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Study on the hydrogen production from methanol steam reforming in supported palladium membrane reactor

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Abstract

This paper presents the effect of palladium membrane on the conversion of methanol reformed to the hydrogen by steam. A supported palladium membrane, which was electrolessly plated on porous stainless steel tube, was incorporated into the reaction system to configurate the membrane reactor. The reaction was carried out over $Cu/ZnO/Al_2O_3$ catalysts at 350°C. The stability of the catalyst was affected by the composition of Cu, Zn, and Al. The higher the content of Al, the better the stability of the catalyst. A double-jacketed membrane reactor was used to conduct both reforming and oxidation reactions simultaneously in separate compartments. The heat released from the oxidation compartment can be directly transferred into the reforming compartment to compensate the heat required from the external furnace. The measured heat supply was found to be strongly depending on the recovery yield of hydrogen. Therefore, a heat balance could be obtained at the recovery yield around 74%, which is consistent with the analysis of energy self-balance. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Supported palladium membrane; Methanol steam reforming; Hydrogen flux; Recovery yield; Energy self-balance

1. Introduction

Hydrogen is conventionally manufactured in large scale by the steam reforming of hydrocarbons such as methane or naphtha oil. For small and medium scale users, it is also produced from the steam reforming of methanol. As a liquid fuel for producing hydrogen, methanol has advantages relative to other hydrocarbons because of its low steam to carbon ratio, relatively low reforming temperatures (250–350°C), consistently high quality (sulfur <5 ppm) and ease of handling. In addition to the use in chemical industry, methanol fueled hydrogen generation is also regarded as the most feasible route to supply a fuel cell for utility power, and particularly, for electric vehicles [1–3]. In steam reformation of methanol, the raw reformate gas contains approximately 75% H_2, 20% CO_2, and 5% CO by volume. The resultant crude hydrogen is further purified to the level of 95% or even higher for industrial purpose. In the chemical industry, the commercially available purification processes such as pressure swing adsorption (PSA) is already used to obtain high purity hydrogen from the reformate gas. Due to the need of extra purification facilities, the whole process becomes complicated and costly. Moreover, the recovery efficiency of PSA is normally lower than 85% [4], which would limit the overall recovery yield of hydrogen.

Membrane reactor was developed to combine the reaction and purification in one system. The reaction product can be removed directly from the reaction system by the selective membrane. In some cases, the

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removal of product can promote the reaction direction toward the product side according to the thermodynamic equilibrium. Therefore, the membrane reactor can carry out the reaction even at lower reaction temperature and achieve enough high conversion. Some equilibrium-limited reactions, such as dehydrogenation and steam reforming, have been investigated by using membrane reactor to increase the conversion due to the shift of equilibrium. In lots of hydrogen related reaction systems, supported palladium membranes were usually used as the hydrogen-permeable membrane [5–7]. Due to the very high permselectivity of palladium membrane, the high purity hydrogen could be obtained directly from the reaction system. Therefore, no extra purification facility is needed.

In the previous paper [8], we have described an integrated purification and production method to directly produce high purity hydrogen with a supported palladium membrane reactor. We successfully demonstrated the one-step production of pure hydrogen without extra purification facilities. In addition, the conversion of methanol could be further enhanced due to the effect of palladium membrane on incipient removal of hydrogen. Without the limitation of equilibrium conversion at the temperature of 350°C, this enhancement was attributed to the kinetic effect which accelerates the reaction by the removal of produced hydrogen that strongly adsorbed on catalyst surface to prevent the reaction progress.

In our recent paper [9], a unique design of double-jacketed membrane reactor was used to carry out the steam reforming of methanol and showed grand possibility to provide energy-efficient and space-compact hydrogen generator in case of use for fuel cell system. The flux and recovery yield of produced hydrogen are determined by two working parameters, i.e. WHSV (weight hourly space velocity) and load-to-surface ratio (inlet flow rate over membrane area). Extremely increasing WHSV or decreasing load-to-surface ratio will decrease hydrogen flux. However, the recovery yield of hydrogen is mainly controlled by the load-to-surface ratio. The higher the load-to-surface ratio, the lower the recovery yield. Both flux and recovery yield are strongly affected by the reaction pressure, too. Increasing the reaction pressure will obviously enhance both parameters.

