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An integrated purification and production of hydrogen with a palladium membrane-catalytic reactor

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Abstract

In this paper, we presented an integrated production and purification process of hydrogen by the use of a defect-free palladium membrane. Hydrogen could be purified from a variety of mixtures providing the purity of 3–7 N depending on the feeding stream. The permeation parameters are accurately predicted by a separation model as established. The membrane is prepared by electroless plating and is stable among 300–400°C. Using an active catalyst, the rate of steam reforming of methanol was found to be significantly faster than that without a membrane module. In the steam reforming of methane, the reaction temperature was lowered to 500°C to achieve a conversion of 45%, which is 15% higher than the thermodynamic equilibrium conversion. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen; Palladium membrane; Steam reforming; Equilibrium

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1. Introduction

Hydrogen is an important chemical raw material as well as an important tool to refine a final product or modify surface properties of a metal or semiconductor. In addition, it is gaining eminence in the future energy supply profile. Traditionally, hydrogen is made in large scale by the steam reforming of hydrocarbons such as methane or naphtha oil. It is also produced from coal gasification or by the recovery from refinery operation. In the production of caustic soda, hydrogen exists as a by-product from electrolysis of brine. In recent years, it is also produced from the steam reforming of methanol for medium scale users and electrolysis of pure water for ultrahigh purity users in small volume. Moreover, it was observed that steam reforming of biomass such as rice hull or bagasse provided attractive alternative route for this important material [1].

In all these processes, production or recovery of hydrogen, additional purification is invariably required and often is a costly step in the whole process. In chemical industry, cryogenic, pressure swing adsorption (PSA) or polymer membrane permeation processes are used. In the semiconductor industry, extra purification by thick palladium alloy membrane is practiced to ensure a purity in the range 6–7 N, i.e., 99.9999–99.99999 mol%. To increase the permeation flux of hydrogen, various types of thin palladium

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membranes have been reported to purify hydrogen to 2–3 N purity in the literature [2,3].

Use of palladium-based membranes to shift the thermodynamic equilibrium towards the product side has attracted more attention for various endothermic reactions, including steam reforming of hydrocarbons. Many works were reported on the steam reforming of methane in the literature. Significant benefits gained by the use of a membrane reactor rather than conventional reactors have been readily described [4–9].

As a liquid source to produce 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. Methanol fueled hydrogen generation is, therefore, regarded as the most feasible route to feed the fuel cell in the application of electric vehicle and on-site electricity [10–13]. Above a reaction of 250°C, the restriction of thermodynamic equilibrium on the steam reforming of methanol is insignificant and almost complete conversion is usual. In this case, displacement of equilibrium conversion is no longer the critical effect to be concerned. Therefore, the present work deals with the observation of kinetic effect that may exist as a palladium membrane is incorporated in such a reaction system.

2. Experimental

2.1. Pd-membrane preparation

The supported palladium membrane was supplied by Worcester Polytechnic Institute, MA, USA. It was tested for its gas permeation character according to literature [14]. This defect-free palladium membrane was electroless plated to 20–25 μm thickness on a porous stainless steel 316L tube after being carefully pretreated. The supports were purchased from Mott Metallurgical, with a rejection grade of 0.2 and 0.5 μm. The membrane tube has a length of 150 mm and 15 mm OD. The effective area is around 70 cm^2.

2.2. Permeation and purification testing

The membrane tube was located inside a 1 in. OD stainless steel tube to form a double-tube module (Fig. 1). As shown in Fig. 1, when hydrogen permeation was in operation, the pure gas or mixture was fed into the annual side without any catalyst existing. The membrane section was heated by a three-zone electric furnace. The pressure of the system was regulated by a back pressure regulator and the flow rate of feeding gas was managed by a mass flow controller. For pure gas permeation testing, a bubble meter was used to measure the flow rate of permeate and, accordingly, calculate the permeation flux and permselectivity of hydrogen relative to other gases such as nitrogen. In the purification of gas mixtures, besides the measurement of flow rate, permeated and rejected gases were analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The TCD allowed only up to 99.9 mol% purity of hydrogen in our laboratory. For those extra high purity tests, a GC equipped with discharge ionization detector (DID) and helium detector was used (Curtsey of San Fu Chemical).

