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HYDROGEN PERMEABILITY OF PALLADIUM MEMBRANE FOR STEAM-REFORMING OF BIO-ETHANOL USING THE MEMBRANE REACTOR

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A Palladium membrane was prepared by electro-less plating method on porous stainless steel. The catalytic hydrogen production by steam-reforming of biomass-derived ethanol (bio-ethanol) using a Pd membrane was analyzed by comparing it with those for the reaction using reagent ethanol (the reference sample). And the hydrogen permeability of the palladium membrane was investigated using the same palladium membrane (H_2/He selectivity = 249, at ΔP = 0.10 MPa, 873 K). As a result, for bio-ethanol, deposited carbon had a negative influence on the hydrogen-permeability of the palladium membrane and hydrogen purity. The sulfur content in the bio-ethanol may have promoted carbon deposition. By using a palladium membrane, it was confirmed that H_2 yield (%) was increased. It can be attributed that methane was converted from ethanol and produced more hydrogen by steam reforming, due to the in situ removal of hydrogen from the reaction location.

Keywords: Bio-ethanol, Palladium membrane, Hydrogen permeability.

1. Introduction

The majority of current energy is supplied by combustion of non-renewable energy sources, such as fossil fuels with the attendant release of large quantities of greenhouse gases, especially carbon dioxide (CO_2) and other harmful emissions. Because of the gradual depletion of these fossil fuels, and increased greenhouse gas emissions, there is considerable interest in using alternative sources of energy.[1-3]

Hydrogen energy is one type of alternative energy that also includes solar light, wind-power, geothermal and biomass, etc. The benefits of hydrogen energy are the reduction of the greenhouse effect and the centralization of the emission sources (ex. H_2O). In addition, hydrogen is the most abundant element on Earth, but less than 1% is present as molecular hydrogen gas. The overwhelming majority is chemically bound as H_2O in water and to liquid or gaseous hydrocarbons.[4] Therefore, high-purity hydrogen

must be separated from the mixture including the products and the un-reacted raw materials under the reaction to generate hydrogen.

The dominant industrial process used to produce hydrogen is the steam reforming (SR) of methane. SR of natural gas is a mature technology. But natural gas is a kind of fossil fuel, and its usage fails to provide a solution to deal with the huge amount of carbon dioxide emissions during the reforming processes. In addition, the use of fossil fuels for secondary energy production is non-sustainable.[5] Moreover, an improvement to the environmental benefits can be achieved if hydrogen is produced from renewable sources, as biomass.[6] Biomass products, such as plants, micro-algae, and organic wastes, are also renewable sources. And bio-fuels, which are produced from biomass (for example, bio-ethanol obtained by the fermentation process) can be used as fuel for vehicles. In addition, an important advantage of bio-fuels for inhibition of increase of greenhouse gas is related to the fact that their use is neutral or nearly neutral with respect to CO_2 emissions.[7] Among the various liquid bio-fuels, ethanol is very attractive as it is relatively non-toxic and easy to store and transport.[8]

The EPR (energy payback ratio) value of produced bio-ethanol from corn is low with 1.3.[9] EPR will be lower if hydrogen is made from the bio-ethanol. In this study, bio-ethanol steam reforming was carried out by using surplus bio-ethanol by-produced in the fermentation process in cornstarch production. Bio-ethanol was supplied by Sanwa cornstarch Co. Ltd.[10, 11]

The reforming reaction is known to be considerably shifted to the product side by the removal of hydrogen, and this can be achieved using a Pd membrane which selectively removes hydrogen from the reaction site. A Pd thin film was plated on the outer surface of a porous stainless steel tube by electro-less plating method. The catalytic hydrogen production by steam-reforming of bio-ethanol using a Pd membrane was analyzed by comparing them to those for the reaction using reagent ethanol (the reference sample). We examined the effects of bio-ethanol on hydrogen permeability of Pd membrane.

2. Experimental

2.1. *Membrane reactor setup and catalyst preparation*

The double tubular membrane reactor consists of a outer tubular stainless steel module (length 375 mm, 25.4 mm O. D.) containing the membrane as a inner tubular Pd layer deposited by electro-less plating onto a porous stainless steel support (12.7 mm O. D. SUS 316 L) having actual pore size 0.45 µm determined by bubble point test.[12] The Pd layer of the membrane is deposited via electro-less plating technique[13-15] onto the porous tube.