In this paper, we further investigate the effect of catalyst composition on the stability for the reaction at 350°C. The influence of reaction pressure and load-to-surface ratio on the hydrogen flux and recovery yield is further presented. The heat effect accompanied with the combination of reforming and oxidation reactions was actually measured and analyzed based on the operation of the double-jacketed membrane reactor.

2. Experimental

2.1. Preparation of supported Pd-membrane

The supported palladium membrane tube was prepared by the electroless plating technique as described in literature [10]. A porous seamless 316L stainless steel tube having an outside diameter of 1.27 cm and a rejection grade of 0.5 μm was used as the support, which were purchased from Mott Metallurgical. The tube was cut to a length of 15 cm and welded to a dense stainless steel tube with the same diameter. The effective membrane area for hydrogen separation was around 60 cm^2. The thickness of palladium membrane deposited on the outer side of the tube was about 20 μm.

2.2. Apparatus and operating procedures of single-jacketed membrane reactor

The steam reforming reaction was primarily conducted in a single-jacketed membrane reactor which is simply constructed with a membrane tube housed by a stainless steel tube as outer jacket. The configuration is similar to that described in the previous paper [8]. The catalyst was loaded in the annular space between the membrane tube and outer jacket. A liquid mixture of methanol and water was fed into the catalyst bed. The produced hydrogen shall permeate through the palladium membrane and exit out of the inner side of membrane tube. The non-hydrogen gases are rejected by the membrane tube. The unreacted methanol and water were condensed and collected from the rejected gas. After weighing and analyzing the liquid effluent, the conversion of methanol could be calculated. A bubble meter was used to measure the flow rate of both permeated and rejected gases. The composition of effluents was analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

2.3. Apparatus and operating procedures of double-jacketed membrane reactor

The double-jacketed membrane reactor was setup to perform the steam reforming and complete oxidation reactions at the same time. The basic configuration is similar to that described in another previous paper [9]. Different from the single-jacketed reactor, the double-jacketed reactor composed of two housing stainless steel tubes as outer jackets and shaped two separate compartments in between them (Fig. 1). In the first compartment, a $Cu/ZnO/Al_2O_3$ catalyst was loaded adjacent to the outer surface of the membrane tube, over where the steam reformation of feeding methanol and water proceeded. In the second compartment, a Pd/Al_2O_3 catalyst was loaded adjacent to the outer surface of the first jacket and the oxidation of rejected gas was made over there. The mixture of methanol and water was fed into the first compartment to produce H_2, CO, and CO_2. Under the driving effect of transmembrane pressure difference, the instantaneously produced H_2 penetrated through the membrane tube and was directly removed as a high purity hydrogen. The rejected gases such as H_2, CO, CO_2, and/or trace amount of unreacted methanol, then entered into the second compartment and were converted into CO_2 and H_2O as a result of complete oxidation with air. To measure the external heat supply during the reaction, an electricity meter was equipped with the power supply device of electric furnace, as shown in Fig. 1. The electricity supplied to the reaction system was measured from the reading of electricity meter. The heat supplied to the reaction was then calculated based on the measured electricity. The procedures to collect flow rates and compositions are the same as that in single-jacketed reactor.

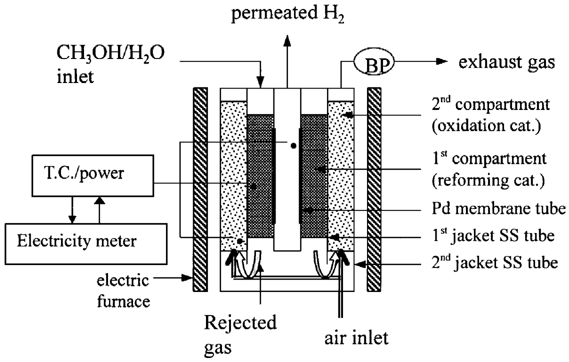

Fig. 1. Schematic diagram of the double-jacketed membrane reactor.

