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Methane steam reforming in a membrane reactor using high-permeable and low-selective Pd-Ru membrane

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Abstract−We performed a methane steam reforming (MSR) reaction through a membrane reactor packed with commercial Ni/Al_2O_3 catalyst and a tubular Pd-Ru membrane deposited on a YSZ modified porous stainless steel support under mild operating conditions: 773 K and a pressure difference range of 100-250 kPa. We prepared the Pd-Ru membrane with thickness of ~6 μm on a tubular stainless steel support (diameter 12.7 mm, length 25 cm) using electroless plating, which was observed for the membrane performance using hydrogen and nitrogen. Gas permeation test carried out at 773 K and 31.4 kPa of pressure difference between retentate and permeate sides showed that the hydrogen permeation rate and nitrogen leakage were ~0.1050 mol s^{-1} m^{-2} and ~0.0018 mol s^{-1} m^{-2}, respectively. The MSR reaction was under the following conditions: temperature 773 K, pressure 100-250 kPa, gas hourly space velocity (GHSV) 837 h^{-1}, and steam-to-carbon feed ratio (S/C) 3. The MSR reaction result showed that methane conversion was increased with increasing pressure difference and reached ~77.5% at 250 kPa. In this condition, the composition of carbon monoxide was ~2%, meaning that no two series of water gas shift reactors were needed in our membrane reactor system. Long-term stability test carried out for ~100 h showed that methane conversion and the hydrogen yield remained constant.

Keywords: Methane Steam Reforming, Membrane Reactor, Pd-Ru Membrane, Hydrogen, Long-term Stability

INTRODUCTION

Methane steam reforming (MSR) is mature technology that has been used industrially to produce hydrogen from natural gas, primarily methane. To obtain high-yield of hydrogen, three successive stages, which are MSR reaction and two water gas shift reactions (high temperature Shift-HTS and low temperature Shift-LTS), are required before purification using a pressure swing adsorption system. [1]. In terms of operating conditions, the MSR reaction is performed at high temperatures (>1,123 K) owing to high endothermic character [2-7].

Many researchers have proposed to apply Pd-based membranes for reactors (MRs) in MSR reaction at milder operating conditions than the conventional ones [8-14]. As an alternative to the conventional systems, the Pd-based MRs can combine two different processes into simultaneous reaction and separation process in the same device. One of the advantages of such an integrated process through the Pd-based MRs is the weakening of thermodynamic equilibrium limitations owing to the removal of hydrogen from the reaction zone. The removal of hydrogen improves the methane conversion due to Le Chatelier's principle on the equilibrium reactions [15]. Consequently, they obtain a high methane conversion at mild operating conditions.

Hydrogen permeates though the membrane by the solution and diffusion mechanism, and the hydrogen permeation flux is proportional to the square root of trans-membrane pressure difference if the diffusion of hydrogen atoms trough the dense metal layer is rate-limiting as in the well-known Sieverts' law [16]. Meanwhile, thermodynamically it would be preferable to conduct the MSR reaction under lower pressures [17]. Many previous studies showed that very high trans-membrane pressure differences are required to obtain sufficient methane conversion by high enough hydrogen removal from the reformed gas to overcome the thermodynamic disadvantage of the MSR reaction [8-14]. Recently, Oyama and Lim [18] showed that hydrogen permeation rate was much more effective than selectivity (H_2/CH_4) in the methane conversion and hydrogen yield. They concluded that hydrogen selectivity from the ratio of single-gas permeances has a substantial effect on conversion and hydrogen yield enhancements in a membrane reactor, and a selectivity of 10 is enough to achieve sufficient conversion enhancement.

In this study, we focused on the decrease of temperature and trans-membrane pressure difference in MSR with Pd-based membrane which had high permeability and moderate selectivity. MSR reaction in a membrane reactor equipped high-permeable and mod-

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erate-selective Pd-Ru membrane under ultimately milder operating conditions (a temperature of ~773 K and a pressure difference of ~250 kPa). The high-permeable Pd-Ru membrane was prepared by electroless plating method on a tubular porous stainless steel support (PSS) coated with YSZ diffusion inter-diffusion barrier. After the MSR in the membrane reactor, the Pd-Ru membrane was analyzed by using SEM/EDS.

