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Experimental Study of Steam Reforming of Methane in a Thin (6 *μ*M) Pd-Based Membrane Reactor

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A novel, thin (6 *μ*m), defect-free Pd/MPSS (macroporous stainless steel) composite membrane tube was prepared by using a multidimensional plating mechanism. A high hydrogen permeation flux of 0.260 mol/(m^2 s) and complete hydrogen selectivity were obtained at a temperature of 500 °C and a pressure difference of 100 kPa. The catalytic membrane reactor for steam reforming of methane was constructed with the as-synthesized thin Pd/MPSS composite membrane and a commercial Ni−Al$_2$O$_3$ reforming catalyst. Methane conversion, hydrogen extraction ratio, and hydrogen production rate of the membrane reactor were studied in detail under different operating parameters such as temperature, pressure, space velocity, steam-to-methane ratio, and sweep gas flux. Some important effects were found for these operating parameters to the three performance factors. Drastic superiority to the traditional reactor was proved by changing the Pd-based membrane tube to a dense stainless steel tube with the same diameter. Moreover, on comparison with the experimental results and the simulation predictions in other catalytic membrane reactors appearing in the literature, the reactor constructed in the present work had a relatively better performance, due to the higher hydrogen permeance of the thin Pd membrane and the proper operating parameters.

1. Introduction

The application field of pure hydrogen has expanded to the operation of fuel cells and mobile vehicles, far from the traditional petroleum refining and semiconductor processing. It is the main energy carrier of the future, due to its light weight, high abundance, and lack of harm to the environment.[1−4] However, the precondition of its realistic application is its production and separation from hydrogen-containing sources such as water, natural gas, and coal. Though the hydrogen source of water has greater potential due to its huge abundance, there is still a long road before its application, due to the high cost of this process. Steam reforming of abundant natural gas (including the water-gas shift step) is one of the most important chemical processes for the production of pure hydrogen, which has been proven more economical than other processes such as coal vaporization, hydrocarbon partial oxidation, and water electrolysis. However, the steam reforming reaction is largely endothermic and limited by equilibrium, and a high operating temperature must be employed to achieve the satisfactory methane conversion. For example, the theoretical calculation results of the thermodynamic equilibrium shown in Figure 1 indicates that a high operating temperature of at least
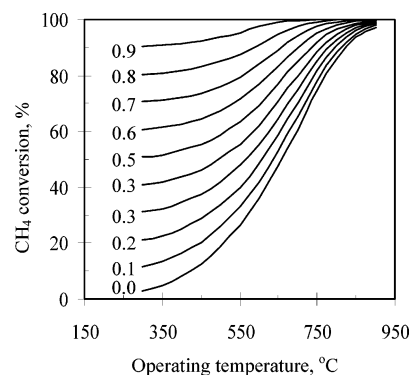

Figure 1. Effect of operating temperatures and H$_2$ removal ratios on CH$_4$ conversion (operating pressure, 1000 kPa; H$_2$O/CH$_4$ = 3).

850 °C is needed for obtaining a satisfactory methane conversion of 90% when the operating pressure and the ratio of H$_2$O/CH$_4$ are controlled to be 1000 kPa and 3.0, respectively. An elevated operating pressure is always used in order to improve the energy efficiency of the overall process. Therefore, the investment cost of equipment of the steam reforming plant is very high, because of the high temperatures and high pressures. In addition, a typical plant for hydrogen production has to use separate water-gas shift and pressure swing adsorption operating units, which makes the operating process more complex and increases the operating cost.

It is fortunate that, as shown in Figure 1, with an increase of the hydrogen removal ratio, a higher methane conversion can also be obtained at relatively lower operating temperatures. This calculation was done by simply setting a residual hydrogen molar amount in the equilibrium composition of the steam reforming reaction. For example, if 90% of the hydrogen is removed

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from the reaction location, a higher methane conversion of 94% can be obtained at the low operating temperature of 500 °C, which is about 350 °C lower than the operating temperature for achieving the same methane conversion under the thermodynamic equilibrium without hydrogen removal. The hydrogen-permeable inorganic membrane reactors[5-9] developed in recent years can remove the hydrogen from the reaction location in situ while the hydrogen is formed, which can largely decrease the operating temperature. Moreover, this catalytic membrane reactor can also combine steam reforming of methane to syngas, the water-gas shift reaction, and hydrogen purification into one operating unit, which makes the hydrogen production process much simpler and the production cost much lower. In comparison with other typical hydrogen-permeable membranes such as mesoporous ceramic membranes (low selectivity), microporous ceramic membranes (low permeability), dense silica membranes (low permeability), and mixed conducting ceramic membrane (low permeability), a Pd-based membrane (high hydrogen permeability and complete hydrogen selectivity) is the best candidate for catalytic membrane reactors to carry out the steam reforming reaction and other hydrogen-related reactions.[10-20]

In recent years, some meaningful work have been published about the steam reforming reaction (including the water-gas shift) in Pd-based membrane reactors.[5-9,21-29] In 1987 the improved reaction performance in a membrane reactor based on a Pd membrane disk with a thickness of 100 μm was first reported by Oertel et al. The hydrogen production was increased greatly. However, the operating temperature was still very high (700 or 800 °C), which was ascribed to a lower hydrogen permeance due to the thickness of the Pd membrane disk.[5] To effectively decrease the operating temperature without impairing the reaction performance, Kikuchi and co-workers developed an electroless plating method and prepared some thin (10-26 μm) Pd-based composite membranes on porous glass substrates.[19-20] In their new membrane reactor, a methane conversion of about 88% for steam reforming of methane was obtained at a lower operating temperature of 500 °C under their experimental conditions.[6] However, some problems such as mechanical and/or thermal stability, high-temperature sealing, and compartment construction resulting from the ceramic substrate must be solved before the industrial application of this membrane reactor. Shu et al. employed a porous stainless steel disk or tube as the substrate and prepared thin Pd and Pd/Ag composite membranes. The steam reforming reaction was also investigated in their membrane reactors. A methane conversion of 63% was obtained at the lower operating temperature of 500 °C. A long-term steady operation of 47 h was achieved.[7] Lin et al. also constructed a membrane reactor by using a thin Pd membrane (20-25 μm) on a porous stainless steel tube, and a methane conversion of 45% was obtained at the operating temperature of 500 °C under their experimental conditions, which was about 15% higher than the methane conversion in a traditional reactor under the same operating conditions.[21] The relatively low methane conversion compared with that of Kikuchi et al. was ascribed to the lower hydrogen permeance or the lower hydrogen selectivity of the Pd membrane on a porous stainless steel substrate. Moreover, Kikuchi et al. also studied the reaction performance of steam

reforming in their membrane reactor based on a Pd membrane by the CVD method.[9] Recently, a cold-rolled Pd/Ag alloy membrane with a thickness of 50 μm was also used to construct a membrane reactor for the steam reforming reaction by Basile and co-workers. The effects of different sweep gases such as nitrogen, air, water, carbon monoxide, and oxygen on the methane conversion in their membrane reactor were investigated, which indicated that a methane conversion of 70% was obtained at an operating temperature of 450 °C while a reactive sweep gas was used.[22] The experimental results showed that it is still very difficult to improve the hydrogen permeance and the stability together. At the same time, some researchers such as Prokopiev,[23] Shu,[7] Jørgensen,[24] Aasberg Petersen,[25] Oklany,[26] Lin,[27] and Gallucci,[28] together with their co-workers, did some math model simulation work for steam reforming of methane in Pd-based membrane reactors, which showed that complete methane conversion could be obtained at an operating temperature of 500-600 °C if the membrane separation efficiency is high enough. In comparison with the reaction kinetics of methane steam reforming and water-gas shift, hydrogen permeation kinetics was the controlling step for the reaction kinetics in this membrane reactor. According to experimental results with model predictions, the hydrogen separation efficiency and stability of the Pd-based composite membrane could be improved continuously. The methane conversion and the operating temperature are not enough to characterize the performance of the membrane reactor.