2.4. Catalysts and operating conditions

Two commercially available copper–zinc catalysts including MDC-3 and G66B, which were provided by Nissan Girdler, Japan, were used for the methanol steam reforming reaction. The activity and stability of both the catalysts were tested. To analyze the metal components, the catalyst was firstly dissolved in chloric acid solution and diluted to appropriate concentration. The diluted solution was then analyzed by induced coupling plasma (ICP) to determine the composition of Cu, Zn, and Al elements. The weight percent of CuO, ZnO, and Al_2O_3 was then calculated based on the metal composition. The reaction temperature was at 350°C. The reaction pressure were ranging from 6 to 15 atm. The pressure of permeate side, i.e. inner side of membrane tube, was under atmosphere. The ratio of steam to methanol was used as 1.2.

3. Results and discussion

The supported palladium membrane used for steam reforming has the hydrogen permeance of $5\,m^3/m^2\,h\,atm^{0.5}$ and permselectivity near 4000 for H_2/N_2. The permeation behavior of membrane follows the Sievert's law. An increase of temperature slightly increased the hydrogen permeation and an Arrhenius relation was followed between the permeance and the temperature. Therefore, the activation energy of the palladium membrane for hydrogen permeation was measured as 3.2 kcal/g mol, being in good agreement with that reported in literature [10,11].

3.1. Influence of catalyst composition on the activity and stability

The stable range of operating temperature for this supported membrane tube is restricted within 300–400°C. Below 300°C, the hydrogen embrittlement occurs [12,13] causing the microcrack and dropping the permselectivity of membrane. Over 400°C,

Table 1
Analyzed composition of CuO, ZnO, and Al_2O_3 in G66B and MDC-3 catalysts

Composition (wt.%)	MDC-3	G66B
CuO	38	31
ZnO	41	60
Al_2O_3	21	9

the intermetallic diffusion occurs between the palladium film and the stainless steel support causing the drop of hydrogen permeance [10]. Under the limitation of operating temperature, the reaction of methanol steam reforming was performed at 350°C. Conventionally, the copper–zinc catalyst, e.g. G66B, is well used for the commercial process of methanol steam reforming [14–16]. The operating temperature is in the range 200–300°C, lower than the operating temperature used in this work.

In order to study the catalyst stability under this high operating temperature, we compared two kind of copper–zinc catalysts, i.e G66B and MDC-3, for the reaction. The comparison for the metal-oxide composition of these two catalysts is listed in Table 1. At high reaction temperature of 350°C, the activity of G66B catalyst was rapidly declined, as shown in Fig. 2. In contrast, the MDC-3 catalyst showed very good stability at this temperature. This could be explained by the higher content of alumina in MDC-3 catalyst, as shown in Table 1. The existence of alumina can stabilize the active copper species and prevent them from the sintering at high temperature to show the higher stability for reaction as reported in literature [17].

When MDC-3 catalyst was used in membrane reactor to produce pure hydrogen, stable conversion of methanol near 95% could be obtained. At the same time, stable hydrogen flux was achieved near $3.5\,m^3/m^2\,h$. As can be seen in Fig. 3, both methanol conversion and hydrogen flux are very stable in a long-term operation near 900 h. This result indicates that, in practical use, the MDC-3 catalyst can constantly provide high conversion of methanol during a long-term operation at 350 h, 15 atm and WHSV of methanol around $1\,h^{-1}$. Also, the result means feasible stability of the supported palladium membrane tube for practical generation of pure hydrogen from methanol.

3.2. Heat effect of combining reforming and oxidation reactions

Different from the conventional fixed bed reactor, the membrane reactor can directly generate a separate stream of pure hydrogen of purity above 99.9% from the feedstock of methanol plus water. The gas rejected by palladium membrane showed lower concentration of hydrogen (~64%) when compared with