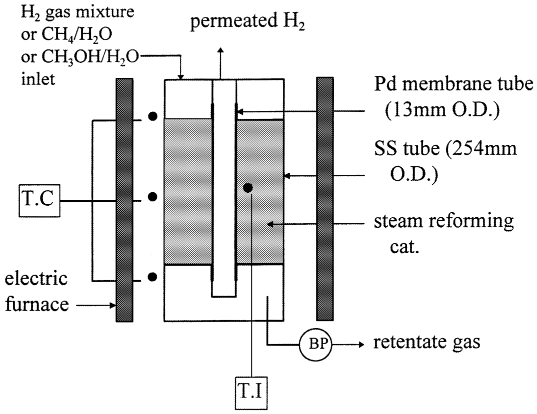

Fig. 1. Schematic diagram of double-tube module of Pd-membrane.

2.3. Steam reforming testing

The steam reforming reaction was carried out with the same double-tube module as shown in Fig. 1. The catalyst was filled on the outside of membrane in between two stainless steel tubes. Steam and carbon source were fed through the annual side on the catalyst bed. The hydrogen product permeates through palladium membrane into the inner tube. Both effluent streams were analyzed for their flow rates and compositions. Several copper-based catalysts including that prepared in our laboratory and commercial G66B of Nissan Girdler and Topsoe's were tested for the methanol steam reforming reaction between 280°C and 350°C. For methane steam reforming, only the industrial catalysts were studied between 400°C and 550°C.

3. Results and discussion

3.1. Behavior of hydrogen permeation and purification

From the results of pure gas permeation testing, the membranes provide high permselectivity of 250–400 for H_2/N_2 on the testing pressure of 2–15 atm (Fig. 2). The permeances of hydrogen were calculated to be 3 and 7 m^3/m^2 h $atm^{0.5}$ depending on the rejection grade of porous supports. The permeation behavior of both membranes follows the Sievert's law as indicated in Fig. 3.

Several permeation tests were carried out for hydrogen mixtures in the range as mole ratio of $H_2/N_2=1–9$, $H_2/CH_4=1–2$, $H_2/N_2/H_2O=1–3/1/1$ and a mixture of $H_2/C_3H_8/CH_4=62/15/23$ mol%. All tests yielded a hydrogen permeate of 99.5–99.9% purity. However, when an industrial grade hydrogen of 4N5 purity was tested, an extremely high purity, 6N8 of hydrogen was obtained in a single step permeation (see Table 1). Presented in Table 2 are the permeation data of separation of $H_2/C_3H_8/CH_4$ mixture. An increasing effect of the pressure difference on both the permeation flux and the recovery yield is observed from Table 2. The permeation flux also increases with the flow rate of feeding stream. However, the recovery yield decreases moderately as the flow rate increases due to insufficiency of membrane surface. At a higher pressure difference and lower flow rate, a recovery yield near 90% could be obtained.

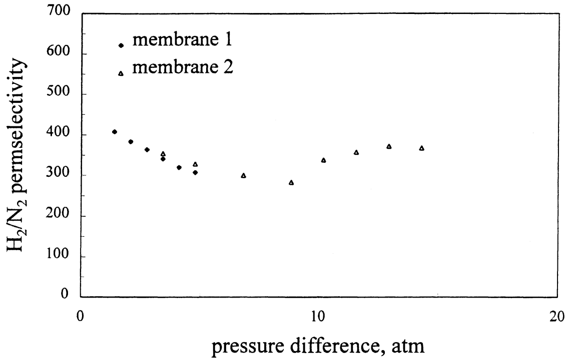

Fig. 2. Permselectivity for H_2/N_2 on two membranes: Membrane 1 with a rejection grade of 0.2 μm; membrane 2 of 0.5 μm.

