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Methane Steam Reforming in a Pd-Ru Membrane Reactor

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Abstract−Methane steam reforming has been carried out in a Pd-Ru membrane reactor at 500-600 °C. The membrane reactor consisted of a Pd-6%Ru tube of 100 μm wall thickness and commercial catalysts packed outside of the membrane. The methane conversion was significantly enhanced in the membrane reactor in which reaction equilibrium was shifted by selective permeation of hydrogen through the membrane. The methane conversion at 500 °C was improved as high as 80% in the membrane reactor, while equilibrium conversion in a fixed-bed reactor was 57%. The effect of gas flow rate and temperature on the performance of the membrane reactor was investigated and the results were compared with the simulated result from the model. The model prediction is in good agreement with the experimental result. In order to apply the membrane in practice, however, the thickness of the membrane has to be reduced. Therefore, the effect of membrane thickness on performance of the membrane reactor was estimated using the model.

Key words: Palladium, Pd Membrane, Membrane Reactor, Methane Steam Reforming, Inorganic Membrane

INTRODUCTION

Palladium-based membranes have been extensively studied in membrane reactor configurations to enhance the conversion or selectivity of dehydrogenation or hydrogenation reactions [Hsieh, 1996; Gryaznov and Orekhova, 1998]. In the case of equilibrium-limited dehydrogenation reaction, the close coupling of the reaction with selective permeation of hydrogen through the membrane significantly increased the conversion of the reaction at constant temperature. Reduction of the operating temperature while keeping the same conversion of the dehydrogenation reaction is also possible in the palladium membrane reactor due to the shift of equilibrium toward the hydrogen-producing side. In the mean time, high purity hydrogen could be obtained from the permeate side of the membrane reactor.

In membrane application, palladium is usually alloyed with other metals to increase the mechanical strength, hydrogen solubility and catalytic activity of the membrane toward hydrogen dissociation. Palladium-silver membrane has been commonly used for purification of hydrogen. Palladium-ruthenium alloy is known to be very stable at high temperature up to 550 °C, and the long-term strength of this alloy at high temperature was greater by a factor of 5 than that of pure palladium [Gryaznov and Orekhova, 1998]. Pure palladium membrane is sensitive to poisoning and coking. On the other hand, it was found that palladium-ruthenium membrane had higher resistivity towards poisoning, stabilizing the hydrogen permeation rate for longer time during hydrogenation reaction. With the increase of ruthenium content, the hydrogen permeability through the palladium-ruthenium membrane attained a maximum at a ruthenium content of about 5.5 wt%.

In this study, we used palladium-ruthenium membrane to investigate the enhancement of the conversion of methane steam reforming reaction. In conventional technology, this reaction is carried out in multi-tubular fixed-bed reactors operated at temperatures up to 850 °C. Previous works on palladium-based membranes showed that the equilibrium of the steam reforming reaction could be considerably shifted, resulting in an increase of methane conversion or reduction of operating temperature [Saracco and Specchia, 1994; Adris et al., 1997; Kim et al., 1999]. The higher stability of the palladium-ruthenium membrane and its higher resistivity toward poisoning would be ideal for this membrane to be applied in methane steam reforming reaction. The aim of this study is first to confirm the enhancement of the conversion of the reaction using Pd-Ru membrane, and then to discuss the possibility of using this membrane in practical application.

EXPERIMENTAL

1. Membrane

Pd-6 wt%Ru membrane tubes of 0.95 mm outside diameter and 100 μm wall thickness were supplied from Russia (Ekaterinburg Plant of Nonferrous Metals Processing). Stainless steel tubes of 1/16" outside diameter were connected at either side of a 12.8 cm-long membrane tube by gold welding.

2. Reactor

The reactor consists of a membrane tube placed concentric to an outer quartz tube of 6 mm inner diameter. The nickel catalysts (ICI 46-1) of 30-40 mesh particle size were packed in the annulus region. The total weight of the catalyst was 3.1 g.

