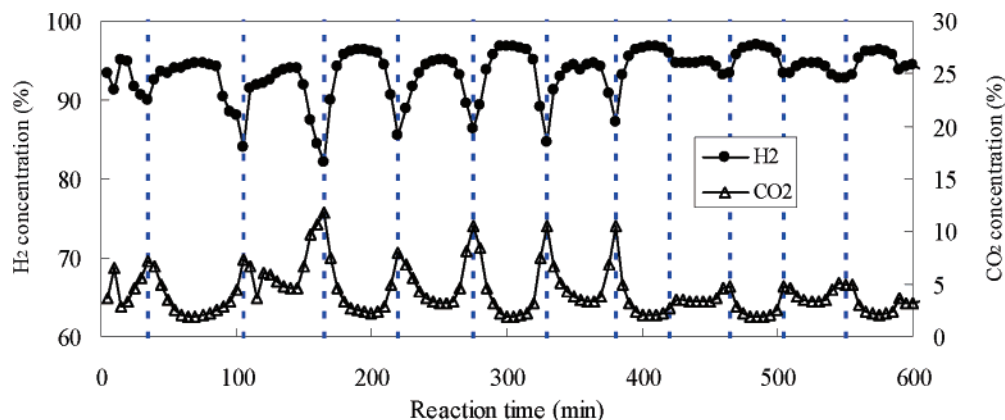


Figure 3. Evolution of H₂ and CO₂ concentrations (dry basis) with time in two fixed-bed reactors. (Dashed lines indicate switching of the reactors. The total solid masses in reactors I and II were ~3 and ~6 g, respectively, and the mass ratio of sorbent to catalyst was 1.)

The thermodynamic analysis was based on the equilibrium constant method. During the reforming period, the SMR, WGS, and CO₂ removal reactions all take place in one reactor. The thermodynamic equilibrium constants for these reactions are functions of reaction temperature only and can be written as

$$K_{\text{SMR}}(T) = \frac{P^2 y_{\text{H}_2}^3 y_{\text{CO}}}{y_{\text{CH}_4} y_{\text{H}_2\text{O}}} \quad (5)$$

$$K_{\text{WGS}}(T) = \frac{y_{\text{H}_2} y_{\text{CO}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} \quad (6)$$

When reactions approach the thermodynamic equilibrium state, the CO₂ partial pressure is equal to CO₂ equilibrium pressure

$$P_{\text{eq,CO}_2} = P_{\text{CO}_2} = y_{\text{CO}_2} P \quad (7)$$

Equations 5–7 describe the equilibrium relationships between the gas-phase mole fractions of various components (CH₄, CO, CO₂, H₂O, and H₂) at a total gas-phase pressure P and reaction temperature T . The CO₂ produced by reaction 2 is removed from the gas phase by reaction 3, if CaO is used as the CO₂ sorbent. At a constant temperature and constant pressure, if the total amount of feed gas is 1 mol, the equilibrium gas-phase mole fractions can be written as^{14,15}

$$\begin{aligned} y_{\text{H}_2} &= \frac{(3x + y)}{(1 + 2x - fy)} \\ y_{\text{CH}_4} &= \frac{1 - x(1 + \alpha)}{(1 + \alpha)(1 + 2x - fy)} \\ y_{\text{CO}} &= \frac{(x - y)}{(1 + 2x - fy)} \\ y_{\text{CO}_2} &= \frac{(1 - f)y}{(1 + 2x - fy)} \\ y_{\text{H}_2\text{O}} &= \frac{\alpha - (x + y)(1 + \alpha)}{(1 + \alpha)(1 + 2x - fy)} \end{aligned} \quad (8)$$

where α is the H₂O/CH₄ molar ratio of the feed introduced into the reactor at P and T , x is the number of moles of CO produced by the SMR reaction per mole of feed gas, y is the number of moles of CO reacted by the WGS reaction per mole of feed gas, and f is the fraction of CO₂ produced by the WGS reaction that is removed from the gas phase by absorption. The variables α , x , and y are related by the thermodynamic equations