Therefore, research interest has been focused on improving the stability of a thin Pd membrane on a ceramic substrate, preparing a much thinner defect-free Pd membrane on an MPSS substrate with marked roughness and large surface pore entrance,[30-37] and performing the steam reforming reaction in this improved catalytic membrane reactor. In the present work, an MPSS (macroporous stainless steel) tube filter was employed as the substrate. The MPSS substrate can solve problems such as the mechanical and/or thermal stability, the high-temperature sealing, and the compartment construction resulting from the ceramic substrate. However, it is very difficult to prepare a defect-free thin Pd membrane of less than 15 μm, due its marked roughness and large surface pore entrance. Here, on the basis of our newly developed multidimensional plating mechanism,[37] a thin (6 μm) defect-free Pd membrane was prepared on an MPSS tube filter. After the higher hydrogen permeance and complete hydrogen selectivity were ensured, the as-synthesized thin membrane was used to construct a catalytic membrane reactor for the steam reforming of methane. The methane conversion in this membrane reactor was studied in detail under different operating conditions, which were compared with some experimental and prediction results appearing in the literature. Moreover, two new factors of the hydrogen extraction ratio and the hydrogen production rate under different operating conditions were studied to characterize the performance of the membrane reactor.

2. Experimental Section

2.1. Membrane Preparation. An MPSS tube filter having a nominal particle retention size of 0.5 μm was purchased from Mott Metallurgical Co. The effective length, outside diameter, and inside diameter are 7.0
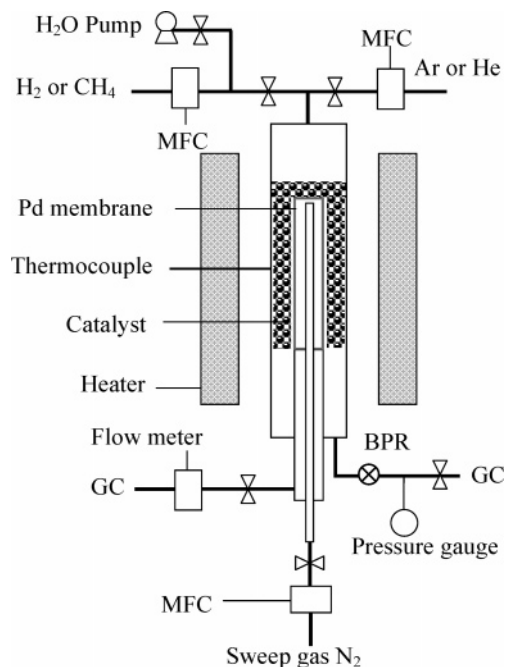
Figure 2. Schematic of gas permeation cell or CH_4 steam reforming membrane reactor.

Figure 3. H_2 permeation flux of thin Pd/MPSS composite membrane versus H_2 pressure difference (temperature, 500 °C).

$\times 10^{-2}$, 9.5×10^{-3}, and 7.0×10^{-3} m, respectively. One end of this MPSS tube was closed, and the other end was welded to a dense stainless tube with the same diameter. After it was cleaned in an ultrasonic bath with dilute alkali, dilute acid, deionized water, and ethanol (in that order), the tube was submitted to the Pd membrane preparation through a multidimensional plating mechanism using commercially available activating solution (OPC-50 inducer and OPC-150 cryster) and plating solution (PALLA TOP) from Okuno Chemical Industries Co., Ltd. A Pd/MPSS membrane having a thickness of 6 μm and effective area of 2×10^{-3} m^2 was prepared in this experiment. The detailed procedure was shown in a previous paper.[37]

2.2. Hydrogen Permeation and Reaction Test. The schematic of the permeation and reaction system at high temperature is shown in Figure 2. The membrane tube was located inside an outer dense stainless steel tube with an inside diameter of 1.7×10^{-2} m to form an annulus reaction chamber (retentate side or reaction side). The volume inside the membrane tube was the permeation chamber (permeation side or sweep side). Inside the permeation chamber, another dense stainless steel tube with an outside diameter of 1.0×10^{-3} m was located near the closed end of the membrane tube for the introduction of sweep gas (N_2). A thermocouple was placed in the middle of the membrane tube for controlling and measuring the operating temperature. All the gases coming into the system were controlled by a mass flow controller, and the exit gases were measured by a data flow meter and analyzed by GC. Connecting with the retentate chamber, a back-pressure regulator was used to control the pressure in the reaction side. For gas permeation experiments, pure hydrogen, pure argon, or pure helium was fed into the catalyst-free retentate side. The permeation flux of hydrogen and the leak of argon or helium through the as-synthesized thin Pd membrane were measured at different pressure differences and different temperatures by the single gas method. For the membrane reactor, the Ni−Al$_2$O$_3$ reforming catalyst (Osaka Gas
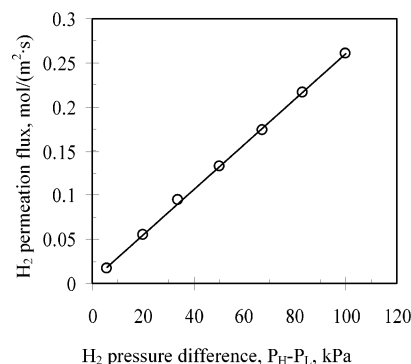
Co., Osaka, Japan) was packed into the reaction chamber. The mixture of methane and water after it was preheated and mixed well was introduced into the reaction side of the membrane reactor. Inside the permeation chamber, a sweep gas of nitrogen was used to remove the permeated hydrogen. The traditional reactor was constructed by simple replacement of the inner membrane tube with a dense stainless steel tube having the same configuration as the membrane tube.

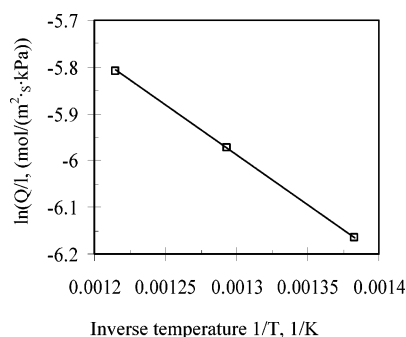## 3. Results and Discussion

3.1. Hydrogen Permeation Behavior. The hydrogen permeation behavior under different hydrogen partial pressure differences and different temperatures were measured by using the single gas method while atmospheric pressure was maintained in the permeation chamber. The hydrogen permeation flux versus the pressure difference at 500 °C is shown in Figure 3, which reveals that the hydrogen permeation flux is proportional to the hydrogen partial pressure difference ($P_H - P_L$, in kPa). The exponent value of the hydrogen partial pressure is about 1, which greatly deviates from Sievert's law (the exponent value is 0.5 for Sievert's law). This means that the hydrogen permeation process is perhaps controlled by the surface reaction rather than bulk diffusion, due to the much thinner Pd layer of this composite membrane. It can also be seen that not only was an increasing hydrogen permeation flux with the increasing hydrogen partial pressure difference observed but also a high hydrogen permeation flux of 0.260 mol/(m^2 s) was obtained at an operating temperature of 500 °C and a hydrogen partial pressure difference of 100 kPa. In addition, the argon or helium flux was measured before and after the hydrogen permeation test at 500 °C and a pressure difference of 300 kPa. The argon or helium permeation flux is about 0 under these operating conditions, which indicates that the separation factor between hydrogen and argon is infinitely high within the measurement range of our experiments. Comparison with some experimental results published in the literature was made, and the results are shown in Table 1. From this table it can be easily seen that the separation efficiency of the as-prepared Pd/MPSS membrane is relatively better.