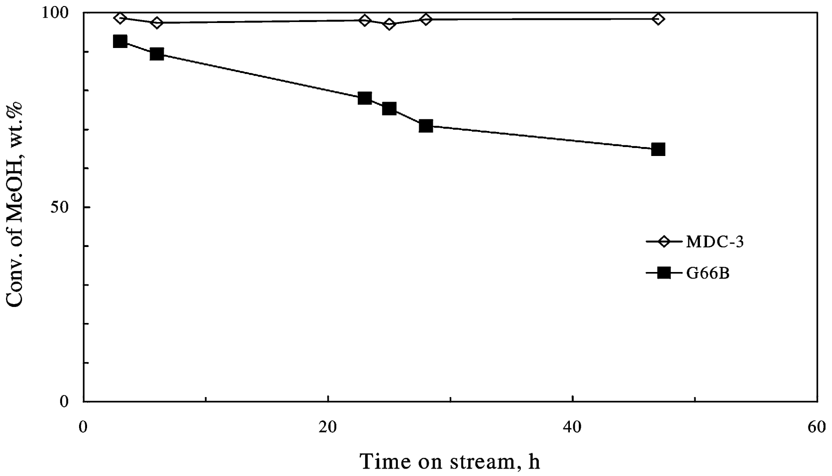

Fig. 2. Comparison for the activity and stability of the MDC-3 and G66B catalysts in methanol steam reforming reaction at 350°C, 6 atm, and WHSV of methanol = $10\,h^{-1}$.

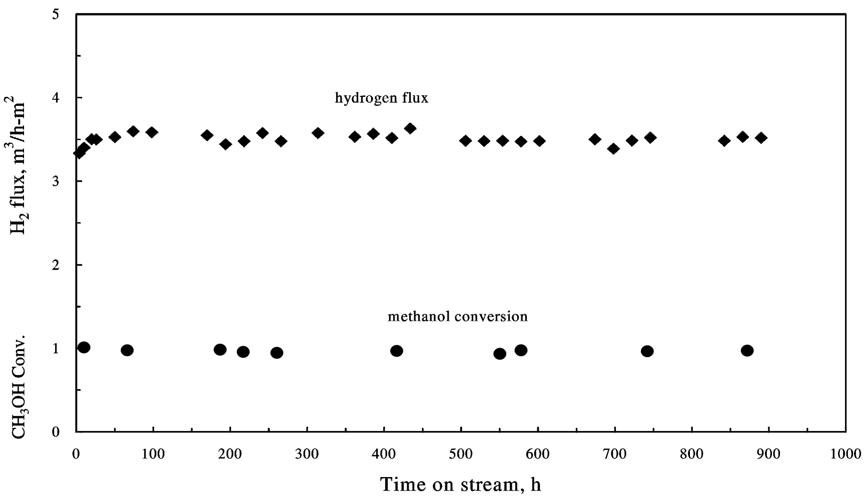

Fig. 3. Long-term test for MDC-3 catalyst and supported Pd-membrane operated in methanol steam reforming reaction at 350°C, 15 atm, and WHSV of methanol $= 1\,h^{-1}$.

the equilibrium value of methanol steam reforming, i.e 75%. Moreover, when double-jacketed reactor was used, the rejected gas was further oxidized by air and converted to CO_2 and H_2O. The much lower hydrogen concentration (~10%) was observed as compared to that from the single-jacketed reactor (Table 2). By coupling an oxidation reaction, the heat of reforming reaction could be compensated in this double-jacketed reactor. Therefore, the electricity consumed by the double-jacketed reactor was measured lower than single-jacketed reactor due to the heat released by the oxidation of a portion of rejected gas. The heat externally supplied by the furnace could be calculated based on the consumed electricity. During the fixed period of operation, the total consumed electricity and feeding amount of methanol were measured to calculate the external heat supply per unit amount of methanol. To maintain the reactor temperature at 350 °C, the heat supply was needed to compensate the heat of reaction, heating of reactants, and particularly, the heat loss by conduction and radiation between the reactor and the ambient. The comparison of the heat supply in the operation of single- and double-jacketed reactors is indicated in Table 2. From the difference between double- and single-jacketed reactor, the heat provided by the oxidation of rejected gas was measured as 214.1 kcal/g mol of feeding methanol. The summary of heat of reaction and heating requirement of reactants, i.e methanol and water, was estimated around 41.7 kcal/g mol methanol [9]. The heat released in Table 2 is obviously larger than the heat demanded. That means the reactor can be operated by internal supply of heat without the external furnace, if the reactor is well insulated.