EXPERIMENTAL

1. Preparation of Pd-Ru Membrane

The Pd-Ru membrane was prepared on a tubular porous stainless steel (PSS) with a 12.7-mm diameter and a 250-mm length (Mott, 0.5 μm grade) using electroless plating (ELP) of Pd and Ru. The tubular PSS was pretreated by ceramic powder filling and blowing coating method, which filled the large pores on the surface of a tubular PSS and fabricated the diffusion barrier between PSS and Pd-Ru alloy layer, respectively. First, we carried out the ceramic powder filling using yttrium stabilized zirconia (YSZ) powder with the average diameter of 5 μm and submicron through the vacuum pump [19], and then the 50 nm sized YSZ was coated on the tubular PSS using newly developed blowing coating method [20]. The YSZ barrier coated on the PSS was dried in the coating equipment overnight and then heat-treated at 873 K for 4 h under hydrogen atmosphere to form stable phase of thin film and eliminate contaminants such as binder and organic solution of a paste. With this method, ~1 μm thick YSZ film could be formed on the tubular PSS as a diffusion barrier.

Table 1. Compositions of electroless plating solution

Components	Concentration or value
$PdCl_2$	3.2 g/L
NH_4OH (28%)	320 ml/L
HCl	4.0 ml/L
N_2H_4 (1%)	200 ml/L
pH	~11

*The ratio of the plating solution volume to the membrane surface area was ~1.3×10^{-3} L cm^{-2}

After these pre-treatment, the PSS was seeded with Pd nuclei by impregnating and drying methods of $PdCl_2$ solution under atmosphere as shown in a previous study [21]. The Pd and Ru layer was deposited on the pre-treated PSS using EDTA-free ELP, and the composition of ELP solution was provided in a previous study [21-23] and Table 1. The Pd and Ru layers were continuously fabricated with thickness of ~5 μm and ~1 μm, respectively.

2. Permeation Test of Pd-Ru Membrane

The permeation flux of hydrogen and nitrogen in the permeation was investigated from the systems containing a membrane module, a furnace, a temperature controller, a pressure controller, and a digital soap-bubble flow meter and a wet gas meter, which was shown in a previous study [21]. Furthermore, the permeation flux of hydrogen and nitrogen in Pd-Ru membranes was periodically observed using a digital soap-bubble flow meter and wet gas meter before and after MSR reaction under a temperature at 773 K