$$K_{\text{SMR}}(T) = \frac{P^2(x - y)(3x + y)^3(1 + \alpha)^2}{(1 + 2x - fy)^2[1 - x(1 + \alpha)][\alpha - (1 + \alpha)(x + y)]} \quad (9)$$

$$K_{\text{WGS}}(T) = \frac{(1 - f)y(3x + y)(1 + \alpha)}{[x - y][\alpha - (1 + \alpha)(x + y)]} \quad (10)$$

The thermodynamic equilibrium equation for the reaction of sorbent with CO₂ is given by

$$P_{\text{eq,CO}_2} = y_{\text{CO}_2} P = \frac{(1 - f)y}{(1 + 2x - fy)} P \quad (11)$$

Equations 9–11 can be simultaneously solved for a given set of values of P , T , and α in order to calculate x , y , and f as functions of temperature and pressure. Then, the equilibrium gas-phase mole fractions of all components and the CH₄ conversion can be calculated.

The CO₂ equilibrium pressure for CaO sorbent, $P_{\text{eq,CO}_2}$, can be obtained by following equation¹⁶

$$P_{\text{eq,CO}_2} (\text{Pa}) = 1.826 \times 10^{12} \exp\left(-\frac{19680}{T}\right) \quad (12)$$

yf is the amount of CO₂ removed from the gas phase by CaO, the flow rate of CH₄ is F_{CH_4} (mL/min), and the mass of CaO added into reactor is m_{CaO} (g). After the prebreakthrough period, the beginning of the breakthrough period corresponds to the leading edge of the CO₂ separation reaction approaching the exit of the fixed bed; the CaO conversion at the beginning of breakthrough period is denoted X_{pre} . The critical feed switchover time is expressed as

$$\begin{aligned} t_{\text{cri}} &= \frac{\frac{m_{\text{CaO}} X_{\text{pre}}}{56}}{yf(1 + \alpha) \frac{F_{\text{CH}_4}}{22.4 \times 10^3}} \\ &= \frac{X_{\text{pre}}}{yf(1 + \alpha)} \frac{\frac{m_{\text{CaO}}}{56}}{\frac{F_{\text{CH}_4}}{22.4 \times 10^3}} \\ &= \frac{X_{\text{pre}}}{yf(1 + \alpha)} \frac{1}{V_{\text{CH}_4/\text{CaO}}} \end{aligned} \quad (13)$$

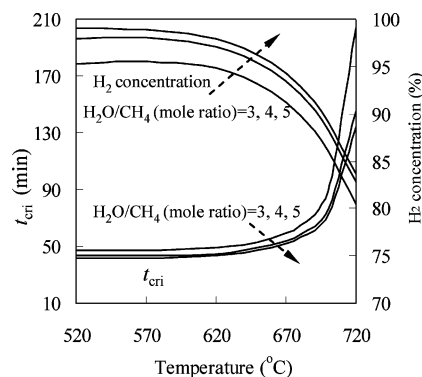


Figure 4. t_{cri} and H_2 concentration at different temperatures and $\text{H}_2\text{O}/\text{CH}_4$ ratios ($P = 1 \text{ atm}$, $X_{\text{pre}} = 0.53$, $V_{\text{CH}_4}/\text{CaO} = 0.0133 \text{ min}^{-1}$).

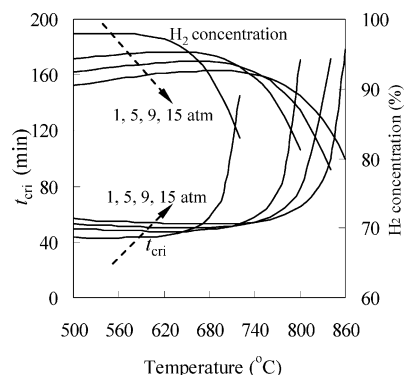


Figure 5. t_{cri} and H_2 concentration at different temperatures and pressures ($\text{H}_2\text{O}/\text{CH}_4 = 4$, $X_{\text{pre}} = 0.53$, $V_{\text{CH}_4}/\text{CaO} = 0.0133 \text{ min}^{-1}$).