Moreover, the temperature effect to the hydrogen permeation behavior is shown in Figure 4. From this Arrhenius plot, it can be seen that the linearity of the curve is very good, which reveals that the apparent activation energy for the hydrogen permeation process through the Pd/MPSS composite membrane remains unchanged within the experimental temperature and

Table 1. Hydrogen Separation Efficiency of Pd-Based Membranes[a]

| membrane	prepn method	thickness, μm	temp, °C	driving force, kPa	H_2 flux, mol/(m² s)	sepn factor, H_2/N_2
Pd/MPSS[30]	ELP/O	10	480	100	0.089	1000
Pd/MPSS[31]	ELP	19−28	500	101	0.015−0.030	≤5000
Pd/MPSS[32]	ELP	5	400	100	0.155	100−200
Pd/PG[20]	ELP	13	500	202	0.189	∞
Pd/Al$_2$O$_3$[32]	ELP	7−15	400	100	0.086−0.134	100−1000
Pd/HF[33]	ELP	3−4	430	100	0.136	1000
Pd/Al$_2$O$_3$[34]	CVD	0.5−1.0	350−450	100	0.050−0.100	100−1000
Pd−Ag/PG[20]	ELP	21.6	400	202	0.067	∞
Pd−Ag/MPSS[35]	ELP	15	500	202	0.103	∞ (H$_2$/Ar)
Pd−Cu/Al$_2$O$_3$[36]	ELP/O	3.5	350	100	0.056	≥7000
Pd−Cu/Al$_2$O$_3$[36]	ELP/O	1.5	350	100	0.499	93
Pd−Ag[22]	cold rolling	50	500	100	0.01	∞
this work	MD-ELP	6	500	100	0.260	∞ (H$_2$/Ar, He)
this work	MD-ELP	6	550	100	0.300	∞ (H$_2$/Ar, He)

[a] Legend: MPSS, macroporous stainless steel; HF, alumina hollow fiber; PG, porous glass; ELP, electroless plating; O, osmotic pressure method; MD, multidimensional plating mechanism.

Figure 4. Arrhenius plot for the Pd/MPSS composite membrane.

Figure 5. Methane conversion versus operating temperature (catalyst amount, 15 g; H$_2$O/CH$_4$ = 3; SV, 400 mL/(g h); pressure, 300 kPa; sweep gas, 500 mL/min).

pressure range. An exact activation energy of 16.7 kJ/mol was calculated from this figure, which is higher than those (10−12 kJ/mol) obtained from Pd/porous ceramic substrate composite membranes.[20,32] The higher activation energy can be ascribed to the surface reaction controlling the hydrogen permeation mechanism rather than a bulk diffusion mechanism, as some other researcher found for their much thinner Pd membranes.[33−34]

3.2. Membrane Reactor. After hydrogen permeation experiments, the system was slowly decreased to room temperature under argon (reaction chamber) and nitrogen (permeation chamber) atmospheres. Continuously, the 15 g of Ni/Al$_2$O$_3$ catalyst was packed into the reaction chamber. As illustrated in Figure 2, the catalyst not only was packed into the annulus volume between the membrane tube and the outer dense stainless steel tube but also was packed at the top of the closed end of the membrane tube, whose bed height was controlled to 1×10^{-2} m. The purpose of this design is to effectively use the membrane and to avoid carbon deposition on the catalyst or the membrane. The temperature of the reactor was slowly increased to 500 °C under argon and nitrogen atmospheres in the reaction chamber and permeation chamber, respectively. Then a mixture of 50 mol % hydrogen and 50 mol % nitrogen was introduced into the reaction chamber for 1 h to activate the Ni/Al$_2$O$_3$ catalyst. After that, a mixture of steam and methane was put on line and the reaction was carried out under different operating parameters.

3.2.1. Effect of Operating Parameters on Methane Conversion. (a) Effect of Operating Temperature. The influence of the operating temperature on the methane conversion is shown in Figure 5, which gives a detailed comparison between the membrane reactor and the traditional reactor at different operating
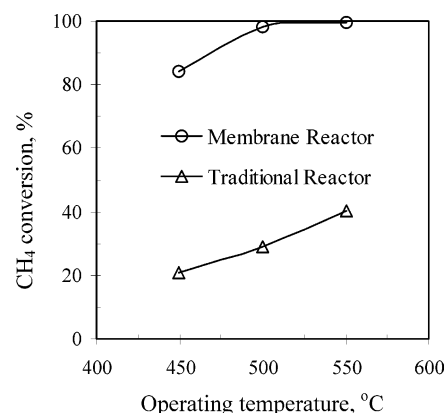
temperatures. It can be seen that the methane conversions in both reactors increase rapidly with an increase of the operating temperature. However, the difference in methane conversions between the membrane reactor and the traditional reactor is large at the same operating temperature. For example, methane conversion in the membrane reactor is 2.5−4 times that in the traditional reactor. Moreover, an almost complete methane conversion (98%) was achieved at the lower operating temperature of 500 °C. The greatly enhanced methane conversion in the membrane reactor is a result of the reaction equilibrium shift due to the in situ removal of hydrogen from the reaction location. A higher operating temperature corresponds to a higher hydrogen permeability of the thin Pd composite membrane, which directly determines the higher hydrogen removal ratio. At the same time, an increase of the operating temperature can also in some degree increase the methane conversion, as it does in the traditional reactor due to the increase of the equilibrium constant. This positive effect of the operating temperature on methane conversion is similar to some published experimental results.[6,7,22,27]

(b) Effect of Operating Pressure. The influence of the operating pressure in the reaction chamber on methane conversion is shown in Figure 6, which provides a comparison between the traditional reactor and the membrane reactor at different operating pressures. As expected, in the traditional reactor, the methane conversion decreases with an increase of the operating pressure. This change trend is in agreement with the limitations of the thermodynamic equilibrium, because
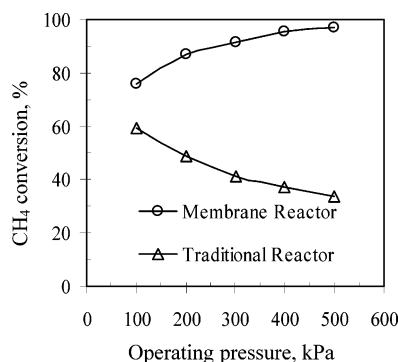
Figure 6. Methane conversion versus operating pressure (catalyst amount, 15 g; $H_2O/CH_4 = 3$; SV, 800 mL/(g h); temperature, 550 °C; sweep gas, 500 mL/min).

