ABSTRACT:

The role of hydrogen as an energy carrier became more important to the future energy system. Methane steam reforming (MSR) is one of the most important chemical processes in hydrogen production. To improve the conversion of methane to hydrogen, a hydrogen-permselective membrane reactor with a carbon dioxide absorbent was proposed and investigated. The conversion at 893K in the integrated reactor with CaO as absorbent was almost equal to that at above 1000K in the conventional reactor. Exergy analyses indicated that the large portion of exergy loss for hydrogen production was chemical exergy loss in the case without methane recycle, while thermal exergy loss in the case with recycle use. The exergy loss of this process using the hydrogen-permselective membrane reactor with the CaO-absorbent was estimated about 70% of that by the conventional catalytic reactor. Efficiencies of the integrated reactor process, based on the energy and exergy losses were compared with those of other hydrogen production processes.

KEYWORDS: hydrogen production, membrane reactor, CO2 absorption, exergy analysis

1. Introduction

Methane steam reforming (MSR) is one of the most important chemical processes in hydrogen production. Methane steam reforming involves five species in two reversible reactions.

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & = \text{CO} + 3\text{H}_2 \quad \Delta G_{298} = 206 \text{ kJ/mol}^{-1} \quad (1) \\
\text{CO} + \text{H}_2\text{O} & = \text{CO}_2 + \text{H}_2 \quad \Delta G_{298} = -41 \text{ kJ/mol}^{-1} \quad (2)
\end{align*}
\]

Reaction (1), reforming reaction, is thermodynamically favored by high temperature and low pressure. Reaction (2), water-gas shift, does not depend on pressure and is favored by low temperature. Reaction (3) is the overall reaction.

\[
\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2 \quad \Delta G_{298} = 165 \text{ kJ/mol}^{-1} \quad (3)
\]

The conventional industrial process is carried out in a furnace containing hundreds of tubes packed with catalyst. One possible way to liberate this reaction from the equilibrium limitation and thus attain a high methane conversion is the removal of hydrogen or carbon dioxide produced in the reactor. By employing a hydrogen-permselective membrane, the hydrogen produced by the MSR is removed from the reaction zone so that the chemical equilibrium shifts towards a higher conversion. Based on this concept, hydrogen-permselective membrane reactors have been proposed and investigated for the MSR process. On the other hand, for the removal of carbon dioxide at higher temperatures, calcium oxide carbonation has been proposed. Some research on hydrogen production from methane, coal and biomass with the aid of regenerable calcium oxide absorbent have been reported.

The purpose of this paper is to propose and investigate hydrogen-permselective membrane reactors, a reactor with a carbon dioxide absorbent and a hybrid reactor with both these separation processes for the improvement of MSR, and to estimate the performance of these MSR processes by exergy analysis.

2. Experimental

2.1 Membrane
Two kinds of hydrogen-permselective membrane were prepared and installed in a membrane reactor for methane steam reforming. The first was a ZrO$_2$/SiO$_2$ composite membrane with expected high thermal stability. The second was a Pd membrane well-known for high hydrogen-permselectivity.

Via a metal-alkoxide method [1], a thin layer of the ZrO$_2$/SiO$_2$ composite membrane was coated on the surface of porous ceramic tubing 10 mm in outer diameter, 7 mm in inner diameter, with an average pore diameter of 100 nm (supplied by NGK INSULATORS LTD.) The composition of the coating solutions are listed in Table 1 and the procedure of preparing the composite membrane is outlined in Fig. 1(a).

The Pd membrane was coated on the surface of the porous ceramic tubing by electroless-plating [2-4]. The base ceramic tubing was sensitized and activated by pretreatment with aqueous solutions of stannous chloride and palladium chloride, respectively. The composition of the plating solution is listed in Table 2 and the procedure of preparing the Pd membrane is outlined in Fig. 1(b).