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A mixture of methane, water vapor and argon with a molar ratio of 1:4:4 was introduced to the feed side (catalyst side) of the membrane. Water was injected to the feed stream with a pump. In the permeate side of the membrane, argon was used as a sweep gas. The gas composition at the outlet of the membrane reactor was analyzed by using a gas chromatograph (HP5890II) after removal of water from the stream. Methane conversion (X_{CH4}) was calculated by carbon balance as:

$$X_{CH4}=\frac{x_{CO}+x_{CO2}}{x_{CH4}+x_{CO}+x_{CO2}} \quad (1)$$

where x_j denotes the mole fraction of component j.

MODEL

A relatively simple mathematical model was established to simulate the performance of the membrane reactor with catalyst on the feed side. Two independent reactions taking place in the reactor are:

$$CH_4+H_2O=CO+3H_2 \quad (2)$$
$$CO+H_2O=CO_2+H_2 \quad (3)$$

The steady-state material balance for component j in the feed side and permeate side of the membrane reactor is derived by considering longitudinal variation.

In the feed side of the membrane

$$-\frac{d}{dz}(Q_f x_j)-\pi d Q_j^{perm}+Wc/L r_j=0 \quad (4)$$

In the permeate side of the membrane

$$-\frac{d}{dz}(Q_p y_j)+\pi d Q_j^{perm}=0 \quad (5)$$

where Q_f, x_j, Q_p, y_j are total molar flow rate and gas composition in the feed side and permeate side, respectively, d is diameter of the membrane, Wc denotes the weight of catalyst, and L is the length of the membrane reactor.

The permeation rate of component j through the Pd-Ru membrane, Q_j^{perm}, is given for hydrogen as:

$$Q_j^{perm}=K_j(\sqrt{P_f x_j}-\sqrt{P_p y_j}) \quad (6)$$

where P_f and P_p are total pressure in the feed side and permeate side, respectively, and K_j is permeation rate constant. Since only hydrogen can permeate through the membrane, $K_j=0$ for components other than hydrogen.

Reaction rate of component j, r_j, in Eq. (4) is based on catalyst weight and can be expressed as follows.

$$r_j=v_{2j}\, r_2+v_{3j}\, r_3 \quad (7)$$

where v_{2j}, r_2, v_{3j}, r_3 are stoichiometric coefficient and reaction rate for reactions (2) and (3), respectively. The following rate expression is used for reaction (2) [Tsotsis et al., 1993],

$$r_2=k_1 P_{CH4} P_{H2O}-k_2 P_{H2}^3 P_{CO} \quad (8)$$

where k_1 and k_2 are reaction rate constants related to the equilibrium constant for reaction (2), as:

Table 1. Typical reaction conditions and parameters

Methane feed: 2-7.5 cm^3[STP]/min
Feed composition: $x_{CH4}:x_{H2O}:x_{Ar}=1:4:4$
Reactor temperature: 500 °C
Feed- and permeate-side pressure: $P_f=P_p=1$ atm
Catalyst weight: Wc=1.3 g
Membrane length and outer diameter: L=12.8 cm, d=0.095 cm
Permeation rate constant for hydrogen: $K_{H2}=4.7$ cm^3[STP]/min-cm^2-$atm^{0.5}$
Reaction rate constant: $k_1=1.209\times10^{-4}$ mol/s-gcat-atm^2
Equilibrium constants: $K_{p2}=9.398\times10^{-4}$ atm^2
$K_{p3}=5.139$

$$K_{p2}=k_1/k_2=\frac{P_{H2}^3 P_{CO}}{P_{CH4} P_{H2O}} \quad (9)$$

We assume that the water-gas shift reaction (3) is always in equilibrium with the following equilibrium constant,

$$K_{p3}=\frac{P_{H2} P_{CO2}}{P_{H2O} P_{CO}} \quad (10)$$

The governing Eqs. (4) and (5) were nondimensionalized and solved together with Eq. (6)-(10) by IMSL subroutines. In the model, there are no adjustable parameters except for the reaction rate constant k_1 which was determined from the result of a fixed-bed reactor. Typical reaction conditions and parameters are summarized in Table 1.