Figure 7. Methane conversion versus operating pressure combined with space velocity (catalyst amount, 15 g; $H_2O/CH_4 = 3$; temperature, 500 °C; sweep gas, 500 mL/min).

the steam reforming reaction is a volume expanded process. In contrast, methane conversion in the membrane reactor increases rapidly with an increase of the operating pressure in the reaction chamber. Moreover, it can be seen that a methane conversion of higher than 97% can be obtained when the operating pressure is higher than 500 kPa (temperature, 550 °C; space velocity, 800 mL/(g h); $H_2O/CH_4 = 3$; sweep gas, 500 mL/min). According to experimental results and model predictions in the literature, the effect of the operating pressure on methane conversion is a complex function.[6,7,21−29] The final net effect of the operating pressure on the methane conversion consists of a negative effect on the thermodynamic equilibrium limitations due to increasing volume at the higher operating pressure and a positive effect on the increasing hydrogen removal ratio at the higher operating pressure. The cooperative effect of the operating pressure is related to the operating temperature, the space velocity of feed, the membrane performance (hydrogen permeance and effective permeation area), etc. Due to the different operating parameters and the membrane performance, different experimental results were reported. For example, Shu et al.[7] and Lin et al.[27] found experimentally a decrease of the methane conversion with an increase in operating pressure under their experimental conditions in their Pd or Pd−Ag/MPSS membrane reactors. However, Oklany,[26] Shu,[7] Prokopiev,[23] and Gallucci[28] together with their co-workers found an increasing trend of the methane conversion with an increase of the operating pressure by using some mathematical models for dense Pd-based membrane reactors. Moreover, the simulation predictions of Gallucci et al.[28] indicated that there may exist a minimum value of methane conversion that depends on the operating parameters and the membrane performance (membrane length, membrane thickness, etc.). In fact, Uemiya et al.,[6] using a tubular hydrogen-permeable membrane reactor, found experimentally an increase of the methane conversion with an increase of the operating pressure under their reaction conditions, which is consistent with our results. In our practical membrane reactor, the membrane performance has been designated beforehand. Here, the synergetic effect of some other operating parameters such as the space velocity of feed and the operating temperature were continuously investigated in detail.

The synergetic effect of the space velocity of feed together with the operating pressure on the methane conversion is shown in Figure 7. It can be seen that the change trends of the methane conversion with an increas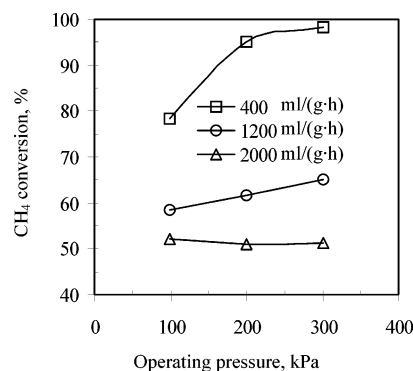e of the operating pressure are different for different space velocities. For the lower space velocity of 400 mL/(g h), the obvious increase trend with increasing pressure is found. When the space velocity is increased to 1200 mL/(g h), the methane conversion still increases with increasing pressure. However, the increase rate is slower than that of the lower space velocity of 400 mL/(g h). For the highest space velocity in our experiments of 2000 mL/(g h), we cannot find the increase trend when the operating pressure is increased from 100 to 200 or 300 kPa. In addition, the methane conversion, when the operating pressure is controlled to be 200 kPa, is slightly lower than the values under the other two operating pressures (100 and 300 kPa). Shu et al.,[7] Gallucci et al.,[28] and Oklany et al.[26] developed several math models for steam reforming of methane in hydrogen-permeable membrane reactors. They calculated the equilibrium conversion of methane in the membrane reactor versus the operating pressure. The increase trend of the equilibrium conversion of methane was obtained on the basis of the complete membrane separation efficiency by assuming that the effective area or length of the membrane or the hydrogen permeance is immense. When the effective area of the membrane is large enough, the membrane reactor can arrive at an equilibrium state. Both the reaction chemical potential and the permeation chemical potential (the pressure difference of different exit gas mixtures is zero) should be zero. For our membrane reactor, when the space velocity is small, the original hydrogen in the feed system is also small. Thus, the membrane effective area is relatively larger, in comparison with the lower hydrogen content on the feed side. (The maximum hydrogen content is 4 times the methane molar amount by assuming the complete conversion of methane to carbon dioxide and hydrogen). The experimental conversion at the lower space velocity is near the equilibrium conversion in our membrane reactor. The increase trend of methane conversion with an increase in the operating pressure is reasonable. With a continuous increase of the space velocity and the corresponding hydrogen content in the reaction chamber, the separation efficiency of the membrane is relatively lower. According to the model prediction by Gallucci et al.,[28] when the effective area of the membrane (separation efficiency) is limited, a minimum value of the methane conversion should emerge with an increase of the operating pressure. Indeed, our experimental results of the highest space velocity of 2000 mL/(g h) is consistent with their model prediction, from which emerged a minimum value of the methane conversion at an operating pressure of 200 kPa.
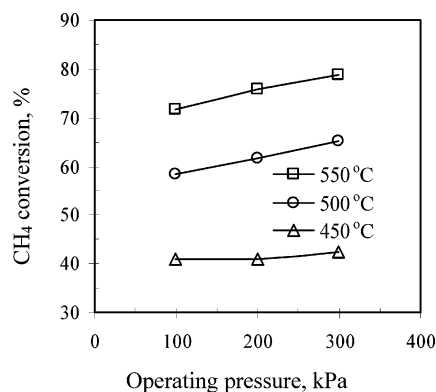
Figure 8. Methane conversion versus operating pressure combined with operating temperature (catalyst amount, 15 g; H_2O/CH_4 = 3; SV, 1200 mL/(g h); sweep gas, 500 mL/min).

Figure 9. Methane conversion versus space velocity (catalyst amount, 15 g; H_2O/CH_4 = 3; temperature, 500 °C; pressure, 300 kPa; sweep gas, 500 mL/min).

The synergetic effect of the operating temperature together with the operating pressure on the methane conversion is shown in Figure 8. It can be seen that the change trends of the methane conversion with an increase of the operating pressure are different at different operating temperatures. At a higher operating temperature, 550 °C for example, the methane conversion increases rapidly with an increase of the operating pressure. In contrast, at a lower operating temperature, 450 °C for example, there emerges a minimum value of the methane conversion at an operating pressure of 200 kPa. It is known that the hydrogen permeability of the membrane increases rapidly with an increase of the operating temperature, which is shown in the measurement results of the hydrogen permeation behavior in Figures 3 and 4. When the membrane reactor is reacted at higher temperatures, the separation efficiency of the membrane based on the other unchanged operating parameters such as space velocity, steam-to-methane ratio, and sweep gas flux is relatively high. Thus, the experimental methane conversion is near the equilibrium methane conversion of the membrane reactor and increases with an increase of the operating pressure. In contrast, when the membrane reactor is operated at lower temperatures, the separation efficiency of the membrane based on the other unchanged operating parameters such as space velocity, steam-to-methane ratio, and sweep gas flux is far from the equilibrium state of the membrane reactor. As predicted by Gallucci et al.,[28] there should also exist a minimum value of the methane conversion with an increase of the operating pressure.