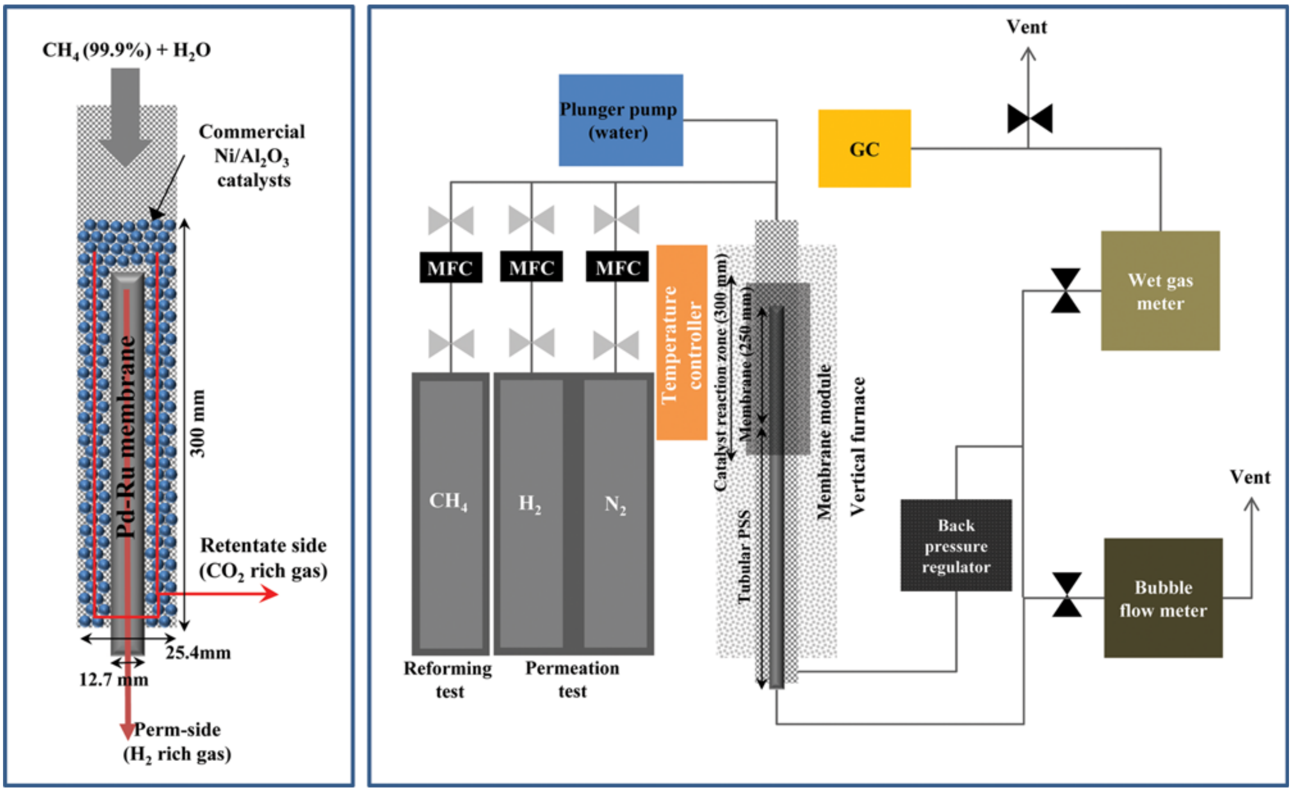

Fig. 1. A schematic of the membrane reactor and testing setup for the methane steam reforming.

and a pressure difference of 31.4 kPa.

3. Methane Steam Reforming Reaction

Fig. 1 shows a schematic of the membrane reactor and testing set-up for the MSR. The Pd-Ru membrane and commercial Ni/Al_2O_3 catalyst were equipped in the membrane reactor with a diameter of 25.4 mm and a length of 1,450 mm. The length of reaction zone packed with catalyst was 300 mm. The membrane reactor was heated in an electric vertical furnace with a programmable temperature controller. The gases containing CH_4, H_2, and N_2 were supplied by mass flow controller (MFC, Brooks 5850 series) under controlling the trans-membrane pressure difference with a back-pressure regulator. A water pump (NS, MINICHEMI PUMP, 1-1,000 μl min^{-1}) was used for feeding liquid water. The liquid water fed by the water pump was vaporized in the pre-heating zone of the reactor and then mixed with methane and fed into a reaction zone of the reactor. The methane was fed at a rate of 1.3×10^{-2} mol min^{-1} and a steam-to-carbon ratio (S/C) was kept constant ~3 (GHSV= ~837 h^{-1}).

When the reactants were introduced with a GHSV of 837 h^{-1}, the pressure on the feed side of the Pd-Ru membrane reactor increased from the pressure difference ranging from 100 to 250 kPa and the perm-side was ambient. This means that the methane steam reforming reaction took place at an absolute pressure of 200-350 kPa. The furnace temperature was controlled to be the reaction temperature ~773 K. To observe the gas compositions, both permeate and retentate stream compositions were analyzed by gas chromatography (HP 7890) with a thermal conductivity detector. To activate the catalyst, nitrogen and hydrogen were supplied during increasing the temperature to 773 K.

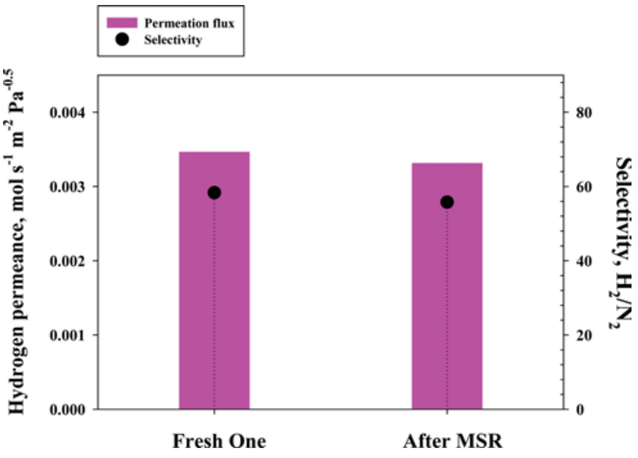

Fig. 2. The hydrogen permeance and H_2/N_2 selectivity before and after MSR.