RESULT AND DISCUSSION

1. Effect of Feed Flow Rate

Fig. 1 shows the effect of the feed flow rate on the methane conversion in the membrane reactor at 500 °C. The methane conversion without a sweep gas flow increased slightly with decreasing the feed flow rate and became close to the equilibrium conversion of 57% which could be obtained in a fixed-bed reactor at relatively low rate of feed flow. With a sweep gas flow of

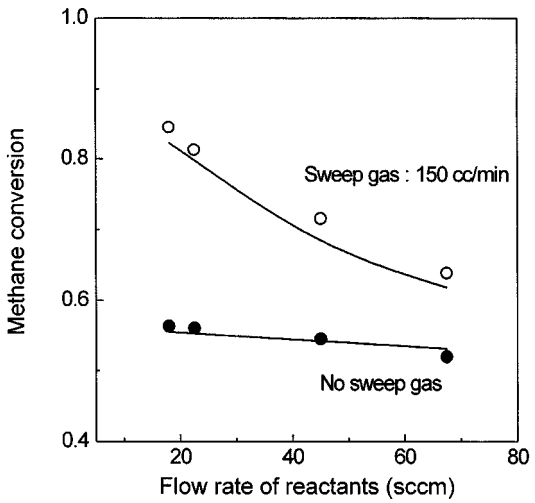

Fig. 1. Effect of feed flow rate on methane conversion at 500 °C.

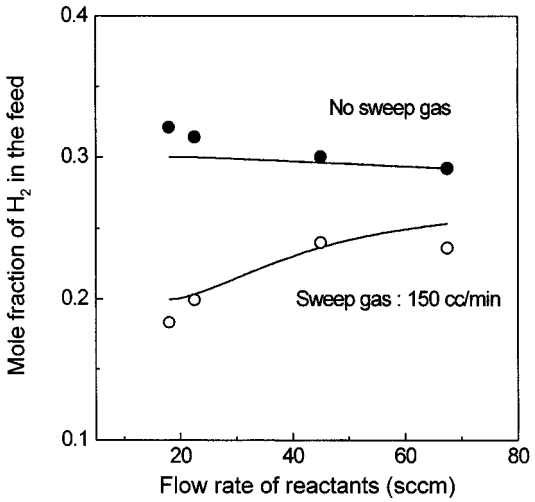

Fig. 2. Effect of feed flow rate on mole fraction of H_2 in the membrane reactor at 500 °C.

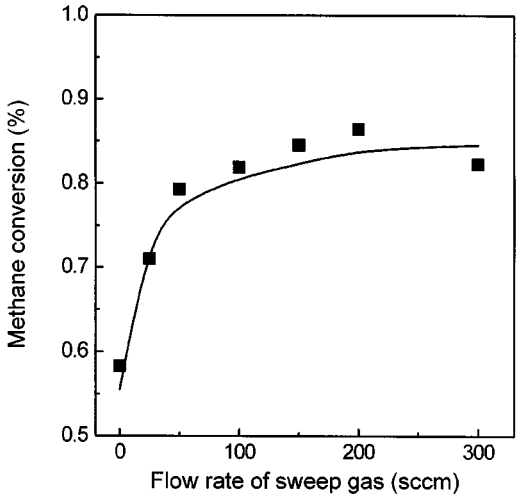

Fig. 3. Effect of sweep gas flow rate on methane conversion at 500 °C.

150 cc/min, the methane conversion increased significantly. At a feed flow of 18 cc/min, the methane conversion was improved to 80%. The difference in conversion with and without sweep gas flow increased with decreasing the flow rate of reactants. The effect of the feed flow rate on the mole fraction of hydrogen at the feed outlet is shown in Fig. 2. Without a sweep gas flow, the hydrogen mole fraction at the feed outlet was about 30% and increased slightly as the feed flow rate decreased. On the other hand, the hydrogen mole fraction in the presence of a constant sweep gas flow decreased below 25% as the feed flow rate decreased.

It's clear from Fig. 1 and Fig. 2 that reaction equilibrium is shifted by using a Pd-Ru membrane reactor in which H_2 partial pressure is lower at the reaction zone due to the continuous removal of H_2 through the membrane. Increasing the feed flow rate in the presence of sweep gas flow decreases the magnitude of the equilibrium shift due to the reduction in the fraction of hydrogen separated by permeation at the same membrane capacity. In addition, at relatively high feed flow rate, the methane conversion is not completely restricted by equilibrium since the methane conversion at higher feed flow rate is lower than equilibrium conversion as shown in Fig. 1. Therefore, methane conversion in the membrane reactor decreases further with increasing the feed flow rate. The solid lines in Fig. 1 and Fig. 2 represent the results estimated from the model indicating that the model predicts closely the performance of a membrane reactor.