1wt% Pt/Al_2O_3 catalysts were prepared by the incipient wetness method of Al_2O_3 (diameter: 1.6 mm, sphere, pore volume: 0.93 mL $\cdot$ g^{-1}) using $H_2(PtCl_6)\cdot6H_2O$ as precursor compounds. Appropriate doses of The $H_2(PtCl_6)\bullet6H_2O$aq calculated from the pore volume was added to the alumina. Then the solid material was dried overnight in an

oven at 383K. The resulting catalyst was calcined for 4 h at 873 K. After calcined, 1wt% Pt/Al_2O_3 catalysts (24.2 g) were packed into the shell side of Pd membrane.

2.2. *Steam reforming of bio-ethanol or reagent ethanol*

The experimental setup, illustrated in Fig. 1, includes a High performance liquid chromatography (HPLC) pump (Shimadzu) used for feeding both liquid H_2O, reagent ethanol or bio-ethanol, which are vaporized before entering into the preheating zone. This bio-ethanol is a slightly brown liquid, comprising mainly ethanol (74.6 vol %) and water, with residual amounts of n-propanol, methanol, acetaldehyde and acetone. The reactant was prepared by adding distilled water to the bio-ethanol until the Steam/Carbon ratio reached a value of 4. An aqueous solution of reagent ethanol (Steam/Carbon ration of 4) was used as a reference sample. The total feed flow rate is 0.070 mL·min^{-1}.

Both non-permeated and permeated streams are analyzed by gas chromatograph equipped with Thermal Conductivity Detector (TCD). And aqueous form in the cold trap was analyzed by gas chromatograph equipped with Flame Ionization Detector (FID). In addition, both non-permeated and permeated flow rates are measured by a soap film meter. Prior to the reaction, the packed catalyst was reduced in situ by H_2 gas flowing at 50 mL/min for 2 h at 873 K. The reactions were carried out at pressure difference of 0.10 MPa. A sweep gas of nitrogen was flowed in the tube side to remove the permeated hydrogen. Hydrogen purity and permeation rate in order to observe the hydrogen permeability was measured for 12 hours. No H_2 removal is constructed by simple replacement of the inner membrane tube with a non porous stainless steel tube having the same configuration as the membrane tube.
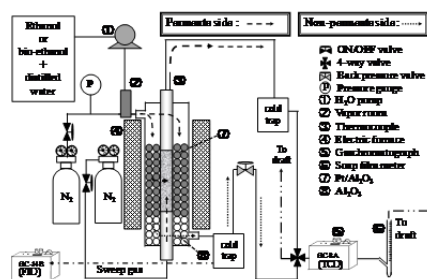

Fig. 1. Experimental setup for steam reforming of bio-ethanol or reagent ethanol.

In this work, the H_2 yield (%) is defined as the ratio of the amount of H_2 produced to that produced when the ethanol steam reforming reaction ($C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$) went to completion.

$$H_2 \text{ yield} = \frac{\text{mol of produced } H_2}{\text{mol of EtOH feed} \times 6} \times 100 \tag{4}$$

And one of by-products, CH_4 yield is defined in terms of the carbon mol% compared to that of the supplied ethanol, and represents carbon recovery as CH_4 gas:

$$CH_4 \text{ yield (carbon mol \%)} = \frac{\text{carbon mol of } CH_4}{\text{carbon mol of EtOH feed}} \times 100 \tag{5}$$

3. Results and discussion

3.1. *Influence of bio-ethanol on hydrogen-permeability of palladium membrane*

To investigate the effect of the bio-ethanol on Pd membrane, the reaction experiments were carried out in order of reagent ethanol (1st), bio-ethanol, reagent ethanol (2nd) using the same Pd membrane (H_2/He selectivity = 249, at ΔP = 0.10 MPa & 873 K). Fig. 2 shows hydrogen permeates flow as a function of time-on-stream for steam reforming for reagent ethanol or bio-ethanol. Fig. 3 shows hydrogen purity as a function of time-on-stream. Ethanol conversions in all these experiments were 100%. Results of bio-ethanol decreased hydrogen permeate flow and hydrogen purity as compared to reagent ethanol (1st).
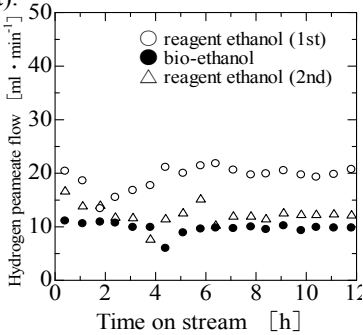