RESULTS AND DISCUSSION

1. Permeation Test and Membrane Analysis

Prior to the steam reforming test, the performance of Pd-Ru membrane was tested using single gas of hydrogen and nitrogen at 773 K and a trans-membrane pressure difference of 31.4 kPa. The hydrogen permeance was, as shown in Fig. 2, 3.46×10^{-3} mol m^2 S^{-1} $Pa^{-0.5}$ (permeation flux ~0.1050 mol s^{-1} m^{-2}) with H_2/N_2 selectivity of ~59. As shown in Table 2 [24-30], the hydrogen permeance was quiet high compared with other reports and selectivity was relatively low. The hydrogen permeation was measured after a long-term reforming test. After the long-term reforming test in the membrane reactor, hydrogen permeance and H_2/N_2 selectivity was slightly decreased. Hydrogen could be transported through dense palladium alloy membrane by a series of different steps [10]:

1. Diffusion of hydrogen to the metal surface.
2. Adsorption of hydrogen on the surface.
3. Splitting of hydrogen molecules and incorporation into the metal.
4. Diffusion of protons in the lattice and of electrons in the electron bands.
5. Regeneration of hydrogen molecules on the permeated side surface.
6. Desorption of the hydrogen molecules.
7. Diffusion of the hydrogen molecules from the surface.

The catalysts in the membrane reactor were in contact with the outer surface of the tubular Pd-Ru composite membrane, and it could reduce the site of hydrogen adsorption causing less hydrogen could be permeated through the membrane consequentially. To verify the reason for hydrogen permeation loss, the tested mem-

Table 2. Comparison of membrane reactor data from the literature for methane steam reforming (MSR)

Membrane	Thickness (μm)	Area (cm^2)	Temperature (K)	Pressure difference (kPa)	Pure H_2 permeance (mol m^2 S^{-1} $Pa^{-0.5}$)	Selectivity (H_2/N_2)	Catalyst	GHSV (h^{-1})	Steam-to-carbon ratio (S/C)	Sweep flow rate (mol/h)	CH_4 conversion (%)	Reference
Pd-Ru/PSS	100	1.2	773	100	1.10E-04	ND	Ni	30	3	0.40	80	[24]
Pd/PSS	11	20	800	100	1.11E-03	ND	Ni	1120	3	1.30	82	[25]
Pd/Al_2O_3	3.8	155.0	823	2500	3.71E-03	97	Ni	150	3	0.13	91	[26]
Pd-alloy/PCS[a]	7.3	93.3	823	800	2.15E-03	ND	Ni	3000	3	None	68	[27]
Pd	11.0	35.8	873	1600	1.70E-03	3000	Ni	600	3	None	37	[28]
Pd-Ru/PSS[b]	5.0	13.3	853	2900	2.70E-3	200	Ni	150	3	None	85	[29]
Pd-Au/PSS	5.0	16.1	784	2800	2.39E-03	6400	Ru	147	3	None	94	[30]
Pd-Ru/PSS	6	100	773	250	3.46E-03	59	Ni	837	3	None	77.5	This study

[a] Porous ceramic support

[b] Porous stainless steel support

Fig. 3. The surface SEM analysis of Pd-Ru membrane after MSR: white spots are dust of alumina catalyst.

brane was analyzed by SEM. After reforming and permeation tests, the reactor was disassembled and the membrane was cut to analyze with SEM analysis. Surface SEM analysis in Fig. 3 shows that some catalyst (white spots) remained on the surface of the membrane and it blocked some of the sites of hydrogen adsorption, reducing the hydrogen permeation value.

