Effect of Co-products on Pd Membrane Performance in Membrane Reforming of Desulfurized Kerosene

Manabu MIYAMOTO¹, Chihiro HAYAKAWA², Yasunori OUMI³ and Shigeyuki UEMIYA¹

¹Department of Chemistry and Biomolecular Science, Gifu University,
1-1 Yanagido Gifu-shi, Gifu 501-1193, Japan

²Department of Materials Science and Technology, Gifu University,
1-1 Yanagido Gifu-shi, Gifu 501-1193, Japan

³Division of Instrument Analysis, Life Science Research Center, Gifu University,
1-1 Yanagido Gifu-shi, Gifu 501-1193, Japan

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Hydrogen production using a Pd membrane reformer from desulfurized kerosene is attractive in view of the portable and domestic use of fuel cells. In the present study, membrane reforming of desulfurized kerosene with a pre-reformer was carried out and compared to that of dodecane, which is the main compound in kerosene. The reactivity of desulfurized kerosene was much lower than that of dodecane, resulting in the low performance of the membrane reformer for desulfurized kerosene. In the pre-reforming and membrane reforming of model kerosene (a mixture of dodecane and *m*-xylene), the performance of the pre-reformer and membrane reformer exhibited a similar trend to those for desulfurized kerosene. This low performance of the membrane reformer may be ascribed to the lowering of Pd membrane performance. From the evaluation of Pd membrane performance in the presence of co-products in the pre-reforming of desulfurized kerosene and model kerosene, polycyclic aromatics such as naphthalenes, anthracene and pyrene reduced the H₂ permeability of Pd membranes.

Introduction

With the increasing attention to global warming, clean and renewable energy is now considered to be essential to solve this world-wide problem. Hydrogen is one of the candidates as clean energy and several hydrogen carrier investigations have been ongoing such as into ammonia (Klerke *et al.*, 2008) and methyl cyclohexane (Okada, 2012). However, since the realization of a hydrogen society through those hydrogen carrier systems will take a long time, fossil fuels assume an important role as a bridging hydrogen carrier for the time being. Steam reforming is a well-established hydrogen production process and has been often used for hydrogen production from a wide variety of hydrocarbons such as natural gas (Kikuchi *et al.*, 1974; Yamaguchi and Iglesia, 2010), liquefied petroleum gas (LPG) (Suzuki *et al.*, 2001; Ahmed *et al.*, 2002), naphtha (Melo and Morlanés, 2005) in petroleum and chemical industries. However, the process efficiency for hydrogen production must be improved before hydrogen can be used as an energy source for fuel cells. Membrane reformers are expected to be one promising technology to produce hydrogen with high energy efficiency because extremely purified hydrogen with higher hydrogen yield than the thermodynamic equilibrium can be obtained

in one-step owing to simultaneous hydrogen separation through palladium membranes in the reformer (Uemiya *et al.*, 1990). Therefore, hydrogen production using a Pd membrane reformer has been extensively investigated from several fuels such as methane (Uemiya *et al.*, 1990; Tong *et al.*, 2005), LPG (Rakib *et al.*, 2010), liquid hydrocarbons (Itoh *et al.*, 2003), and alcohols (Gallucci and Basile, 2008).

Considering portable and domestic use with an increasing attention to fuel cells, kerosene is an attractive hydrogen source because of its easy availability and safety. Owing to the low reactivity of desulfurized kerosene, catalyst development has been the main research for steam reforming of desulfurized kerosene so far (Muramoto *et al.*, 2009; Miyamoto *et al.*, 2015) and less investigation concerning membrane reforming of desulfurized kerosene has been reported. Previously, we investigated the membrane reforming of dodecane to evaluate the membrane reforming of desulfurized kerosene and found that the pre-reforming was essential to achieve sufficient performance of Pd membrane reformers because of its low reactivity (Miyamoto *et al.*, 2011). In this study, we evaluated the performance of pre- and membrane reforming of desulfurized kerosene. From the comparison to dodecane, we report the negative effect of co-products in the membrane reforming of desulfurized kerosene on the Pd membrane performance, which is one of the significant lowering factor for the performance of membrane reformer.