Fig. 2. Hydrogen permeates flow
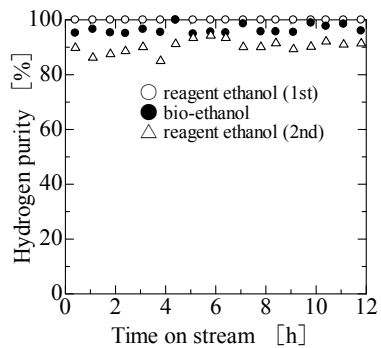as a function of time on stream.

Fig. 3. Hydrogen purity as a function of
time on stream.

In addition, the amount of produced CO was measured in the case of bio-ethanol and reagent ethanol. In the case of bio-ethanol the amount of produced CO was increased as compared to reagent ethanol. Then, steam reforming of reagent ethanol (2nd) was carrie d out under the same operating conditions, but the result shows hydrogen permeate flow and hydrogen purity were not equal to the results of reagent ethanol (1st).

For this reason, it was assumed that produced CO from a minor component contained (detected components: n-propanol, methanol, acetaldehyde, acetone) in the bio-ethanol used as raw materials, have a negative influence on hydrogen-permeability of palladium membrane and hydrogen purity. Similar results were reported in our previous paper.[16] (1) After CO gets dissociated on the palladium membrane, where carbon was deposited. (2) It has exposed that the deposited carbon is not easily reduced in the presence of hydrogen. It is clear that methane was detected with TCD when hydrogen was fed to into the palladium membrane after carbon monoxide and it took time to exceed 9 hours until methane was no longer detected.[16] And so, CO generated from a minor component contained in the bio-ethanol decreased hydrogen-permeability of palladium membrane.

3.2. *Effect of Palladium membrane on steam reforming reaction*

Table 1 shows the reagent ethanol (1st), bio-ethanol and reagent ethanol (No H_2 removal) of average H_2 yield (%) and CH_4 yield (%) in steam reforming, respectively.

Table 1. Average H_2 yield and carbon yield in steam reforming of ethanol.

	H_2 yield [%]	carbon yield [%]
Reagent ethanol (1st)	59.6	4.8
Bio-ethanol	55.6	5.6
Reagent ethanol (No H_2 removal)	40.5	20.4

As described above 3.1. , ethanol conversions in all these experiments were 100%. Nevertheless, H_2 yield (%) value of reagent ethanol (1st) and bio-ethanol was higher than reagent ethanol (No H_2 removal). As reason of these results, it can be explained that this CH_4 yield (%) was lower than the result of reagent ethanol (No H_2 removal). Steam reforming of CH_4 was carried out in the case of hydrogen removal and the CH_4 conversion was greatly enhanced compared with that for No H_2 removal. In other words, in an ordinary catalytic reaction, it may be said that ethanol is converted to mostly CH_4. And then CH_4 is converted to hydrogen. This is why H_2 yield (%) was increased by using a palladium membrane. In addition, the in situ removal of hydrogen from the reaction location may be simplifying the separation step.

3.3. *Effect of contaminants in bio-ethanol on steam reforming reaction*

In order to examine the cause of the hydrogen-permeability degradation of palladium membrane in the bio-ethanol steam reforming reaction, reaction tests were carried out using an aqueous solution of reagent ethanol with added sulfurous acid solution. Table 2 shows the amount of carbon deposition for the reagent ethanol (1st), bio-ethanol, reagent ethanol (No H_2 removal) and reagent ethanol with added 0.1wt% sulfurous acid solution (No H_2 removal), respectively. Although residues of sulfur species in the bio-ethanol could not be detected by the supplier, a sample containing added sulfurous acid was prepared. The poisoning effect of sulfur compounds on the Pt sites of Pt/ZrO_2 was responsible for the deactivation of the bio-ethanol steam reforming reaction.[11]