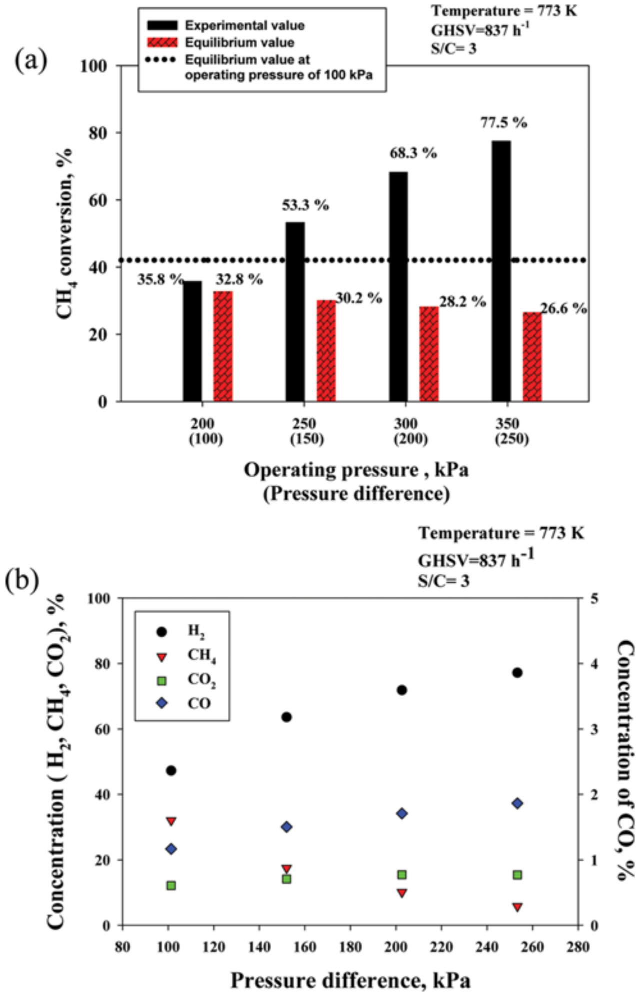

Fig. 4. Results of the MSR reaction through Pd-Ru membrane reactor: (a) methane conversion, (b) gas compositions.

2. Methane Steam Reforming in Pd-Ru Membrane Reactor

The major advantage of MSR reaction through Pd-based MRs is the significant improvement of the methane conversion at lower temperature [17]. It is well known that the major gaseous products of MSR reaction are hydrogen and carbon monoxide. Carbon dioxide is also a major component of reformed gas and is produced via the water-gas shift (WGS) reaction. The methane steam reforming reaction is highly endothermic, so a large amount of heat is therefore required [2-7]. For conventional reactors, the operating temperature is kept in the range of 1,073-1,273 K to achieve the complete conversion of methane. Since the MSR reaction is limited by the thermodynamic equilibrium of the reversible reactions, one possible method of enhancing the reaction rate is to remove one of the products [31,32]. If hydrogen is selectively removed from the reaction system, thermodynamic equilibrium of these reactions is shifted to the products sides, and highly efficient conversion of reactants can be attained; consequently, it can be accomplished even at lower temperatures. Fig. 4(a) shows that methane conversion increased with increasing the pressure difference and exceeded the equilibrium value at absolute pressure of 100 kPa, except at the pressure of 100 kPa. MSR is thermodynamically predominant at a lower pressure because the volume of the products is higher than the reactants. To overcome the equilibrium value, sufficient hydrogen should be removed from the products. Hydrogen permeation rate is dependent on the pressure difference, and high enough pressure is required to surpass the equilibrium conversion by the sufficient removal of hydrogen from the product. The methane conversion reached ~77.5% at a pressure difference of 250 kPa, which was about twice higher than that of equilibrium value at absolute pressure of 100 kPa. Table 2 compares the MSR performance in Pd-based membrane reactors. Some results [26,29,30] showed higher methane conversion (80-90%) than our result at a similar temperature. They operated it very high pressure differences (2,500-2,800 kPa) to remove hydrogen in the reformed stream sufficiently. Nam et al. got ~80% methane conversion at 773 K and a pressure difference of 100 kPa. They used sweep gas to remove hydrogen from the reformed gas and tested their reactor at a very low GHSV (30 h^{-1}). Our results confirmed that the Pd-Ru membrane with high permeation flux for hydrogen could remove the produced hydrogen and then achieve higher methane conversion at relatively low temperature. Furthermore, the moderate selectivity (H_2/N_2 ~59 at 31.4 kPa) of membrane was sufficient for achieving the improvement of the methane conversion. The thickness of ~6 μm is somewhat thick to compare the other membranes shown in Table 2. We tried to make a high permeability and moderate selectivity membrane to increase MSR efficiency. It was the first time to develop tubular Pd based composite membrane in our group. It means that the diffusion barrier coating and electroless plating of Pd-Ru was the first stage of tubular membrane development in our group. We are trying to decrease the membrane thickness without selectivity loss and expect to report it in the foreseeable future.