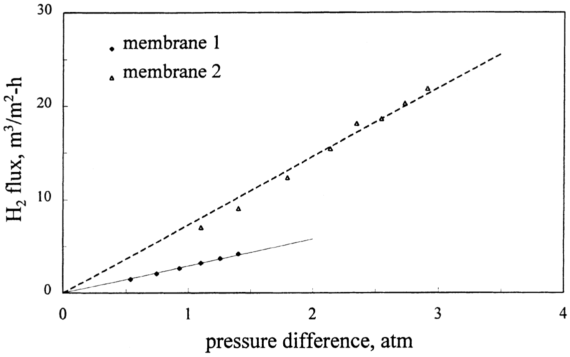

Fig. 3. Sievert's type permeation pattern on the two membranes: Membrane 1 with a rejection grade of 0.2 μm and a permeance of 3 m^3/m^2 h $atm^{0.5}$; membrane 2 of 0.5 μm and 7 m^3/m^2 h $atm^{0.5}$.

Table 1

Purity analysis of permeated hydrogen via Pd-membrane depending on the feeding stream

	N_2 content	CO content (ppb)	CO_2 content (ppb)
Feeding H_2 (4N5 purity)[a]	17.6 ppm	245.6	158.2
Permeated H_2 (>6 N purity)[b]	0.603 ppm	84.8	122.1
Feeding H_2 (40%)[a]	60%	—	—
Permeated H_2 (>3 N purity)[b]	336.9 ppm	—	—

[a] Feeding H_2 was provided by San Fu Chemical.

[b] Impurity analysis of permeated H_2 was done by GC with DID of San Fu Chemical.

Table 2
Permeation of $H_2/C_3H_8/CH_4$ (62/15/23 mol%) mixture at 350°C via Pd-membrane with permeated H_2 (~99.9% purity) under atmospheric pressure

F/S[a] ($m^3/h\ m^2$)	FP[a] (atm)	PF (ex.)[a] ($m^3/m^2\ h$)	PF (ca.)[a] ($m^3/m^2\ h$)	RY (ex.)[a] (%)	RY (ca.)[a] (%)	RY (eq.)[a] (%)
1.79	3.7	0.78	0.76	70	69	77
2.07	4.4	0.97	0.95	76	75	82
2.26	5.1	1.10	1.11	80	80	85
2.25	5.8	1.17	1.17	85	85	87
11.85	3.7	1.16	1.18	16	16	77
12.65	4.4	1.49	1.48	19	19	82
12.64	5.1	1.78	1.76	23	23	85
12.94	5.8	2.08	2.03	26	26	87

[a] F/S: feed flow rate to membrane surface area; FP: feeding pressure; PF: permeation flux; RY: recovery yield; ex.: experimental; ca.: calculated; eq.: equilibrium.

A separation model was developed to predict the permeation results of hydrogen in a gas mixture (see Appendix A). According to the model, the permeation flux and the recovery yield can be calculated. Excellent agreement between calculated and experimental result was found from Table 2.

Significantly, the prepared membrane is stable enough to operate under a pressure difference up to 14 atm at a temperature between 300°C and 400°C. Over 450°C, however, the membrane deteriorates significantly, possibly due to the intermetallic diffusion of metal atoms in SS support into the palladium film [14]. On the other hand, the hydrogen embrittlement occurs as the temperature is below 300°C [15,16], leading to microcrack and resulting in selectivity drop of palladium membrane. Nevertheless, this membrane shows outstanding purification capability in its stable region, exhibiting high permeation flux, recovery yield and permeate purity. It may offer a very attractive device for on-line purification in the future industrial supply pattern of hydrogen.

