Preparation of Double Layer Membrane Combined with Palladium Metal and FAU Zeolite for Catalytic Membrane Reactor

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The preparation of a double-layer membrane by the combination of Pd metal and FAU zeolite was attempted to enhance the catalytic activity of the membrane reactor. The membrane was successfully synthesized on a porous α-Al2O3 support tube by the hydrothermal synthesis of the FAU zeolite layer followed by chemical vapor deposition of the Pd layer. The thicknesses of the FAU and Pd layers were ca. 5 µm and 1 µm, respectively. The membrane functioned efficiently as a hydrogen separation membrane without deterioration, due to the rigid connection of each layer. During the model reaction, such as the reaction of benzene and permeated hydrogen species from Pd membrane, the inner surface of the Pd layer that was in contact with the FAU layer exhibited high hydrogenation activity, in contrast to the outer surface. Scanning electron microscope observations reveal that one of the reasons for this observed difference is the roughness of the inner surface. Loading of Pd particles in the micropores of FAU zeolite layer by ion-exchange treatment resulted in enhancement of the hydrogenation activity. The FAU zeolite layer is suitable for loading of the highly dispersed active metal particles. The combination of Pd metal membrane and fine metal particles has potential for acceleration of catalytic membrane reactions. [doi:10.2320/matertrans.MF201402]

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1. Introduction

Pd thin metal membrane can separate hydrogen from mix gas by the lattice diffusion mechanism. Considerable attention has been paid to Pd membranes due to their applicability to the separation of high-purity hydrogen and catalytic membrane reactions. The catalytic Pd membrane reactor has been extensively investigated for dehydrogenation and hydrogenation reactions.1,2) For example, in the steam reforming of methane, the combination of a Pd membrane and a catalyst can be used to separate high-purity hydrogen with a single reactor and reduce the influence of the equilibrium limitation by removing the hydrogen. Our group investigated the direct hydroxylation of benzene to phenol. The active oxygen species for a direct hydroxylation is produced by the reaction of oxygen and permeated hydrogen on a Pd membrane.3,4) In this case, the Pd membrane functioned both as the hydrogen separator and as the catalytic active site. Although the surface of the Pd membrane functions effectively as a catalytically active site due to the supply of dissociated hydrogen species through the membrane, the surface area is relatively small compared with that of common supported catalysts.

In general, the Pd membrane is prepared by deposition on a porous support tube, i.e., stainless steel and ceramic tubes. Some researchers have used the porous support tube as the site for the loading of active metal species in order to enhance the catalytic performance. Tokyo Gas Co. Ltd. reported the combination of a Pd membrane and a NiO-yttrium stabilized zirconia support for use in the steam reforming of natural gas.5) Our group reported the effect of loading various metal particles into the macropores of α-Al2O3 on the direct hydroxylation of benzene.6) Loading with Cu enhanced the catalytic activity by the bi-functional effect of the Cu and Pd combination. Although effects on the catalytic activity were observed based on the metal loading, the surface area of the α-Al2O3 tube was too small for effective functioning as a catalytically active site.

In contrast to the supports with macropores described above, zeolite membranes have ordered micropores and high surface area, and can be prepared on the porous support tube by hydrothermal synthesis. In the last two decades, a number of studies have reported the preparation of zeolite membranes and their application to the selective separation of gases and membrane reactions.7–9) Recently, attempts were made to prepare a zeolite layer on a porous support for use as a Pd membrane. Bosko et al. reported the preparation of NaA zeolite on porous stainless steel as a diffusion barrier.10) Guo et al. reported the preparation of a silicate-1 layer on porous α-Al2O3 for benzene hydroxylation.11)

In this study, we attempted the preparation of a double layer membrane combining FAU zeolite (faujasite) and Pd metal on a porous α-Al2O3 tube (Fig. 1(a)). FAU zeolite has a three-dimensional microporous structure with a pore size of 0.74 nm, and a surface area of ca. 600 m²/g. FAU is mainly used as the cracking catalyst in the production of petroleum fractions by the fluid catalytic cracking process. Consequently, in the double layer membrane produced by the combination of Pd and FAU zeolite, the zeolite layer is expected to act as the loading site for highly dispersed metal particles by ion-exchange treatment. In addition, the FAU zeolite layer is expected to accelerate the membrane reaction by concentrating the reactant in the micropore of the zeolite. FAU zeolite might also be effective for membrane reactions with hydrogen, and the removal of gases that interfere with the Pd membrane might be expected. In fact, the FAU membrane has been used for CO2 separation.12)

In the current study, the optimal method for preparing the Pd-FAU double layer membrane was investigated. FAU zeolite was initially prepared by hydrothermal synthesis under various synthesis conditions. Subsequently, a Pd layer was deposited on the FAU membrane. FAU zeolite is not
stable in highly alkaline solutions, which makes the conventional electroless plating method for the preparation of the Pd membrane unsuitable. Hence, Pd was deposited by chemical vapor deposition (CVD) treatment. The catalytic activity of the prepared membrane was investigated by a model catalytic reaction, in this case, the hydrogenation of benzene, to evaluate the features of the membrane. The ion-exchanged Pd-FAU membrane was then prepared (Fig. 1(b)). The effect of loading Pd metal into the micropores of the FAU zeolite layer was evaluated by the model reaction.