As mentioned in the previous paragraph, the increase of operating pressure in the MSR would result in decreased methane conversion due to the thermodynamically unfavorable impact. The increasing of the operating pressure has two competitive effects on methane conversion [17]. First, a negative effect proceeds with an increase of the moles number and is not favored by higher pressure owing to the thermodynamic features of the reaction. On the contrary, a positive effect induced a higher pressure difference makes a higher hydrogen recovery due to the increase of the hydrogen permeation driving force (Fick-Sieverts law and Arrhenius-like equation) [17]. A low value of the pressure difference indicates that the driving force for hydrogen permeation is low. Fig. 4(a) shows that the methane conversion as a function of pressure difference at 773 K. The reaction pressure should be added 100 kPa to the pressure difference because the atmospheric pressure is ~100 kPa in our place. The methane conversions were higher than the equilibrium value at the whole the range of the reaction pressure, and the difference between the experimental value and the equilibrium increased with the pressure. It is because the equilibrium value decreases with increasing reaction pressure thermodynamically. The dotted line in Fig. 4(a) is the equilibrium value at an absolute pressure of 100 kPa. Compared with the equilibrium value at the absolute pressure of 100 kPa, a negative effect was shown at the pressure difference of 100 kPa (absolute pressure 200 kPa), and it turned out to be a positive effect when the operating pressure difference was ≥150 kPa (absolute pressure 200 kPa). The negative effect at the pressure difference of 100 kPa was that selective hydrogen removal was not sufficient to overcome the thermodynamically reduced methane conversion at an absolute pressure of 100 kPa. The methane conversion enhancement at the pressure difference of ≥150 kPa was due to the prevalence of the "shift effect" related to the selective removal of hydrogen over the above mentioned detrimental (negative) effect [17].

Gas compositions containing the H_2, CH_4, CO_2, and CO in retentate and permeate sides of the reaction system are presented in Fig. 4(b), depending on a function of pressure differences. The retentate and permeate stream were combined in one stream and analyzed by gas chromatography. The concentrations of hydrogen, carbon monoxide, and carbon dioxide increased with the increasing of pressure differences corresponding to the increase of the methane conversion. It is general that two series of water gas shift reactors, i.e., HTS (~400 °C) and LTS (200 °C), follow the MSR reaction to obtain higher hydrogen yield and reduce carbon monoxide [26]. And the carbon monoxide was ~1% at the outlet of the LTS. The gas composition in Fig. 4(b) shows that the concentration of carbon monoxide remained <2% at the pressure difference range from 100 to 250 kPa. It means that the water gas shift reaction ($CO+H_2O \leftrightarrow H_2+CO_2$) was additionally enhanced by the selectively removal of hydrogen and no two series of water gas shift reactors were needed in our membrane reactor system.

Fig. 5 shows the long-term stability test of the Pd-Ru membrane reactor carried out for ~95 h. As presented in Fig. 5, the methane conversion and the hydrogen production rate were ~77.5% and 54×10^{-3} $Nm^3\ h^{-1}$ under the pressure difference of 250 kPa at the temperature of 773 K, respectively, and then remained constant during the testing period.

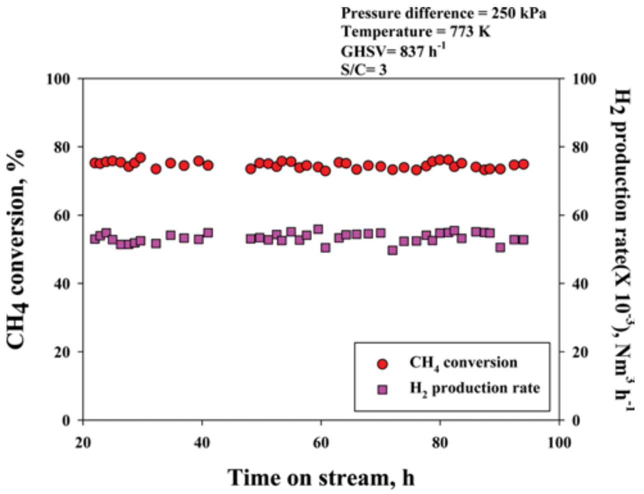

Fig. 5. The methane conversion and hydrogen yield for long-term stability test of ~100 h in Pd-Ru membrane reactor.

CONCLUSION

Our membrane reactor promoted the reaction due to the shift of the equilibrium by the Pd-Ru membrane with high permeability and moderate-selectivity, which led to the improvement of methane conversion under the mild operating conditions. Moreover, the methane conversion and hydrogen yield in Pd-Ru membrane reactor remained constant during the long-term reforming testing (~100 h). Consequently, we confirmed that our Pd-Ru membrane and membrane reactor could be effectively used for the MSR reaction and the alternative for two series of water gas shift reactors.

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