### Table 1. Coating solution for alkoxide

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(OC$_3$H$_7$)$_4$</td>
<td>22.4 ml</td>
</tr>
<tr>
<td>Si(OC$_2$H$_5$)$_4$</td>
<td>0.9 ml</td>
</tr>
<tr>
<td>Y(CH$_3$COO)$_3$·4H$_2$O</td>
<td>1.0 g</td>
</tr>
<tr>
<td>i-C$_3$H$_7$OH</td>
<td>84.8 ml</td>
</tr>
</tbody>
</table>

### Table 2. Electroless-plating

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd[(NH$_3$)$_4$]Cl$_2$</td>
<td>4.7 g</td>
</tr>
<tr>
<td>EDTA·2Na</td>
<td>67.2 g</td>
</tr>
<tr>
<td>NH$_3$ (28% solution)</td>
<td>651.3 ml</td>
</tr>
<tr>
<td>H$_2$NNH$_2$</td>
<td>0.35 ml</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>348.4 ml</td>
</tr>
</tbody>
</table>

2.2 CaO-absorbent
The CaO-absorbent was prepared by thermal decomposition of a powder reagent of calcium carbonate (Junsei Kagaku Co., Assay 99%). After grinding with a mortar and pestle, this powder mixture was formed into column pellets of 4 mm in diameter and length, and dried at 383K for 24 hours. The annealing of the reaction solid was controlled by a programmable temperature controller in an electric furnace. After drying the solid reactants in the furnace at 473K for 4 hours, the temperature of the furnace was raised to 1273 K at 10 K/min, maintained at 1273 K for 3 hours, and decreased to 773 K at 10K/min. All reaction solids were kept at 773 K until just before reaction experiments to prevent reactions with moisture.

2.3 Apparatus
A schematic flow diagram of the experimental apparatus is shown in Fig. 2. A schematic view of the reactor cell is shown in Fig. 3. The column was divided into two sections: adsorbent and membrane.
For the measurement of membrane separation, no catalyst was packed in the reactor cell. For the investigation of reaction, Ru/Al₂O₃ catalyst pellets and alumina balls were packed in the annular region between two coaxial circular cylinders for the length of effective membrane. The inner cylinder was perforated with circular holes of 2 mm, and of 22% open area ratio, protecting the active surface of the membrane from direct contact with the catalyst pellets. The Ru-catalyst, alumina cylinder pellets containing 0.5% ruthenium (diameter: 3.2 mm, length: 3.4 mm, pore volume: 0.33-0.37 cm³/g, superficial density: 1.55 g/cm³; N. E. Chemcat, Co. Ltd.) was used for the steam reforming reaction experiment. The catalyst concentration and the height of catalyst zone were adjusted using alumina balls (diameter: 3.2 mm, superficial density: 3.45 g/cm³). Flexible heaters were used to prevent condensation of water contained in reacted gas mixtures in the tubing, the temperature of which was kept above 423K.

2.3 Evaluation of membrane performance

Pure gas and mixed gas permeations of Pd membrane were evaluated. Each feed pure gas of H₂ and He was introduced from a gas cylinder into the cell. The pressure in the cell was controlled by the pressure-control valve. The pure gas (H₂, He) permeation rates were measured by soap-bubble flow meter. The permeation experiment was carried out at 773K and at 0.15-0.30 MPa absolute on the feed side.

Separation performance of gas mixture was evaluated by the separation factor, \( \alpha_{ij} \), defined by the following equation.

\[
\alpha_{ij} = \frac{y_j}{x_j} \div \frac{y_i}{x_i}
\]  

where \( x_i \) (or \( x_j \)) and \( y_i \) (or \( y_j \)) are the molar fractions of the component \( i \) (or \( j \)) in the feed and permeated gas, respectively.

2.4 Reaction experiment

Reaction experiment was carried out with the following conditions: reaction temperature 623 – 973 K, molar ratio of \( \text{H}_2\text{O} \) to \( \text{CH}_4 \) 1 : 3, gas feed rate 100 – 300 Nml/min, superficial space velocity 0.08 - 0.4 l/s, reaction pressure 0.15-0.3 MPa absolute. The permeation rate of the product gas was measured by the same method used for the gas permeation experiment. The compositions of the gas mixture of the feed and permeated gas were determined by gas chromatography.

3. Experimental Results and Discussions

3.1 Performance of ZrO₂/SiO₂ composite membrane

Figure 4 shows the relationship between the pure gas permeation fluxes of H₂, CO₂, CH₄ and H₂O through the ZrO₂/SiO₂ composite membrane and trans-membrane pressure at 523 K. Permeation fluxes for each gas increase with an increase in pressure.
The permeance of each gas is defined by the slope of the relationships shown in Fig. 4. The main permeation mechanism for all the gases tested except H\textsubscript{2}O was estimated as Knudsen diffusion, while that for H\textsubscript{2}O was estimated as surface diffusion. Figure 5 shows the relationship between the separation factor of gaseous mixture of CH\textsubscript{4}-CO\textsubscript{2} and trans-membrane pressure. Applying the equation of Present-de Bethune [5] to this relationship, the average mean pore diameter of the membrane was estimated at about 4nm.