(c) Effect of Space Velocity. The influence of the space velocity of the feed on methane conversion is shown in Figure 9, which provides a comparison between the traditional reactor and the membrane reactor at different space velocities of the feed. As expected, the methane conversion in the traditional reactor remains unchanged with an increase of the space velocity. It is known that the equilibrium methane conversion of the traditional reactor is determined by the operating temperature, the operating pressure, and the steam-to-methane ratio. It is independent of the space velocity when the activity of the catalyst is high enough. However, a rapid decrease of the methane conversion with an increase of the space velocity is found for the membrane reactor. For example, the methane conversion decreases from 98.2% to 51.3% with an increase of the space velocity from 400 to 2000 mL/(g h). Though a decreasing trend was found, the methane conversion of
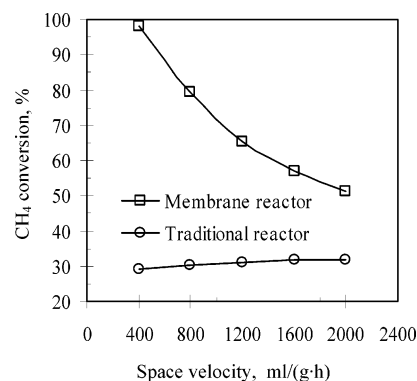
the membrane reactor is still much higher than that of the traditional reactor. For example, the lowest methane conversion of 51.3% for the space velocity of 2000 mL/(g h) for the membrane reactor is still higher than the methane conversion of 31.9% for the traditional reactor. As for the space velocity effect on methane conversion in hydrogen-permeable reactors, there have also been some experimental studies and math model predictions in the literature. For example, Kikuchi[9] found the same decrease trend of methane conversion with an increase of feed rate of town gas (operating temperature, 550 °C; operating pressure, 620 kPa; steam-to-carbon ratio, 2.4). Moreover, the lowest methane conversion of his report was also higher than that of the equilibrium conversion of the traditional reactor. Lin et al.[27] predicted the effect of the weight hourly space velocity to the methane conversion by a simulation calculation. The results predicted that the methane conversion would decrease gradually with an increase of the weight hourly space velocity. At the two extremes of the highest and the lowest weight hourly space velocity, the methane conversion of the membrane reactor has approached the equilibrium conversion of the traditional reactor and the equilibrium conversion of the membrane reactor, respectively. Therefore, the change trend of the methane conversion in our membrane reactor is analogous to some published experimental and model predicted results. In fact, a catalyst with higher activity was used in most membrane reactors and the steam reforming reaction kinetics was assumed to be much faster than the hydrogen permeation rate. Therefore, the reaction in the membrane reactor was thought to be under a continuous reaction equilibrium through the length of the membrane reactor after the removal of hydrogen, which is similar to the description in Figure 1. The lower hydrogen removal ratio is related to the lower methane conversion. In the continuous study, we have found a decreasing trend of hydrogen extraction ratio with an increase of the space velocity.

(d) Effect of Steam-to-Methane Ratio. Steam reforming of methane usually proceeds in the presence of an excess of steam to prevent carbon deposition over the catalyst surface and to enhance methane conversion. The influence of the steam-to-methane ratio on methane conversion is shown in Figure 10, which provides a comparison between the traditional reactor and the membrane reactor at different steam-to-methane ratios. The methane conversion in the traditional reactor exhibits a monotonic increase with an increase of the steam-to-methane ratio. This is in agreement with thermodynamic equilibrium calculations. In the mem-
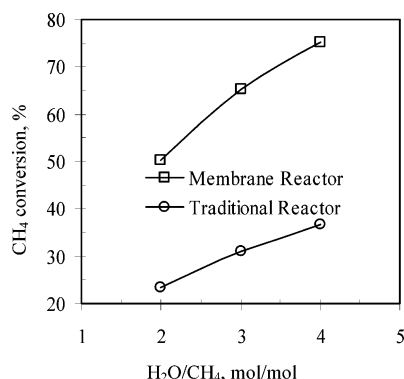
Figure 10. Methane conversion versus steam-to-methane ratio (catalyst amount, 15 g; SV, 1200 mL/(g h); temperature, 500 °C; pressure, 300 kPa; sweep gas, 500 mL/min).

Figure 11. Methane conversion versus sweep gas flux (catalyst amount, 15 g; $H_2O/CH_4 = 3$; temperature, 500 °C; pressure, 300 kPa).

brane reactor, the same monotonic increase trend is also found in the range of our experiments (ratios of 2−4). Moreover, the methane conversion in the membrane reactor is much higher than that in the traditional reactor. For example, at the same steam-to-methane ratio of 4, the methane conversion in the membrane reactor is about 75.2%, which is much higher than the value of 36.7% in the traditional reactor under the same operating conditions. Shu et al.[7] gave a detailed study of the effects of the steam-to-methane ratio on methane conversion by using Pd/SS- and Pd−Ag/SS-based membrane reactors. The same increase trend of the methane conversion with an increase of the steam-to-methane ratio was reported in their experimental results. Aasberg Petersen et al.[25] gave a simulation prediction on the effect of steam-to-methane ratio. They found that too great an excess of steam would dilute the hydrogen in the reaction mixture, which could result in a decrease of the hydrogen partial pressure difference between the reaction chamber and the permeation chamber. This continuously resulted in a decrease of the membrane separation efficiency. Therefore, not only the energy savings but also the membrane reactor performance do not permit a much higher steam-to-methane ratio. Moreover, according to the report of Jørgensen et al.,[24] a steam-to-methane ratio higher than 2.5 was enough to avoid carbon deposition on the reforming catalyst while operating in the membrane reactor mode. Indeed, for most of our membrane reactor experiments, the steam-to-methane ratio was controlled to be 3. No deactivation of catalyst and membrane was found during the whole operating process.

(e) Effect of Sweep Gas Flux (N_2). Introducing sweep gas into the permeation chamber is an effective method of maintaining or increasing the hydrogen partial pressure difference between the two sides of the membrane and moving out hydrogen product from the reaction system. The different hydrogen partial pressure driving forces resulted from the different sweep gas fluxes having a huge effect on the methane conversions in the membrane reactor mode. The experimental results of the effect of the sweep gas flux on the methane conversion for the membrane reactor are shown in Figure 11. It can be seen that the methane conversion for the membrane reactor increases rapidly with an increase of the sweep gas (N_2) flux at the beginning. The value is much higher than the value of 29.1% obtained in the traditional reactor. For example, the lowest methane conversion of 77.7% corresponding with the lowest sweep gas flux of 100 mL/min for the membrane reactor is still much higher than the methane conver-
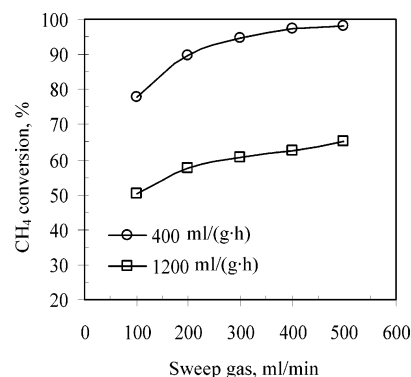
sion value of 29.1% for the traditional reactor. However, it should also be noted that, for a sweep gas flux higher than 300 mL/min, the methane conversion of the membrane reactor levels off with a continuous increase of the sweep gas flux. Moreover, the curve of the methane conversion of the membrane reactor at the higher space velocity of 1200 mL/(g h) is also shown in the same figure. It can be seen that the same change trend of the methane conversion is found with an increase of the sweep gas flux at this higher space velocity of 1200 mL/(g h). Most of the published experimental and model works deal with the effect of the sweep gas. Uemiya et al.,[6] Shu et al.,[7] Oklany et al.,[26] Lin et al.,[27] and Gallucci et al.[28] found the increase trend of the methane conversion of the membrane reactor with an increase of the sweep gas flux in their experimental results or model predictions. Their prediction is that the methane conversion continues to increase gradually with an increase of the sweep gas flux. In fact, the experimental methane conversion at a sweep gas flux higher than 140 mL/min also has leveled off, according to the report of Shu et al.[7] This means that a continuous increase of the sweep gas flux will play a minor role in enhancing the methane conversion. Shu et al. ascribed the flattening effect of the higher sweep gas flux on the methane conversion to the operating temperature difference. On the other hand, Dittmeyer et al.[32] studied the effect of the sweep gas flux on the hydrogen permeation flux in detail. They found that for a higher sweep gas flux no real improvement of the hydrogen permeation flux is observed, even at higher retentate pressure (i.e. high hydrogen feed flux), although the hydrogen partial pressure on the permeation side decreases substantially with an increasing sweep gas flux. Thus, the flattening hydrogen permeation flux with a continuous increase in the sweep gas flux is perhaps another reason the flattening methane conversion was found with increasing sweep gas flux.