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Correspondence concerning this article should be addressed to S. Uemiya (E-mail address: uemiya@gifu-u.ac.jp).

1. Experimental

1.1 Preparation of Pd membrane

A porous α -alumina tube (OD: 10 mm, ID: 7 mm, length: 30 cm, pore size 0.1 μ m, NGK INSULATORS, Ltd.) was used as a support. A Pd thin layer was deposited by electroless plating on the support. The details of the electroless plating are described in our previous study (Uemiya *et al.*, 1988). The porous α -aluminum tube was washed ultrasonically by ethanol. After drying, Pd nuclei were supported on the outer surface of the porous α -alumina tube by sensitization and activation treatments with stannous chloride and palladium chloride solutions, respectively. These treatments were repeated three times. Then, the palladium nuclei was sufficiently reduced in a hydrazine solution. Palladium was autocatalytically deposited on the outer surface of the porous α -alumina tube in an electroless plating bath containing a tetraammine complex of palladium, ethylenediamine tetraacetic acid, ammonium hydroxide and hydrazine. Except for the effective membrane area (5 cm length at the center of the support), a thick Ag layer was deposited by electroless plating to inhibit hydrogen permeation.

1.2 Reaction tests

Pre-reforming was carried out by using a fixed bed reactor over Ru/ α -Al₂O₃ (2.0 wt% Ru, N.E. CHEMCAT Corporation) at 873 K. Dodecane, desulfurized kerosene and model kerosene (20 wt% *m*-xylene/dodecane mixture) were used as fuel. Fuel and water were vaporized and mixed at the steam to carbon ratio, S/C, of 3 and supplied to the pre-reformer. The outlet gas passed through an ice trap to recover heavy residual oil including the feed fuel. For the performance evaluation of Pd membrane reformer, the outlet gas from the pre-reformer was successively introduced to the Pd membrane reformer. The membrane reforming was performed at 773 K and atmospheric pressure. The heavy residual oil at the retentate side was recovered from the outlet gas of membrane reformer by the ice trap. The outlet gas composition through the ice trap was analyzed by gas chromatography and the flow rate was measured by a soap film meter. The composition of heavy residual oil was confirmed by gas chromatography mass spectroscopy analysis (GC-MS). The flow rate and gas composition at the permeate side were analyzed as well.

1.3 Permeation tests

H₂ permeation tests using Pd membranes were performed at 773 K and atmospheric pressure. The permeated H₂ was swept under an Ar flow. The flow rates in both the retentate and permeate sides were measured by soap film meters, and the gas composition in the permeate side was analyzed by gas chromatography. To evaluate the effect of hydrocarbons/aromatics on the Pd membrane performance, hydrocarbons or aromatics (C₂–C₃ mixture, dodecane, desulfurized kerosene, *m*-xylene, naphthalene, anthracene and pyrene) were supplied with H₂. It was noted that polycyclic aromatics were supplied by dissolving in dodecane. During the per-

Table 1 Partial pressure of additives in H₂ permeation tests

	Partial pressure [kPa]		
	Hydrocarbons/ Aromatics	H ₂	Dodecane (solvent)
C ₂ –C ₃	6.3	95.0	—
Dodecane	2.2	99.1	—
Desulfurized kerosene	2.2	99.1	—
<i>m</i> -Xylene	3.4	97.9	—
Naphthalene	4.9×10^{-1}	91.4	9.3
Anthracene	3.5×10^{-3}	99.6	1.7
Pyrene	3.5×10^{-3}	99.6	1.7

meation tests, the mixture of H₂ and Ar (balance) was supplied in the first 20 min, and vaporized hydrocarbons and aromatics co-existed with the H₂ flow for the next 20 min. This procedure was repeated and the performance deterioration of Pd membranes was determined by the relative H₂ permeability, which is the ratio of H₂ permeability in the co-existence of additives to that under H₂/Ar mixture feed without additives. The partial pressures of the feed components is summarized in **Table 1**.