3.2 Performance of Pd membrane

The theoretical permeation flux through Pd membrane defined by the following equation [6].

\[ J_{H_2} = k e^{(-E/RT)} \left( P_{H_2}^{0.5} - P_{He}^{0.5} \right) \]  \hspace{1cm} (5)

The permeances of H\textsubscript{2} and He through this Pd membrane are shown in Table 3. These results showed that the prepared Pd membranes A and B were highly hydrogen-permselective dense membranes as the permeance of H\textsubscript{2} was about 65 times and 600 times that of He, respectively. For numerical analysis these Pd membranes were considered only H\textsubscript{2} permeable. Pd membranes were used below 773K because of its thermostability.

### Table 3. Permeance through Pd membrane

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeance of H\textsubscript{2}</th>
<th>Permeance of He</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.1 x 10\textsuperscript{-7} [mol/(m\textsuperscript{2} · Pa · s)]</td>
<td>ca. 3.5 x 10\textsuperscript{-10} [mol/(m\textsuperscript{2} Pa s)]</td>
</tr>
<tr>
<td>B</td>
<td>3.1 x 10\textsuperscript{-6} [mol/(m\textsuperscript{2} Pa s)]</td>
<td>4.7 x 10\textsuperscript{-8} [mol/(m\textsuperscript{2} Pa s)]</td>
</tr>
</tbody>
</table>

3.3 Membrane reactor test

Figure 6 and 7 show the effect of space velocity and temperature on methane conversion for three reactors: without membrane, with a ZrO\textsubscript{2}/SiO\textsubscript{2} composite membrane, and with a Pd membrane. Each solid line indicates the equilibrium conversion for each condition. In Fig. 6 the methane conversion for the reactors installed with hydrogen perm-selective membrane became greater than the equilibrium conversion in the case of the ZrO\textsubscript{2}/SiO\textsubscript{2} composite membrane below the space velocity of 0.2 [1/s], and of the Pd membrane below 0.4 [1/s]. In Fig. 7 the methane conversion for both the membrane reactors became greater than the equilibrium conversion in all tested temperature ranges.

![Fig. 6 Conversion vs. space velocity](image1)

![Fig. 7 Conversion vs. Temperature](image2)
3.4 CaO-absorbent reactor test

Figure 8 shows the effect of temperature on methane conversion for the reactor with CaO-absorbent and without a membrane. The solid line indicates the equilibrium conversion for the given condition. In Fig. 6 the methane conversion became greater than the equilibrium conversion in the range from 893 to 1023K. The ranges without absorbent effectiveness, below 873K and above 1023K are in agreement with the equilibrium temperatures for the formation of calcium hydroxide and the pyrolysis of calcium carbonate. Based on this result, 973K as the temperature of the absorbent section was adopted for numerical analysis.

4. Numerical Analysis

4.1 Reactor model

The schematic diagrams of the systems without and with absorbent or membrane are shown in Fig. 9 (a), (b) and (c). Plug flow in the reactor and permeate chamber, uniform temperature in each chamber and no concentration gradient in the vertical direction to the flow are assumed. Material balances of each gaseous component across a longitudinal length dl of the reactor yields the following ordinary differential equations. More detailed derivation of the equations and the numerical integration method were described in previous papers [7-9].

\[
\frac{d\left(s_i \cdot f_i \cdot r_i\right)}{dl} = s_R \cdot \alpha_i \cdot r_{CH_4} \tag{6}
\]

(reactor with catalyst)

\[
\frac{d\left(s_i \cdot f_i \cdot r_i\right)}{dl} = s_R \cdot \alpha_i \cdot r_{CH_4,R} - s_R \cdot \beta_i \cdot r_{CaO} \tag{7}
\]

(reactor with catalyst and absorbent)

(reactor with catalyst and membrane)