(f) Comparison with Other Membrane Reactors. The methane conversion in our thin Pd/MPSS-based membrane reactor was compared with that in some other membrane reactors published in the literature. The comparison results are shown in Table 2. It can be easily seen that all of the listed methane conversions in the membrane reactors are higher than the equilibrium methane conversions in traditional reactors under the same operating temperatures, pressures, and steam-to-methane ratios. Also, the methane conversion has a close relationship to the membrane properties and the operating parameters. A change of factors such as increasing membrane area, decreasing membrane thick-

Table 2. Methane Conversion in Different Membrane Reactors[a]

membrane	membrane properties	operating conditions	methane conversn, %
Pd/PG[6]	ELP, $\delta = 20$ μm, A = 25.1 cm^2	T = 500 °C, P = 100 kPa, Ni/Al$_2$O$_3$ 13 g, CH$_4$ 25 mL/min, S/C = 3.0, SG(Ar) 400 mL/min	88
Pd/MPSS[7]	ELP, $\delta = 19.8$ μm, A = 10.7 cm^2	T = 500 °C, P = 136 kPa, Ni/Al$_2$O$_3$ 11 g, CH$_4$ 40 mL/min, S/C = 3.0, vacuum pumping	63
Pd−Ag/MPSS [7]	ELP, $\delta = 10.3$ μm, A = 10.7 cm^2	T = 500 °C, P = 136 kPa, Ni/Al$_2$O$_3$ 11 g, CH$_4$ 40 mL/min, S/C = 3.0, SG(He) = 40 mL/min	51
Pd−Ag[22]	cold rolling, $\delta = 50$ μm, A = 46.1 cm^2	T = 450 °C, P = 122 kPa, Ni/Al$_2$O$_3$ 3.1 g, CH$_4$ 7.29−17.80 mL/min, S/C = 3.0, SG(O$_2$) = 49 mL/min	70
Pd/MPSS[21]	ELP, $\delta = 20-25$ μm, A = 70 cm^2	T = 500 °C, P = 300−600 kPa, G56H, SV = 1600 L/h, S/C = 3.0, SG = 0 mL/min	~45
Pd/porous Inconel disk[38]	ELP, $\delta = 70-100$ μm, A = 5.0 cm^2	T = 750 °C, P = 2200 kPa, Ni/Al$_2$O$_3$, S/C = 2.2, SG = 0 mL/min	55
Pd or Pd−Ag/Al$_2$O$_3$[39]	ELP, $\delta = 5.2-22.5$ μm, A = 12.6 cm^2	T = 500 °C, P = 100 kPa, Ni/Al$_2$O$_3$, SV = 672 mL/(g h)	60−80
this work	MD-ELP, $\delta = 6$ μm, A = 20 cm^2	T = 450 °C, P = 300 kPa, Ni/Al$_2$O$_3$ 15 g, CH$_4$ 25 mL/min, S/C = 3.0, SG = 500 mL/min	84
this work	MD-ELP, $\delta = 6$ μm, A = 20 cm^2	T = 500 °C, P = 300 kPa, Ni/Al$_2$O$_3$ 15 g, CH$_4$ 25 mL/min, S/C = 3.0, SG = 500 mL/min	98
this work	MD-ELP, $\delta = 6$ μm, A = 20 cm^2	T = 550 °C, P = 500 kPa, Ni/Al$_2$O$_3$ = 15 g, CH$_4$ = 50 mL/min, S/C = 3.0, SG = 500 mL/min	97

[a] Legend: MPSS, macroporous stainless steel; PG, porous glass; ELP, electroless plating; MD, multidimensional plating mechanism.

ness, increasing operating temperature, decreasing space velocity, and increasing sweep gas flux is related to higher methane conversion. The operating pressure has complicated effects on methane conversion. Depending on the different membrane properties and different operating parameters, it can have a positive or a negative effect on the methane conversion. However, it is obvious that the methane conversion in this work is much higher than the other results. The better results can be ascribed to the better hydrogen separation performance, which has been shown in Table 1, and the proper operating parameters, which have been discussed above.

3.2.2. Hydrogen Extraction Ratio. The main purpose of steam reforming of methane is to produce pure hydrogen. To decrease the operating temperature without impairing the methane conversion, a hydrogen-permeable membrane reactor was used in the literature and in the present work. Methane conversion is a commonly studied performance factor of steam reforming of methane in a hydrogen-permeable membrane reactor. Moreover, the hydrogen extraction ratio is defined as the ratio between the permeated hydrogen and theoretical hydrogen content, which is 4 times the methane molar amount by assuming the complete conversion of methane to carbon dioxide and hydrogen. The effects of different operating parameters such as temperature, pressure, space velocity, steam-to-methane ratio, and sweep gas flux on the hydrogen extraction ratio were experimentally studied, and the results are shown in parts a−e of Figure 12, respectively. From Figure 12a it can be seen that an increase in the operating temperature can result in an increase of the hydrogen extraction ratio. At an operating temperature of 500 °C, the hydrogen on the reaction side can be almost completely extracted (the extraction ratio is higher than 96.6%). It is well-known that the hydrogen permeance increases with the operating temperature. Therefore, the hydrogen separation efficiency increases with an increase of the operating temperature, while other operating conditions such as pressure, space velocity, steam-to-methane ratio, and sweep gas flux remain unchanged. Moreover, an increase of the hydrogen extraction ratio with temperature is consistent with the aforementioned increasing trend of the methane