Table 2 The amount of carbon deposition in steam reforming of ethanol

	Reagent ethanol (1st) (H_2 removal)	Bio-ethanol (H_2 removal)	Reagent ethanol (No H_2 removal)	Added 0.1wt% sulfurous acid solution (No H_2 removal)
carbon deposition [g]	0.006	0.017	0.013	0.028

The amount of carbon deposition is calculated based on produced methane after the each reaction experiment. The membrane and the catalyst were reduced in the presence of hydrogen at 873 K. The calculated results were in the following order: Added 0.1wt% sulfurous acid solution (No H_2 removal) > Bio-ethanol > Reagent ethanol (No H_2 removal) > Reagent ethanol (1st). These show that the sulfur content promoted carbon deposition. And that leads to degradation of hydrogen permeability palladium membrane and/or deactivation of the catalysts.

The amount of carbon deposition was lower when using a palladium membrane. It can be attributed that methane, which is one of the causes of carbon deposition was consumed more by removing of hydrogen from the reaction location. This means that using a palladium membrane leads to inhibit carbon deposition. But the fact that the sulfur content in bio-ethanol promotes the carbon deposition gives the negative influence on hydrogen-permeability of palladium membrane.

4. Conclusions

The steam reforming reactions for bio-ethanol or reagent ethanol using a palladium membrane over Pt/Al_2O_3 catalyst were examined. As a result, by using a palladium membrane (H_2 removal), H_2 yield (%) increased compared with no H_2 removal. And hydrogen selectivity of a palladium membrane was only permeated hydrogen when reagent ethanol (1st). But the hydrogen permeability and the purity were depressed when bio-ethanol was used as a raw material. It has exposed that the deposited carbon was not easily reduced in the presence of hydrogen. And so, CO generated from a minor component contained in the bio-ethanol decreased hydrogen-permeability of palladium membrane.

References

1. D. Cortright, R.R. Davda, J.A. Dumesic, Nature, **418**, 964 (2002).
2. F. Haga, T. Nakajima, K. Yamashita, S. Mishima, React. Kinet. Catal. Lett., **63**, 253 (1998).
3. J. Abayomi, O. Raphael, K. Ajay, Appl. Catal. A, **287**, 159 (2005).
4. L. Schlapbach, A. Züttel, Nature, **414**, 353 (2001).
5. M. Ni, D. Y.C. Leung, M. K.H. Leung, Int. J Hydrogen Energy **32**, 3238 (2007).
6. L. Barelli, G. Bidini, A. Corradetti, U. Desideri, Energy, **32**, 697 (2007).
7. J. Comas, F. Marino, M. Laborde, N. Amadeo., Chem. Eng. J., **98**, 61 (2004).
8. M. Benito, J.L. Sanz, R. Isabel, R. Padilla, R. Arjona, L. Dazaa, J. Power Sources, **151**, 11 (2005).
9. H. v. Blottnitz, M. A. Curran, J. Cleaner Production, **15**, 607 (2007).
10. M. Katoh, T. Yamazaki, N. Kikuchi, Y. Okada, T. Yoshikawa, M. Wada, Kagaku Kogaku Ronbunshu, **34**, 396 (2008).
11. T. Yamazaki, N. Kikuchi, M. Katoh, T. Hirose, H. Saito, T. Yoshikawa, M. Wada, Appl. Catal. B, **99**, 81 (2010).
12. ISO 4003-1977, JIS K 3832-1990.
13. P. P. Mardilovich, Y. She, Y. H. Ma, M. H. Rei, AIChE. J, **44**, 310 (1998).
14. M. Katoh, A. Sondoh, T. horikawa, T. Tomida, Int. J. Mod. Phys. B., **20**, 3866 (2010).
15. M. Katoh, K Chohama, E. Sakata, T. Horikawa, T. Tomida, J. Chem. Eng. Japan, **43**, 745 (2010).
16. M. Katoh, K. Nishihara, K. Kinouchi, K. Chohama, T. Horikawa, T. Tomida, K. Sotowa, Int. J. Mod. Phys. B, **24**, 2833 (2010).