3.2. *Methane steam reforming*

In the steam reforming of methane, the prepared membrane with a permeance of 7 $m^3/m^2\ h\ atm^{0.5}$ was used to investigate the effect of equilibrium displacement. The reaction was performed on a conventional catalyst of G56H of Nissan Girdler Catalyst. The temperature was at 500°C and the pressure was about 3–6 atm. The mole ratio of steam to methane was 3. A conversion of around 15 mol% higher than that without using a membrane, i.e., 45 versus ~30%, was observed as shown in Fig. 4. Compared to the equilibrium conversion, the so-called "drain-off effect" of Pd-membrane reactor [17,18] was clearly demonstrated in such an endothermic reaction. This result is compatible with those of the literature [4,7,8]. Successfully developed in the future, this could lead to a substantial saving of furnace material as reaction temperature is decreased from 700–800°C down to 500–550°C, allowing the use of SS316 which is about half the price of special alloy of HK-40 now in use for such a kind of furnace reactor.

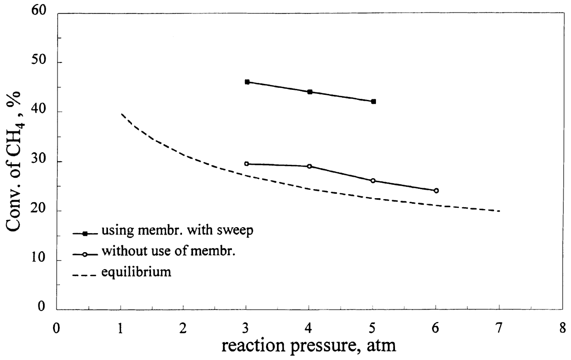

Fig. 4. Equilibrium displacement of methane steam reforming. Reaction temperature: 500°C; gas hourly space velocity: 1600 h^{-1}; steam to methane mole ratio: 3.

3.3. *Methanol steam reforming*

Due to the restriction of operating temperature of this membrane, the reaction of methanol steam reforming was performed at 350°C in this work. Under

Table 3
Rate effect of a Pd-membrane on the steam reforming of methanol at 350°C, 6 atm and $H_2O/CH_3OH=1.2$

WHSV[a] (h^{-1})	Conversion[a] (wt%)	Permeate[b] (ml/min)	Retentate (ml/min)	Composition of retentate (vol%)		
				H_2	CO	CO_2
1.3	99.4	76	33	24.8	4.7	70.5
8	99.4	304	339	54.0	6.3	39.7
20	91.4	273	1147	73.7	2.2	24.1

[a] WHSV and conversion were based on the weight of methanol.
[b] H_2 permeate from reaction products.

Table 4
Steam reforming of methanol without the use of the membrane at 350°C, 6 atm and $H_2O/CH_3OH=1.2$

WHSV[a] (h^{-1})	Conversion[a] (wt%)	Effluent (ml/min)	Composition of effluent (vol%)		
			H_2	CO	CO_2
1.3	97.6	98	76.1	5.4	18.4
8	95.5	613	77.2	3.9	18.9
20	69.0	894	78.9	1.1	20.0

[a] WHSV and conversion were based on the weight of methanol.

this temperature, the methanol should be completely converted by steam without the thermodynamic limitation [10]. Unlike the effect of a membrane on the thermodynamic equilibrium, the effect of inorganic membrane on the reaction rate receives relatively little attention. According to the reported kinetic results, the reaction rate of methanol could be enhanced with the increase of both methanol and water concentration and the decreasing hydrogen concentration [19,20]. Therefore, an enhancement of methanol conversion can be expected as the continuous withdrawal of produced hydrogen from the reaction system is done by the use of a palladium membrane. This was actually observed as shown in Tables 3 and 4. By comparing the results in Tables 3 and 4, the conversion is almost quantitative when WHSV is increased from 1 to 8 with the use of the membrane. Although the conversion does drop to 91% at WHSV=20, it is still much higher than 69% without the membrane. This enhancement of conversion could be attributed to the effect of palladium membrane on incipient removal of hydrogen.

High capacity of pure hydrogen could be produced by this process on the use of a very thin supported palladium membrane in which only a one step membrane-reactor is needed without an additional costly purification system. Therefore, it is definitely able to reduce the capital spending, production cost and the facility volume. This unique feature will provide a grand opportunity for using such a hydrogen generation process in the future fuel cell system, particularly in the application of electric vehicle for which highly space-compact device is strongly required.