The heat, released from oxidation compartment and transferred into the reforming compartment, was found

Table 2
Methanol steam reforming conducted in double- and single-jacketed membrane reactor at 350°C, 6 atm, $H_2O/CH_3OH = 1.2$, and WHSV of methanol $= 1\,h^{-1}$. The GHSV of air in DJR is $1200\,h^{-1}$

	H_2 flux (m^3/m^2 h)	Recovery yield (mol%)	Rejected composition (vol.%)			External heat supply (kcal/g mol CH_3OH)
			H_2	CO	CO_2	
DJR[a]	3.70	50	10.4	0	89.6	343.3
SJR[b]	2.85	38	64.7	6.0	29.3	557.4

[a] Double-jacketed reactor.
[b] Single-jacketed reactor.

Table 3
Effect of recovery yield of hydrogen on the external heat supply in the operation of double-jacketed membrane reactor

	Blank run	Recovery yield (%)					
		38	59	63	70	87	97
Consumed electricity (kW/h)[a]	0.85	0.73	0.735	0.72	0.835	0.89	0.94
Heat supply (Kcal/h)	292.7[b]	251.4	253.1	248.0	287.6	306.5	323.7
Net heat (Kcal/h)	–	−41.3	−39.6	−44.7	−5.1	+31	+13.8

[a] Measuring period of consumed electricity is 2.5 h.

[b] Equivalent to the heat loss between the reactor and ambient during process.

strongly depending on the recovery yield of hydrogen, as shown in Table 3. High recovery yield means less H_2 is rejected by the membrane and then oxidized over oxidation compartment to deliver heat for reforming reaction. Before measuring the electricity consumption during the reaction, a blank run was performed to determine the heat loss by conduction and radiation during the process. Net heat was obtained as the heat loss was subtracted from the measure of heat supply. A minus net heat means the heat released from the oxidation compartment is larger than that required in reactor, i.e the overall reactor system is exothermic. In contrast, a plus net heat means endothermic system and the heat released is less than required. Increasing the recovery yield could shift the reactor system from exothermic to endothermic. Therefore, a self-balance of heat, i.e zero net heat, should exist at an appropriate recovery yield (Fig. 4). According to the analysis of energy self-balance developed in the previous paper [9], the dependence of net heat could be presented on the recovery yield of hydrogen. The status of heat balance was calculated at recovery yield of 74%. This estimation was very consistent with the experimental measure as shown in Fig. 4.

3.3. Influence of reaction pressure and load-to-surface ratio on hydrogen flux and recovery yield

The study in previous paper [9] showed that increasing the load-to-surface ratio moderately increased the hydrogen flux but significantly decreased the recovery yield. An optimum load-to-surface ratio should be, therefore, undertaken to compromise these two output

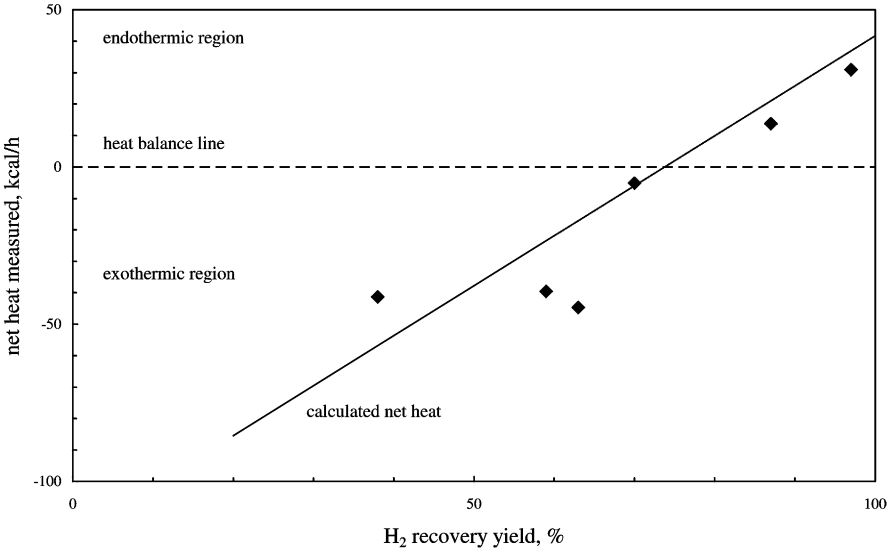

Fig. 4. Net heat measured as a function of recovery yield of hydrogen in the operation of double-jacketed membrane reactor at 350°C.