$V_{\text{CH}_4}/\text{CaO}$ is defined as the CH_4 gas minutely space velocity over CaO sorbent (GMSV-CaO , min^{-1}). From eq 13, the effects of temperature, pressure, steam/methane mole ratio, and GMSV-CaO on the critical feed switchover time can be obtained.

Figure 4 shows t_{cri} and the dry-basis equilibrium mole fraction of H_2 as functions of temperature and $\text{H}_2\text{O}/\text{CH}_4$ mole ratio for the sorption-enhanced steam methane reforming reaction. At a fixed pressure, the equilibrium content of H_2 initially does not change with increasing reaction temperature and then decreases slightly with further increase in temperature. When the mole ratio of $\text{H}_2\text{O}/\text{CH}_4$ increases, more CH_4 is converted to H_2 , resulting in an increase in the H_2 concentration. The critical feed switchover time remained nearly constant with increasing temperature in the range of 520–640 °C and then increased rapidly with further increase in temperature, as shown in Figure 4. At lower temperature and higher $\text{H}_2\text{O}/\text{CH}_4$ mole ratio, most of the CO_2 produced by the reforming and shift reactions are removed from the gas phase by the sorbent, and the sorbent approaches X_{pre} rapidly. The CO_2 equilibrium pressure, $P_{\text{eq,CO}_2}$ increased with increasing temperature, resulting in an increase in y_{CO_2} and a decrease in y_f under the condition of constant total pressure. The fraction of CO_2 removed by the sorbent decreases with increasing temperature, and therefore, the critical feed switchover time would increase with increasing temperature.

Because reactions 1–3 involve an increase in the total number of gas-phase moles of hydrogen, y_{H_2} , and the amount of available CO_2 decreases with increasing pressure, t_{cri} increases with increasing pressure, as shown in Figure 5. However, an increase in pressure shifts the CaCO_3 decomposition temperature to higher temperatures, and it can be seen in Figure 5 that the temperature at which the hydrogen concentration begins to decrease and t_{cri} begins to increase increases with increasing pressure.

From the experimental conditions used in Figure 3, the total solid mass in reactor I was $\sim 3 \text{ g}$ and the mass ratio of sorbent to catalyst was 1, so the CaO contained in $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (75/25 wt %) sorbent was calculated to about 1.125 g. The value of X_{pre} was calculated from experimental results by material balance and found to be about 0.53 at the beginning of breakthrough. The CH_4 flow rate was 6 mL/min, so $V_{\text{CH}_4}/\text{CaO}$ could be calculated as 0.0133 min^{-1} . At 630 °C and 1 atm, it can be seen in Figure 4 that the value of the critical feed switchover time would be about 45 min, with a $\text{H}_2\text{O}/\text{CH}_4$ ratio of 5. Therefore, when the feed switchover time was reduced to 40 min, a continuous stream of hydrogen with purity higher than 90% could be obtained, as shown in Figure 3.

When designing a reactor for sorption-enhanced hydrogen production, in addition to t_{cri} , the hydrogen concentration is also an important parameter. It can be seen from Figures 4 and 5 that a large value of t_{cri} can be accomplished by operating at high temperature, say, above 700 °C. At higher temperature, the sorbent is almost completely ineffective, so that the CO_2 produced by steam methane reforming and water shift reactions cannot be absorbed effectively by the sorbent and the value of f becomes zero, causing t_{cri} to become infinitely large. However, Figures 4 and 5 also suggest clearly that the hydrogen concentration decreases rapidly with increasing temperature. When the reactor is operated at high temperature where the sorbent is almost completely ineffective, the hydrogen concentration decreases, and high-purity hydrogen cannot be obtained from a single step. In designing a reactor, one would want first a high-purity hydrogen stream and then a large value of t_{cri} . Although a large value of t_{cri} can be accomplished by operating at high temperature, the hydrogen concentration decreases rapidly. The attainment of a large t_{cri} value must satisfy first that a high concentration of hydrogen can be obtained simultaneously, as shown in Figures 4 and 5.