2. Effect of Sweep Gas Flow Rate

Fig. 3 shows the effect of sweep gas flow rate on the methane conversion. Increasing the sweep gas flow increases the methane conversion. This is due to the reduction of hydrogen partial pressure in the permeate side, increasing the driving force for permeation and resulting in the higher rates of hydrogen removal from the reaction zone. The increase in conversion, however, becomes relatively small as the sweep gas flow increases. The simulated result from the model depicted as a solid line in Fig. 3 agrees well with the experimental result.

3. Effect of Temperature

As the temperature increases, hydrogen permeation rate through the membrane as well as the reaction rate increase, resulting in the increase of methane conversion as shown in Fig. 4. At 600 °C, the equilibrium conversion in a fixed-bed reactor is 89% while nearly complete conversion of methane can be obtained in a membrane reactor.

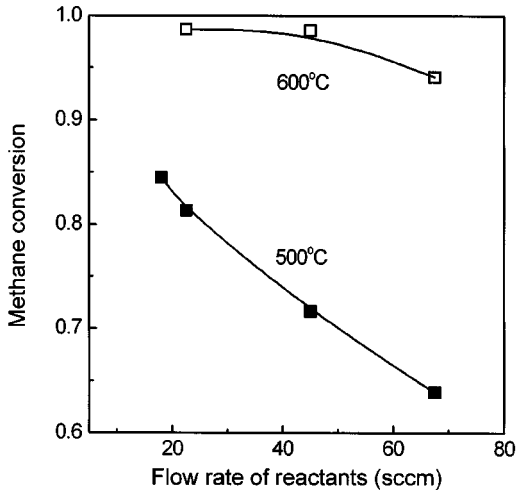

Fig. 4. Effect of temperature on methane conversion in the membrane reactor.

4. Comparison with an SiO_2 Membrane Reactor

Previously, we carried out methane steam reforming in an SiO_2-carrying porous glass membrane reactor which was produced by chemical vapor deposition of SiO_2 on porous glass [Ha et al., 1993]. The performance of a 16 cm-long SiO_2 membrane reactor containing the same amount of catalyst is compared with that of Pd-Ru membrane reactor. Fig. 5 shows that much higher methane conversion can be obtained in the Pd-Ru membrane reactor due to the higher permeation rate of hydrogen through the Pd-Ru membrane. Permeation rate of hydrogen through the SiO_2 membrane at 500 °C is one order of magnitude lower than that through the Pd-Ru membrane: 0.106 cm^3[STP]/min-cm^2-atm for SiO_2 membrane and 4.7 cm^3[STP]/min-cm^2-$atm^{1/2}$ for Pd-Ru membrane. So the extent of equilibrium shift

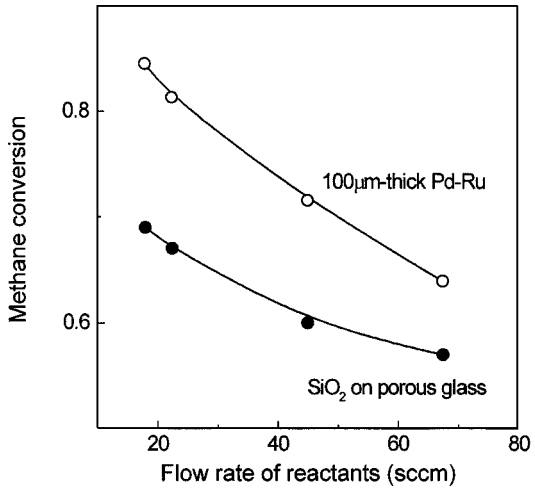

Fig. 5. Comparison of the performance of membrane reactors at 500 °C.