2. Results and Discussion

2.1 Pre-reforming of dodecane, desulfurized kerosene and model kerosene

Figure 1 shows the conversion of fuels to C₁ products as a function of W/F. The conversion of dodecane was achieved up to 93.7% at 873 K and W/F = 3000 g-cat min C-mol⁻¹. In contrast, the conversion of desulfurized kerosene was only 83.1% at the same reaction condition, and was achieved at a similar conversion to those in pre-reforming of dodecane at more than 6000 g-cat min C-mol⁻¹ (94.3% and 96.8% at the W/F = 6000 and 9000 g-cat min C-mol⁻¹, respectively). These results clearly exhibited that the reactivity of desulfurized kerosene was lower than that for dodecane, although the H₂ yield in pre-reforming of desulfurized kerosene was slightly lower or comparable to those of dodecane. The low reactivity of desulfurized kerosene may be attributed to the variety of compounds containing aromatics which was nearly 20 vol%. **Figure 2** shows the selectivity of C₁ products (C₁ selectivity) in reference to **Figure 1**. For dodecane, the chemical composition of C₁ products corresponded to the thermodynamic equilibrium even at slightly lower conversion to C₁ products. On the other hand, the CO₂ composition was relatively high with low CH₄ composition at W/F = 3000 g-cat min C-mol⁻¹ for desulfurized kerosene compared to those of dodecane. This implies that the reaction rate in C₁ chemistry was possibly lower in pre-reforming of desulfurized kerosene than that of dodecane owing to a large number of components in desulfurized kerosene. With an increase in conversion to C₁ products, the C₁ selectivity approached the thermodynamic equilibrium in pre-reforming of desulfurized kerosene and no significant difference in conversion to C₁ products and C₁ selectivity was observed at 3000 g-cat min C-mol⁻¹ for dodecane and

Fig. 1 Conversion to C_1 products after 180 min reaction in the pre-reforming of dodecane and desulfurized kerosene at 873 K. $S/C=3$; circles: dodecane, squares: desulfurized kerosene; filled symbol: conversion to C_1 products, open symbol: H_2 yield

Fig. 2 C_1 selectivity in pre-reforming of dodecane and desulfurized kerosene at 873 K; DK: desulfurized kerosene, DD: dodecane, T.E.: thermodynamic equilibrium, figures in parentheses were W/F [g-cat min/C-mol]

Fig. 3 Conversion to C_1 products and H_2 yield in pre-reforming of model kerosene as a function of xylene concentration at 873 K. $S/C=3$, $W/F=3000$ g-cat min/C-mol; circles: H_2 yield, squares: conversion to C_1 products

6000 g-cat min $C\text{-mol}^{-1}$ for desulfurized kerosene, respectively, assuming that the membrane reformer shows the comparable performance at those pre-reforming conditions in both reactants.

Figures 3 and 4 show the conversion to C_1 products and

Fig. 4 C_1 selectivity in pre-reforming of model kerosene as a function of xylene concentration at 873 K. $S/C=3$, $W/F=3000$ g-cat min/C-mol

Fig. 5 Performance of membrane reformer in steam reforming of dodecane (DD), desulfurized kerosene (DK) and model kerosene (MK, 20 wt% *m*-xylene/dodecane) at 773 K. $S/C=3$. $W/F=3000$ g-cat min/C-mol; pre-reforming condition: 873 K, $W/F=3000$ g-cat min/C-mol for dodecane and model kerosene, 6000 g-cat min/C-mol for desulfurized kerosene

C_1 selectivity as a function of xylene concentration in pre-reforming of model kerosene. As expected, the conversion to C_1 products and H_2 yield were gradually decreased with an increase in xylene concentration, which indicates the aromatics have a negative effect to catalytic activity. However, the C_1 selectivity was stable at all xylene concentrations and very similar to those of dodecane. Considering the difference in C_1 selectivity in pre-reforming of desulfurized kerosene from those of dodecane and model kerosene, xylene may decrease the degradation rate of reactants to C_1 products, but that did not influence the reaction kinetics of C_1 products.