4. Conclusion

Defect-free, very thin palladium membrane can be made on the porous stainless steel tubes by electroless plating method. The membrane showed high permselectivity in the range 250–400 for H_2/N_2 and hydrogen permeance of 3–7 $m^3/m^2\,h\,atm^{0.5}$ for which Sievert's law is obeyed. High purity hydrogen of 3–7 N can be obtained depending on the purity of feeding stream. The permeation flux and recovery yield of hydrogen from gas mixtures can be calculated according to the derived separation model, which is in excellent agreement with the experimental results.

In the steam reforming of methane, a conversion of 15 mol% higher than the thermodynamic equilibrium conversion was observed. As expected for the effect of equilibrium shift, the reaction temperature might be decreased from 700–800°C to 500–550°C. This could lead to a substantial saving of furnace material due to the use of SS316 rather than the twice-priced special alloy of HK-40.

Using an active reforming catalyst in the membrane reactor, we were able to achieve constantly complete conversion of methanol by steam under WHSV from 1 even up to 8. This higher WHSV should imply higher permeation capacity of hydrogen generated on the relatively small size of the reactor. Without additional purification, this will provide an opportunity for using such a hydrogen in the future fuel cell system, especially in the electric vehicle.

Appendix A

Derivation of separation model to calculate hydrogen permeation flux and recovery yield

Making a material balance for a section of palladium membrane as shown in Fig. 5, then

$$-\mathrm{d}R_\mathrm{H} = J\mathrm{d}A, \tag{A.1}$$

where R_H is the flow rate of H_2 in retentate side, J the permeance of H_2 and A is the surface area of the membrane.

If the permeation behavior of H_2 follows the Sieverts law, then

$$J = \beta(P_\mathrm{H}^{0.5} - P_1^{0.5}), \tag{A.2}$$

where β is the permeance of H_2, P_H the H_2 partial pressure in the retentate side and P_1 is the pressure of the permeate side in which 100% H_2 is assumed.

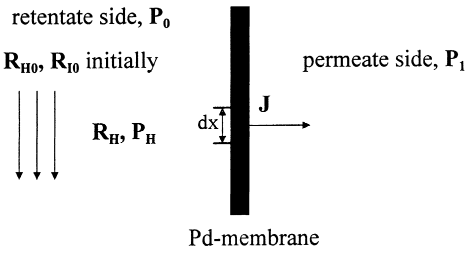

Fig. 5. Schematic diagram of permeation crossing the Pd-membrane.

Substituting (2) into (1),

$$-\mathrm{d}R_\mathrm{H} = \beta(P_\mathrm{H}^{0.5} - P_1^{0.5})\mathrm{d}A \quad \text{and}$$
$$-\mathrm{d}R_\mathrm{H}/\mathrm{d}x = \pi DL\beta(P_\mathrm{H}^{0.5} - P_1^{0.5}), \tag{A.3}$$

where D is the diameter of the membrane, L is the length of the membrane, and $x=z/L$, where z is the axial position of the membrane.

Let

$$P_\mathrm{H} = P_0R_\mathrm{H}/R = P_0R_\mathrm{H}/(R_{I_0} + R_\mathrm{H}),$$

where P_0 is the pressure of the retentate side, R the total flow rate in the retentate side and R_{I_0} is the nonhydrogen flow rate in the retentate side. Then

$$-\mathrm{d}R_\mathrm{H}/\mathrm{d}x = \pi DL\beta\{P_0^{0.5}[R_\mathrm{H}/(R_{I_0} + R_\mathrm{H})]^{0.5} - P_1^{0.5}\}.$$

Let

$$a = \pi DL\beta P_1^{0.5}/R_{\mathrm{H}_0}, \quad b = (P_0/P_1)^{0.5},$$
$$c = R_{I_0}/R_{\mathrm{H}_0}, \quad y = R_\mathrm{H}/R_{\mathrm{H}_0},$$

where R_{H_0} is the initial H_2 flow rate in the retentate side.