Fig. 9 Schematic diagram of reactor for numerical analysis

Fig. 8 Effect of temperature on methane conversion
(In the main chamber (reactor))
\[
\frac{d(f_i \cdot s_R)}{dl} = s_R \cdot \alpha_i \cdot \gamma_{CH_4,R} - \frac{s_R}{h} \cdot j_i \tag{8}
\]

(In the permeate chamber)
\[
\frac{d(u_i \cdot s_P)}{dl} = s_p \cdot \alpha_i \cdot \gamma_{CH_4,P} + \frac{s_R}{h} \cdot j_i \tag{9}
\]

where \(f_i\) (or \(u_i\)), \(\alpha_i\), and \(j_i\) are the flow rate, the stoichiometric coefficient, the permeation flux of component \(i\), respectively, \(s_R\) and \(s_P\) are the cross-sectional area of reactor and permeate chamber, and \(\gamma_{CH_4,R}\), \(\gamma_{CH_4,P}\) are the reaction rate of methane and CaO, respectively. \(\alpha_i\) was used as the value of 1 for \(i = CO_2\) and 0 for the other components.

Fig. 10 Conversion profiles for each reactor

Fig. 11 Gas flux profiles for each reactor (10 min. after start)

Figures 10 and 11 show the results of the simulation [7] using numerical analysis. The reactor is divided into two zones, the absorbent zone and the membrane zone at 0.5 of the dimensionless reactor length. The conversion drop in the case of no absorbent found at 0.5 is caused by the equilibrium conversion drop from
893K to 773K. On the other hand, the reverse reaction is suppressed in the reactor with absorbent because CO₂ is absorbed. It was found that gas mixture through the CaO-absorbent could be utilized in a membrane reactor without the conversion drop occurring at lower temperatures in Fig. 10 and permeated hydrogen flux increases about twice in the reactor with absorbent in Fig. 11.

4.2 Exergy analysis

To consider hydrogen as the secondary energy, the required energy to obtain hydrogen needs to be evaluated on a reasonable basis. In this study the quantitative comparison of the obtained exergy of product and the total exergy supplied in the reaction system was proposed as the evaluation method.

The exergy of a mixture is the sum of the following exergies: the sum of the chemical exergy $E_0$, the sum of the exergy due to temperature change $E_T$, the exergy due to compression $E_P$, the sum of the exergy due to mixing $E_M$. Each exergy is defined by the following equations [10].

$$E = E_0 + E_T + E_P + E_M$$

$$E_0 = \sum n_i e_i^0$$

$$E_T = \frac{1}{T} \int_0^T \left( 1 - \frac{T_0}{T} \right) C_P dT$$

$$E_P = NRT_0 \left( \frac{1}{P_0} - \frac{P}{P^2} \right) \int_0^P dP$$

$$E_M = NRT_0 \sum x_i \ln(x_i)$$

The exergy of each system was calculated by using these equations on the basis of the flow schemes [10-13] shown in Fig.12. On the supposition of ideal heat input and output, the exergy loss of each system was evaluated by converting to the basis per one mole product hydrogen.

Figure 12 Process flow diagram for exergy analysis

The relationship between the exergy loss and temperature is shown in Fig. 13. The exergy loss decreases rapidly with a temperature rise in the lower range, while the decrease becomes gentle in the higher range. Compared with the exergy loss for the conventional reactor, that for the membrane reactor installed with a ZrO₂/SiO₂ composite membrane and a Pd membrane saved 5 – 10 % and 30 – 50%, respectively.

Figure 14 shows the breakdown of the total exergy loss of process in each reactor. Heat exergy loss accounted for most of the total exergy loss in all process. The heat exergy loss of conventional process (MSR) at 893K was smaller than that at 773K because the increase of conversion surpassed that of the required heat exergy. Negative value of chemical exergy loss was derived from unreacted methane. In this analysis unreacted methane was regarded as reusable. The total exergy loss of process with Pd membrane at 773K became as small as that of conventional process at 893K. The processes with CaO-absorbent
indicated smaller exergy loss as the chemical exergy included in CaO was used in addition to the conversion rise mentioned above. Figure 15 shows the details in the heat loss for each unit operation.

Fig. 13 Relationship between exergy loss and temperature

Fig. 14 Breakdown of the total exergy loss of process

Fig. 15 Details in the heat loss for unit operation
5. References