2.2 Performance of membrane reformer

Figure 5 summarizes the performance of membrane reformer in steam reforming of dodecane, desulfurized kerosene and model kerosene. H_2 removal ratio and H_2 recovery are defined as follows.

$$H_2 \text{ removal ratio} = \frac{H_2 \text{ permeation rate}}{H_2 \text{ production rate}} \times 100$$

$$H_2 \text{ recovery} = \frac{H_2 \text{ permeation rate}}{\text{Stoichiometric } H_2 \text{ production rate}} \times 100$$

Fig. 6 C₁ selectivity in membrane reforming of dodecane (DD), desulfurized kerosene (DK) and model kerosene (MK, 20 wt% *m*-xylene/dodecane), T.E.: thermodynamic equilibrium at 773 K. S/C=3. W/F=3000 g-cat min/C-mol; pre-reforming condition: 873 K, W/F=3000 g-cat min/C-mol for dodecane and model kerosene, 6000 g-cat min/C-mol for desulfurized kerosene

The conversion to C₁ products in the membrane reforming of desulfurized kerosene was slightly high compared to that for dodecane because of higher W/F in the pre-reforming, but the H₂ yield was significantly low and found to be similar to those for model kerosene where the conversion to C₁ product was the lowest in those fuels. It should be noted that the H₂ yield was clearly related to both the H₂ removal ratio and H₂ recovery. These two factors exhibit the performance of Pd membranes in the membrane reformers, and the low H₂ removal ratio and H₂ recovery suggest that these fuels and/or co-products after pre-reforming reduced the Pd membrane performance. From the C₁ selectivity as shown in **Figure 6**, in the membrane reforming of dodecane, the CH₄ selectivity was unchanged from that in the pre-reforming and the increased CO₂ selectivity indicates that selective H₂ removal through the Pd membrane effectively shifted the thermodynamic equilibrium, resulting in high H₂ yield. Indeed, the H₂ yield was the same as the theoretical one at the thermodynamic equilibrium estimated by H₂ recovery as shown in **Figure 7**. Contrary to dodecane, in the membrane reforming of desulfurized kerosene and model kerosene, a significant increase of CH₄ selectivity was observed, although CO₂ selectivity was slightly increased as well. Comparing the equilibrium C₁ selectivity between 773 and 873 K, the C₁ selectivity is likely to approach the thermodynamic equilibrium at 773 K. In other words, high CH₄ selectivity is due to preferential CO hydrogenation rather than CO shift reaction, indicating that the Pd membrane performance was lower than that in the membrane reforming of dodecane. As a result thereof, the H₂ yield in the membrane reforming of desulfurized kerosene and model kerosene decreased from those in the pre-reforming (Figure 7).

Considering the results in membrane reforming, the reactants and/or co-products possibly have a negative effect on the Pd membrane performance. Thus, the co-products were analyzed in the pre-reforming of desulfurized kerosene and model kerosene. **Figure 8** shows the C₂ and C₃ composition in the outlet gas of pre-reforming as a function of xylene

Fig. 7 H₂ yield in the membrane reforming dodecane (DD), desulfurized kerosene (DK) and model kerosene (MK, 20 wt% *m*-xylene/dodecane) at 773 K; solid line: thermodynamic equilibrium estimated by H₂ recovery, dashed line: H₂ yield in pre-reforming