conversion with the operating temperature. From Figure 12b it can be seen that the hydrogen extraction ratio increases gradually with an increase of the operating pressure. At a higher operating pressure of 300 kPa, a hydrogen extraction ratio of 84.5% can be achieved while the other operating conditions such temperature, space velocity, steam-to-methane ratio, and sweep gas flux are kept unchanged. In comparison with the complex effect of the operating pressure on methane conversion, the effect of the operating pressure on the hydrogen extraction ratio is a monotonically increasing function of the operating pressure. The monotonic increase trend is consistent with the monotonic increase of the hydrogen partial pressure driving force with an increase of the operating pressure. From Figure 12c it can be seen that the hydrogen extraction ratio decreases gradually with an increase of the space velocity. For the highest space velocity of 2000 mL/(g h), the lowest hydrogen extraction ratio of 31.5% was obtained in our experiments. With an increase of the space velocity, the potential hydrogen maximum in the feed mixture of methane and steam increases rapidly while the hydrogen separation efficiency remains unchanged, due to the other unchanged operating parameters such as temperature, pressure, steam-to-methane ratio, and sweep gas flux. Many other researchers have investigated the effect of space velocity on methane conversion. All the results showed that the methane conversion decreased with an increase of the space velocity in their membrane reactors. The reason the methane conversion decreased with an increase of space velocity was ascribed to the decrease of the removal ratio of hydrogen from the membrane system with an increase of the space velocity. In fact, a catalyst with higher activity was used in most membrane reactors and the steam reforming reaction kinetics was assumed to be much faster than the hydrogen permeation rate. Therefore, the reaction in the membrane reactor was thought to be in the new reaction equilibrium after hydrogen removal, which is similar to the description in in Figure 1. The lower hydrogen removal ratio is related to the lower methane conversion. On the other hand, the lower methane conversion is related to lower methane conversion. Here, the removal ratio has the same definition as the hydrogen extraction ratio. Moreover, Li et al.[30] studied the effect of mixture feed
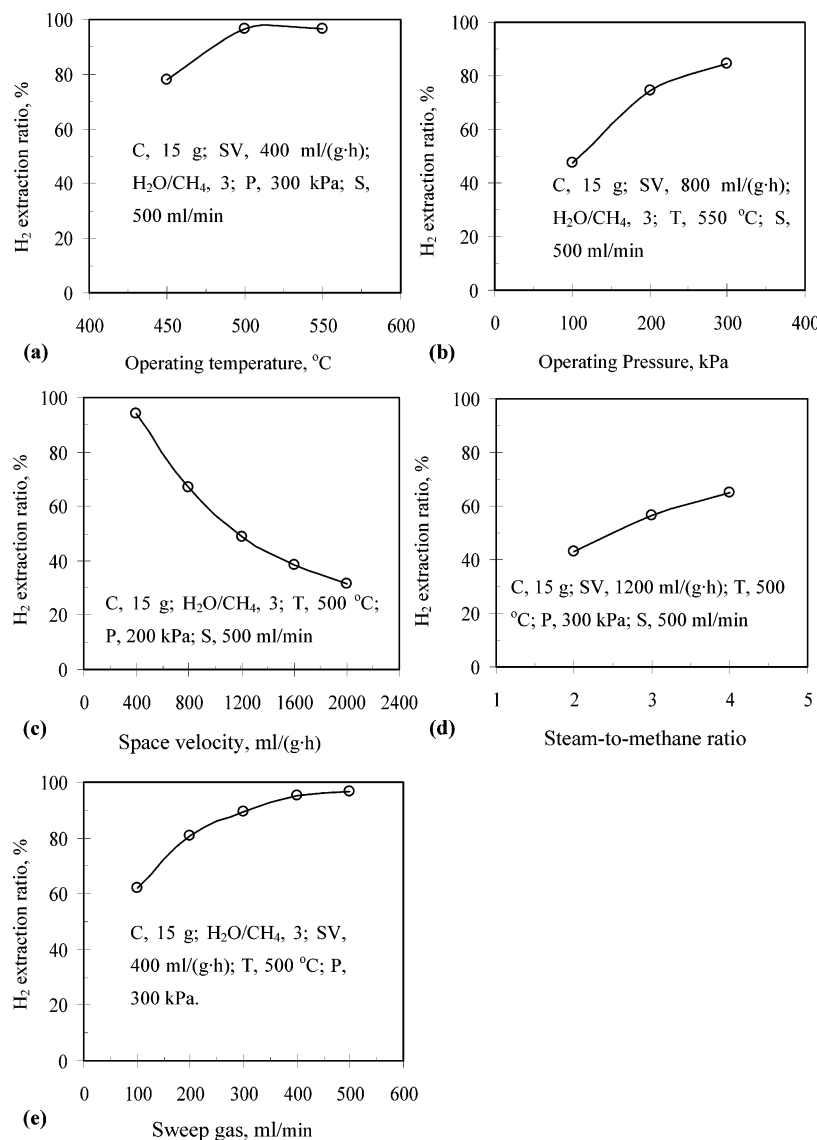
Figure 12. Hydrogen extraction ratio versus the operating parameters (a) operating temperature, (b) operating pressure, (c) space velocity, (d) steam-to-methane ratio, and (e) sweep gas flux (C, catalyst amount; SV, space velocity; H_2O/CH_4, steam-to-methane ratio; T, operating temperature; P, operating pressure; S, sweep gas (N_2) flux).

flux on the hydrogen permeation flux in their Pd/MPSS-based permeation cell. From their data an analogous ratio between permeate hydrogen and the original hydrogen content can be calculated and the results show that an analogous ratio also decreases with an increase of the mixture feed flux. This is similar to our results. From Figure 12d it can be seen that the hydrogen extraction ratio increases gradually with an increase of the steam-to-methane ratio. With the increase of the steam-to-methane ratio, the feed mixture is diluted and the steam amount increases. By the prediction of Aasberg Petersen et al.,[25] the hydrogen partial pressure driving force decreases with an increase of the steam-to-methane ratio. Thus, the resulting hydrogen separation efficiency also decreased with an increase of the steam-to-methane ratio. According to this, the hydrogen extraction ratio should decrease with an increase of the steam-to-methane ratio. However, another factor we should note is that the original hydrogen-containing amount in the feed mixture decreases rapidly with an increase of the steam-to-methane ratio. Overall, the net effect of the increase of the steam-to-methane ratio to the hydrogen extraction ratio is positive under our

experimental conditions for our membrane reactor. From Figure 12e it can be seen that the hydrogen extraction ratio increases gradually with an increase of the sweep gas flux at the beginning. When the sweep gas flux is higher than 300 mL/min, the hydrogen extraction ratio levels off with the continuous increase of the sweep gas flux. This trend is also consistent with the change trend of the methane conversion with the sweep gas flux. The change trend can be simply ascribed to the effect of the sweep gas flux on the hydrogen separation efficiency of the membrane reactor while the other operating conditions such as temperature, pressure, space velocity, and steam-to-methane ratio remain unchanged.

The hydrogen extraction ratio has a close relationship to the methane conversion in the membrane reactor. In the normal case, a higher hydrogen extraction ratio (removal ratio) corresponds to a higher methane conversion in the membrane reactor. However, in some cases, the effects of operating parameters on the hydrogen extraction ratio and the methane conversion are different. For example, the operating pressure has a complicated effect on the methane conversion rather than the
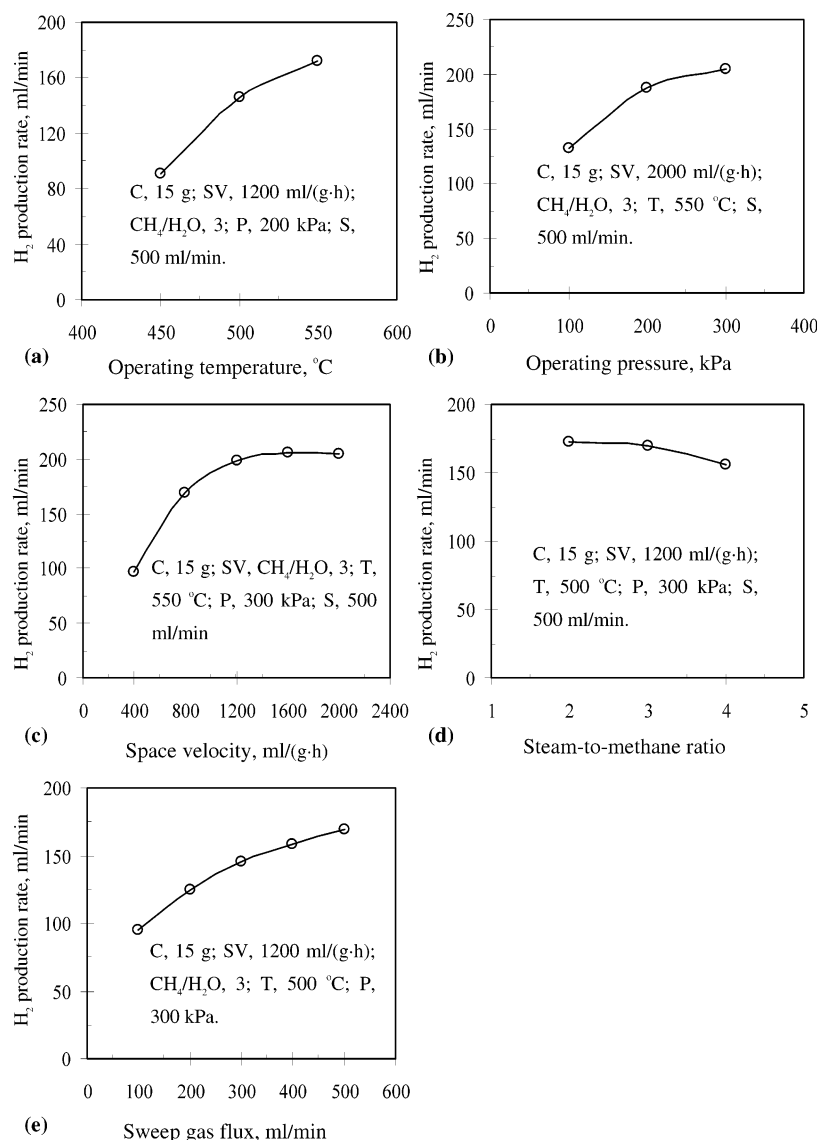
Figure 13. Hydrogen production rate versus the operating parameters (a) operating temperature, (b) operating pressure, (c) space velocity, (d) steam-to-methane ratio, and (e) sweep gas flux (C, catalyst amount; SV, space velocity; H_2O/CH_4, steam-to-methane ratio; T, operating temperature; P, operating pressure; S, sweep gas (N_2) flux).

monotonic effect on the hydrogen extraction ratio. Moreover, the steam-to-methane ratio has a complicated effect on the hydrogen extraction ratio.