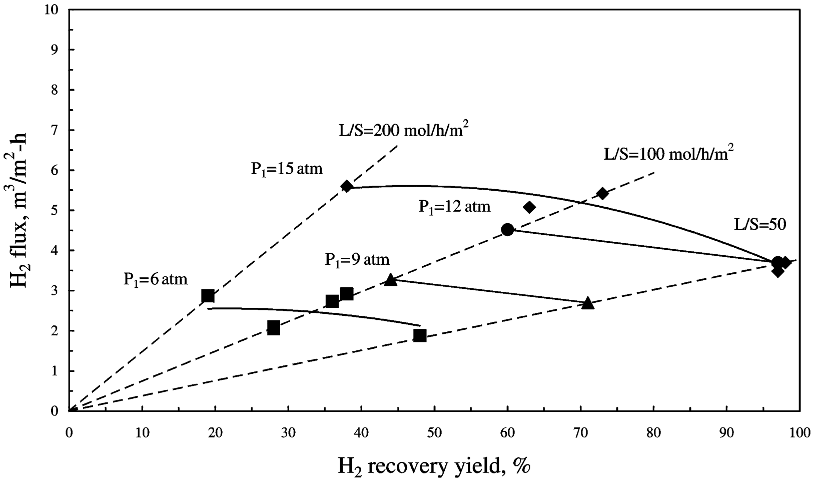

Fig. 5. Chart of hydrogen flux and recovery yield determined by the reaction pressure and load-to-surface ratio. Reaction temperature: 350°C; permeate pressure: 1 atm.

values. In contrast, both the hydrogen flux and recovery yield increased with increasing reaction pressure. A chart relating hydrogen flux and recovery yield was established on the load-to-surface ratio and reaction pressure as shown in Fig. 5. When higher reaction pressure is used, the load-to-surface ratio should increase to provide sufficient hydrogen flow. In other words, at lower load-to-surface ratio, the hydrogen flux and recovery yield cannot be further enhanced by simply increasing pressure due to the shortage of hydrogen in product stream. At 350°C and above 12 atm, neglecting the self-balance of heat, a recovery yield of 97% and hydrogen flux of 3.7 m^3/m^2 h was obtained when a lower load-to-surface ratio of 50 g mol(CH_3OH)/h m^2 was used. This recovery yield of 97% is much higher than the commercially existing process, in which the recovery yield of pure hydrogen is usually below 85% due to the limitation of purification efficiency of PSA method [4].

4. Conclusion

The supported palladium membrane has been promisingly demonstrated to produce high purity hydrogen from catalytic steam reforming of methanol. At reaction temperature of 350°C, the activity and stability of catalyst was promoted by increasing the content of alumina. A double-jacketed reactor has successfully demonstrated the generation of high purity hydrogen directly from the steam reforming of methanol. No external purification device is needed, as is often the case with conventional method. Also, the recovery yield as high as 97% could be obtained at 350°C and 12 atm. It provides much higher recovery yield than conventional one. Combining the reforming and oxidation reactions, the double-jacketed reactor can be operated in self-heating mode. The heat released was mainly determined by the recovery yield. Reducing the recovery yield would increase the heat released and shift the reactor system from endothermic to exothermic. A self-balance of heat was then achieved at the hydrogen recovery yield around 74%, which is in good agreement with the analysis of energy self-balance. With features of high recovery yield of hydrogen, compact-space of the facility and adequate efficiency of energy, this palladium membrane reactor can afford a very attractive device of pure hydrogen generator either for the purpose of chemical usage or as an energy source for the electricity converter like fuel cell system.

Acknowledgements

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