Fig. 8 C₂-C₃ product composition in pre-reforming of model kerosene as a function of xylene concentration

concentration in model kerosene. In the pre-reforming of dodecane (0% xylene concentration in Figure 8), the concentration of C₂ and C₃ gases were under the detection limits, suggesting degraded dodecane was immediately converted to C₁ products. In contrast, the composition of C₂-C₃ products increased with an increase in xylene concentration in the feed. It is well-known that olefins (ethylene and propylene) are readily reacted and produce carbonaceous species (Cai *et al.*, 2002). Additionally, considering the concentration of aromatics decreased the conversion to C₁ products (Figure 3), the changes in aromatics contents have an impact on the performance of membrane reformer because aromatics also pose coking problems (Trimm, 1997). The product distributions of heavy residual oil, which was recovered from an ice trap in the pre-reforming of desulfurized kerosene, exhibited the residual oil included much more heavy compounds than desulfurized kerosene, and polycyclic aromatics such as alkyl naphthalenes, anthracene and pyrene were notably increased as in the **Figure 9**, although the estimated concentration of those polycyclic aromatics in the outlet gas was very low as summarized in **Table 2**. For pre-reforming of dodecane, however, no polycyclic aromatics

Fig. 9 Gas chromatograph of (a) desulfurized kerosene, (b) dodecane, and residual oil in pre-reforming of (c) desulfurized kerosene and (d) dodecane; the numbers in the figure are (1) 2-methylnaphthalene, (2) 1-methylnaphthalene, (3) 1,5-dimethylnaphthalene, (4) anthracene and (5) pyrene

Table 2 Concentration of polycyclic aromatics in products in pre-reforming of desulfurized kerosene

	Concentration [%]
Naphthalene	0.18
Anthracene	$<1.0 \times 10^{-3}$
Pyrene	$<1.0 \times 10^{-3}$

were observed in the residual oil.

2.3 Influence of additives on Pd membrane performance

From the results as mentioned above, the decrease in Pd membrane performance may be ascribed to reactants and/or co-products, particularly olefins and aromatics. Then, the Pd membrane performance was evaluated in the presence of those compounds. **Figure 10** shows the relative H_2 permeability which is defined as the ratio of H_2 permeability with additives and without additives. The concentration of additives shown in Table 1 was adjusted over those in the outlet gas of pre-reforming as shown in Table 2. The relative H_2 permeability for dodecane, *m*-xylene, desulfurized kerosene and C_2 - C_3 mixture was found to be over 1, indicating those compounds did not reduce the Pd membrane performance. It should be noted that the relative permeability for *m*-xylene and desulfurized kerosene reached 1.05 at the initial stage. This is attributed to the gradual activation of Pd membranes during the permeation tests. On the other hand, it is interesting to note that the relative H_2 permeability for naphthalene, anthracene and pyrene was less than 1 and the results clearly exhibited that these polycyclic aromatics decreased the Pd membrane performance. However, as shown in **Figure 11**, the decreased H_2 permeation flux by polycyclic aromatics could be recovered to the initial value by the feed of H_2 and Ar. Therefore, this lowering of Pd membrane performance might be caused by physical adsorption of those compounds on the Pd membrane surface.

Fig. 10 Effect of hydrocarbons and aromatics on Pd membrane performance at 773 K

Fig. 11 H_2 permeation flux on Pd membrane with co-existing of anthracene at 773 K with anthracene (triangles) and without anthracene (circles)

Conclusions

Pre-reforming and membrane reforming of desulfurized kerosene and model kerosene were evaluated and compared to those of dodecane. The reactivity of desulfurized kerosene in pre-reforming was significantly lower than that of dodecane. From the pre-reforming of model kerosene, the conversion to C_1 products decreased with an increase in xylene concentration. For membrane reforming, the H_2 yield for desulfurized kerosene was significantly lower compared to that for dodecane, owing to the lower H_2 membrane performance, although the conversions were similar. From the

evaluation of co-products, C₂–C₃ gases and polycyclic aromatics were found to increase after pre-reforming and the effect of these compounds on Pd membrane performance was evaluated. As a result thereof, lowering of the H₂ permeability of the Pd membrane was observed in the presence of polycyclic aromatics. This indicates that polycyclic aromatics are poisoning compounds to Pd membranes which caused the lowering of membrane reformer performance. However, this negative effect is expected to be reversible.

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