3.2.3. Hydrogen Production Flux. Apart from the methane conversion and the hydrogen extraction ratio, the hydrogen production rate is another factor in evaluating the performance of the membrane reactor for steam reforming of methane in the hydrogen-permeable membrane reactor. In the present work, the effect of operating parameters on the hydrogen production rate was also studied experimentally. The hydrogen production rate from analysis of the gas mixture in the permeation side versus operating parameters such as temperature, pressure, space velocity, steam-to-methane ratio, and sweep gas flux is shown in parts a–e of Figure 13, respectively. From Figure 13a it can be seen that the hydrogen production rate increases rapidly with an increase of the operating temperature. For example, the increase of the operating temperature from 450 to 550 °C corresponds to about a doubling of the hydrogen production rate from 90.8 to 171.6 mL/min. This trend is consistent with the change trend of the methane conversion and the hydrogen extraction ratio with an

increase of the operating temperature. All the increase trends of these three performance factors can be attributed to an increase of the hydrogen separation efficiency and an increase of thermodynamic equilibrium in concert with an increase of the operating temperature. From Figure 13b it can be seen that the hydrogen production rate increases gradually with an increase of the operating pressure. For example, a higher hydrogen production rate of 204.4 mL/min was obtained at the high operating pressure of 300 kPa. The effect of the operating pressure on the hydrogen production rate is different from the case of the methane conversion. The increase trend of the hydrogen production rate with an increase of the operating pressure is monotonic, which is similar to the change trend of the hydrogen extraction ratio with an increase of the operating pressure. This change trend can be simply attributed to an increase of the hydrogen separation efficiency with an increase of the operating pressure. From Figure 13c it can be seen that the hydrogen production rate increases rapidly with an increase of the space velocity at the beginning. With a continuous increase of the space velocity, the hydrogen production

rate levels off gradually. For example, when the space velocity increases from 400 to 1200 mL/(g h), the hydrogen production rate increases rapidly from 96.5 to 197.8 mL/min. However, when the space velocity is continuously increased to 2000 mL/(g h), the hydrogen production rate only increases 3.3%, compared with the original value of 197.8 mL/min for the space velocity of 1200 mL/(g h). This change trend is very different from those of the methane conversion and the hydrogen extraction ratio, which decrease gradually with an increase of the space velocity. The increase trend of the hydrogen production rate can be attributed to the rapid increase of the potential hydrogen amount in the reaction chamber with an increase of the space velocity. Also, the change trend is the synergetic net result of a rapid increase of the hydrogen amount and a slowly decreasing rate of hydrogen extraction ratio. From Figure 13d it can be seen that the hydrogen production rate decreases slowly with an increase of the steam-to-methane ratio. This change trend is also very different from those of the methane conversion and the hydrogen extraction ratio, which increase with an increase of the steam-to-methane ratio. This decrease trend of the hydrogen production rate can be simply attributed to a decrease of the hydrogen separation efficiency resulting from the diluted feed mixture and a decrease of the hydrogen partial pressure driving force with an increase of the steam-to-methane ratio. From Figure 13e it can be seen that the hydrogen production rate increases rapidly with an increase of the sweep gas flux. For example, when the sweep gas flux is increased from 100 to 500 mL/min, the hydrogen production rate increases from 94.8 to 169.7 mL/min rapidly. This change trend is consistent with those of the methane conversion and the hydrogen extraction ratio on an increase of the sweep gas flux. It can be attributed to an increase of the hydrogen separation efficiency due to an increase of the sweep gas flux.

The hydrogen production rate has a close relationship with the other two performance factors of the methane conversion and the hydrogen extraction ratio. In some cases, the higher hydrogen production rate corresponds to a higher methane conversion and a higher hydrogen extraction ratio in the membrane reactor. For example, with an increase of the operating temperature and the sweep gas flux, all three of these performance factors increase gradually. However, in some other cases, the effect of the operating parameters on the hydrogen production rate is very different from that of the other two performance factors. For example, with an increase of the space velocity of the feed both the methane conversion and the hydrogen extraction ratio decrease rapidly. In contrast, the hydrogen production rate increases quickly with an increase of the space velocity.

4. Conclusions

A thin defect-free Pd membrane with a thickness of 6 μm was prepared by using a multidimensional plating mechanism. A higher hydrogen permeation flux of 0.260 mol/(m² s) was achieved at an operating temperature of 500 °C and a hydrogen partial pressure difference of 100 kPa. At the same temperature and pressure difference, the hydrogen selectivity versus argon or helium is complete.

Then the membrane reactor was constructed by packing the Ni$-$Al$_2$O$_3$ catalyst into the annulus volume between the membrane tube and the outer dense stainless steel tube. The effects of operating parameters of temperature, pressure, space velocity, steam-to-methane ratio, and sweep gas flux on the methane conversion, the hydrogen extraction ratio, and the hydrogen production rate were studied in detail. The operating temperature and the sweep gas flux had a positive effect on all three of these performance factors. The operating pressure has a complicated effect on the methane conversion. The synergetic effect of the space velocity and the operating temperature together with the operating pressure was also studied in detail, which showed that the operating pressure would have a positive effect on the methane conversion when the space velocity is low and the operating temperature is high. Otherwise, there might exist a minimum value of the methane conversion with a change in the operating temperature. The operating pressure had a positive effect on both the hydrogen extraction ratio and the hydrogen production rate. The space velocity had a negative effect on the methane conversion and the hydrogen extraction ratio, while it had a positive effect on the hydrogen production rate. The steam-to-methane ratio had a monotonic negative effect on the hydrogen production rate and a monotonic positive effect on the methane conversion. However, it has a complicated effect on the hydrogen extraction ratio. Overall, to achieve better comprehensive operating performance, operating parameters such as temperature, pressure, space velocity, steam-to-methane ratio, and sweep gas flux should be chosen carefully according to the hydrogen separation efficiency of the membrane reactor.

At the same time, a comparison of the membrane reactor performance with the traditional reactor and some published experimental and model prediction results was also done, which showed that superior performance has been achieved by using our membrane reactor, due to the better hydrogen separation efficiency of the thin Pd/MPSS-based composite membrane and the proper operating parameters. For example, a comprehensive result of a methane conversion of 96.9%, a hydrogen extraction ratio of 90.4%, and a hydrogen production flux of 180.8 mL/min was achieved under the properly designed operating conditions (temperature, 550 °C; pressure, 500 kPa; space velocity, 800 mL/(gh); steam-to-methane ratio, 3; sweep gas flux, 500 mL/min).

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