In this study, the CH_4 gas minutely space velocity over CaO sorbent (GMSV-CaO , min^{-1}), $V_{\text{CH}_4}/\text{CaO}$, is defined that the CH_4 flow rate (mol min^{-1}) divided by the number of moles of CaO packed into the reactor. The increase of GMSV-CaO means that the amount of CO_2 produced by the reforming and shift reactions also increases, resulting in a rapid decreases of t_{cri} . X_{pre} corresponds to the CaO conversion at the beginning of the breakthrough period. The value of t_{cri} increases linearly with X_{pre} . For different sorbents, the values of X_{pre} are different; therefore, the critical feed switchover time will vary. The activities of most Ca-based sorbents decay during multiple reforming/sorbent regeneration reaction cycles, and therefore, X_{pre} will decline with increasing number of cycles, resulting in a decrease of t_{cri} . It should be noted that the fractional sorbent conversion at the beginning of breakthrough is a function of the space velocity. At the same time, temperature, pressure, and $\text{H}_2\text{O}/\text{CH}_4$ ratio all have some effects on the value of X_{pre} . It is beyond the scope of this short article to analyze in detail the complicated mechanism of this process.

4. Conclusions

It is feasible to produce a continuous stream of hydrogen with purity higher than 90% by conducting the sorption-enhanced steam methane reforming and sorbent regeneration reactions in two parallel fixed-bed reactors operated in a cyclic manner. The feed switchover time between two fixed-bed reactors has a critical value for achieving the best performance in the process. When the feed switchover time is smaller than the critical value, a hydrogen stream with purity higher than 90% can be obtained continuously by the cyclic switching the two parallel fixed-bed

reactors. When the feed switchover time is larger than the critical value, high-purity hydrogen cannot be produced continuously. The critical value of the feed switchover time is determined by the temperature, pressure, steam/methane mole ratio, and GMSV-CaO.

Acknowledgment

This work was supported by the National High Technology Development Program of China (No. 2003AA501330).

Nomenclature

α = molar ratio of $\text{H}_2\text{O}/\text{CH}_4$

F_{CH_4} = methane flow rate, mL min^{-1}

f = fraction of CO_2 removed from the gas phase by absorption

K_{SMR} = thermodynamic equilibrium constant of the steam methane reforming reaction

K_{WGS} = thermodynamic equilibrium constant of the water–gas shift reaction

m_{CaO} = molecular weight of CaO, 56 g mol^{-1}

P = total pressure, Pa

P_{CO_2} = CO_2 partial pressure, Pa

$P_{\text{eq,CO}_2}$ = CO_2 equilibrium pressure, Pa

t_{cri} = critical feed switchover time, min

$V_{\text{CH}_4/\text{CaO}}$ = CH_4 gas minutely space velocity over CaO sorbent (GMSV-CaO), min^{-1}

X_{pre} = CaO conversion at the beginning of the breakthrough period

x = number of moles of CO produced by the SMR reaction per mole of feed gas, mol

y = number of moles of CO reacted by the WGS reaction per mole of feed gas, mol

y_i = gas-phase mole fraction of component i ($i = \text{H}_2, \text{CO}, \text{CO}_2, \text{H}_2\text{O}, \text{CH}_4$)

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Received for review August 2, 2006

Revised manuscript received September 7, 2006

Accepted October 11, 2006

IE061010X