So

$$-\mathrm{d}y/\mathrm{d}x = a\{b[y/(c+y)]^{0.5} - 1\}. \tag{A.4}$$

Integrating Eq. (A.4), we obtain

$$a = \int_y^1 \mathrm{d}y/\{b[y/(c+y)]^{0.5} - 1\}. \tag{A.5}$$

From Eq. (A.5), the parameter y can be solved by numerical method and then the recovery yield of H_2 is calculated as $1-y$. Permeation flux of H_2 is calculated as $R_{\mathrm{H}_0}(1-y)/A$. At $b[y/(c+y)]^{0.5}-1=0$, the H_2 partial pressure is in equivalence across the membrane, i.e. reaching its equilibrium state. So $y_{\mathrm{eq.}} = c/(b^2-1) = (R_{I_0}/R_{\mathrm{H}_0})/(P_0/P_1 - 1)$ and equilibrium recovery yield of H_2 is obtained as $1-y_{\mathrm{eq.}}$.

References

[1] M.H. Rei, F.S. Lin, T.B. Su, Appl. Catal. 26 (1986) 27.
[2] E. Kikuchi, S. Uemiya, Gas Sep. Purif. 5 (1991) 261.
[3] J.P. Collins, J.D. Way, Ind. Eng. Chem. Res. 32 (1993) 3006.
[4] E. Kikuchi, Catal. Today 25 (1995) 333.

[5] M.P. Harold, C. Lee, A.J. Burggraaf, K. Keizer, V.T. Zaspalis, R.S.A. de Lange, MRS Bulletin (1994) 34.
[6] Y. Ohta, M. Gondaira, K. Kobayashi, Y. Fujimoto, K. Kuroda, AIChE Annual Meeting, San Francisco, USA, 1994.
[7] J. Shu, B.P.A. Grandjean, S. Kaliaguine, Catal. Today 25 (1995) 327.
[8] S.L. Jorgensen, P.E.H. Nielsen, P. Lehrmann, Catal. Today 25 (1995) 303.
[9] S. Uemiya, N. Sato, H. Ando, T. Matsuda, E. Kikuchi, Appl. Catal. 67 (1991) 223.
[10] J.C. Amphlett, M.J. Evans, R.A. Jones, R.F. Mann, R.D. Weir, Can. J. Chem. Eng. 59 (1981) 720.
[11] J.C. Abens, M. Lambrech, P. Marchetti, I. Michalko, D. Patel, Final Technical Report, Energy Research Corporation, Danbury, CT, USA, 1978.
[12] J.C. Amphlett, K.A.M. Creber, J.M. Davis, R.F. Mann, B.A. Peppley, D.M. Sokes, Int. J. Hydrogen Energy 19 (1994) 131.
[13] N.E. Vanderborgh, The Second International Fuel Cell Conference Proceedings, Kobe, Japan, 1996, pp. 323.
[14] P.P. Mardilovich, Y. She, Y.H. Ma, M.H. Rei, The Fourth International Conference on Inorganic Membranes, Gatlinburg, TN, USA, preprint, 1996.
[15] F.A. Lewis, Int. J. Hydrogen Energy 20 (1995) 587.
[16] F.A. Lewis, Int. J. Hydrogen Energy 21 (1996) 461.
[17] J. Shu, B.P.A. Grandjean, E. Ghali, S. Kaliaguine, J. Membr. Sci. 77 (1993) 181.
[18] J. Shu, B.P.A. Grandjean, A. van Neste, S. Kaliaguine, Can. J. Chem. Eng. 69 (1991) 1036.
[19] C.J. Jiang, D.L. Trimm, M.S. Wainwright, N.W. Cant, Appl. Catal. A 93 (1993) 245.
[20] J.C. Amphlett, M.J. Evans, R.F. Mann, R.D. Weir, Can. J. Chem. Eng. 63 (1985) 605.