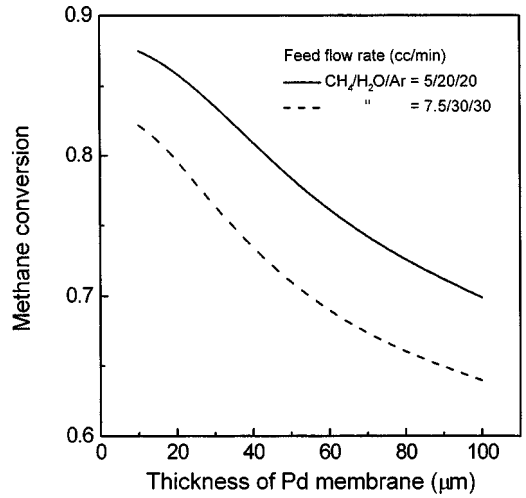

Fig. 6. Estimated methane conversion with respect to the membrane thickness at 500 °C.

is more pronounced in the Pd-Ru membrane reactor.

5. Estimation of the Effect of Membrane Thickness

Since the result from the model prediction agrees well with the experimental result, the effect of membrane thickness on conversion of methane was estimated. Fig. 6 shows that, with decreasing the membrane thickness from 100 μm to 10 μm, the methane conversion increases by 50% due to the enhancement of the hydrogen removal from the reaction zone.

The practical application of the Pd-Ru membrane is quite limited due to the high cost of palladium and relatively low hydrogen permeation capacity of the membrane. Therefore, many attempts have been made recently to produce thinner membranes [Shu et al., 1994]. It is expected from Fig. 6 that Pd-Ru membrane of 10 μm thickness would be used for practical applications. Research is now underway to fabricate thin films of Pd-Ru films on porous ceramic support.

SUMMARY

Methane steam reforming has been carried out at 500-600 °C in a membrane reactor made of a Pd-6% Ru tube. The methane conversion was significantly enhanced in the membrane reactor. The conversion at 500 °C was improved as high as 80% in the membrane reactor while equilibrium conversion in a fixed-bed reactor was 57%. With decreasing the feed flow rate or increasing the sweep gas flow rate, the methane conversion increased considerably. Nearly complete conversion could be obtained at 600 °C. The model estimation is in good agreement with the experimental data. It was found from model prediction that Pd-Ru membrane of 10 μm thickness would have practical applications.

REFERENCES

Adris, A. M., Lim, C. J. and Grace, J. R., "The Fluidized-bed Membrane Reactor for Steam Methane Reforming: Model Verification and Parametric Study," *Chem. Eng. Sci.*, **52**(10), 1609 (1997).

Gryaznov, V. M. and Orekhova, N. V., "Reactors with Metal and Metal-Containing Membranes," in "Structured Catalysts and Reactors," Cybulski, A. and Moulijn J. A., eds., Marcel Dekker, Inc., New York (1998).

Ha, H. Y., Nam, S. W., Hong, S. A. and Lee, W. K., "Chemical Vapor Deposition of H_2-permselective Silica Films on Porous Vycor Glass Supports Form TEOS," *J. Membrane Sci.*, **85**, 279 (1993).

Hsieh, H. P., "Inorganic Membranes for Separation and Reaction," Elsevier Science B. V., Amsterdam (1996).

Kim, J.-H., Choi, B.-S. and Yi, J., "Simulation on the Methane Steam Reforming in Pd-Membrane Reactor," *HWAHAK KONGHAK*, **37**, 210 (1999).

Saracco, G. and Specchia, V., "Catalytic Inorganic Membrane Reactors: Present Experience and Future Opportunities," *Catal. Rev.-Sci. Eng.*, **36**, 305 (1994).

Shu, J., Grandjean, P. A. and Kaliaguine, S., "Methane Steam Reforming in Asymmetric Pd- and Pd-Ag/porous SS Membrane Reactors," *Appl. Catal. A*, **119**, 305 (1994).

Tsotsis, T. T., Champagnie, A. M., Vasileiadis, S. P., Ziaka, Z. D. and Minet, R. G., "The Enhancement of Reaction Yield through the Use of High Temperature Membrane Reactors," *Sep. Sci. Tech.*, **28**, 397 (1993).