2. Experimental

2.1 Preparation of membrane

The double layer membrane was prepared on a porous support tube by the consecutive deposition of FAU zeolite prepared by hydrothermal synthesis and a thin Pd layer by CVD. A porous $\alpha$-Al$_2$O$_3$ tube (200 mm length, 2.0 mm OD, 1.6 mm ID, 0.15 $\mu$m average pore size, and 4.5 m$^2$/g specific surface area) was prepared as the support material.

First, the FAU zeolite layer was prepared by hydrothermal synthesis based on a previous report.13) Powdered FAU zeolite (NaY; Tosoh Corporation 320NAA) was rubbed on the surface of the porous $\alpha$-Al$_2$O$_3$ tube as nucleation sites for growing of the zeolite crystals. The synthesis solution was composed of sodium aluminate (0.33 g), sodium hydroxide (1.31 g), sodium silicate solution (3.23 g) and water (40 g: H$_2$O = 3000 or 50 g: H$_2$O/Al = 4000), which were stirred for 4h at room temperature. The tube and solution were kept in an autoclave equipped with a Teflon inner case (250 mm inner length, 12 mm inner diameter). The autoclave was horizontally settled in the heating chamber at temperatures of 80°C, 85°C, and 90°C for 19 h. After removing the heating chamber, the sample was washed in distilled water and dried in air at 90°C. The structure of the zeolite was confirmed by X-ray diffraction (XRD; Mac Science MXP-18) and scanning electron microscopy (SEM; Hitachi S-800).

After confirming the FAU structure, the Pd layer was deposited on the outer surface of the zeolite layer.5) Both ends of the FAU membrane tube were connected to the dense $\alpha$-Al$_2$O$_3$ tube (70 mm length, 2.0 mm OD, 1.0 mm ID) using silicon sealant (Permatex, Ultra copper) for setting in the CVD chamber. The chamber was composed of stainless steel and equipped with two electric heaters for efficient heating of the membrane tube and Pd source (Pd(COOCH$_3$)$_2$ powder), which were placed at the bottom of the chamber. Two rotary pumps were connected to the chamber to evacuate the inner and outer chambers of the tube, separately. Under the vacuum conditions, the membrane tube was heated to 250°C, while the Pd(COOCH$_3$)$_2$ powder on the flat plate was heated at 160–230°C for 2 h. The sublimated Pd(COOCH$_3$)$_2$ was deposited on the outer surface of the FAU zeolite membrane. During the deposition of Pd, the partial pressure of the inner tube was kept lower than that of the outer tube, resulting in a defect free Pd layer that rigidly adhered to the membrane tube.

Ion exchange of Na with Pd in the FAU zeolite layer was performed for several samples. Ion exchange was carried out in a 1 mmol/l [Pd(NH$_3$)$_4$](NO$_3$)$_2$ solution for 17 h at 25°C. After ion exchange, the membrane tube was washed in distilled water for 12 h and dried in air at 110°C. This treatment was repeated for two cycles. The loading amount of Pd was calculated from the Pd remaining in the solution as determined by ICP analysis.

2.2 Model reactions

Hydrogen permeation measurement and catalytic reaction were carried out in a continuous flow reactor (Fig. 2). In this reactor, the inside gas and outside gas can be alternatively varied using a 4-way valve in order to evaluate the catalytic activity of both the inner and outer membrane surfaces. The flow rate of the gases was controlled by mass flow controllers. The membrane tube was cut to a length of 6 cm and placed inside a stainless steel tube reactor with an inner diameter of 3 mm. Both ends of the tube were fixed with a stainless steel joint, which can be supplied with the reaction gases for the inner and outer membrane surfaces, separately. The membrane tube was connected to the joints using perfluoro plastic O-rings. The reactor was heated up to 200°C in the heat chamber. The products could be analyzed using the on-line sampling valves and two on-line gas chromato-
One GC was equipped with a thermal conductivity detector (TCD), and the other was equipped with a flame ionization detector (FID). The TCD-GC used packed columns (Molecular sieve 13X, 2 m; Gasukrupak 54, 2 m) for the analysis of inorganic gases, and the FID-GC used a TC-WAX capillary column (30 m, GL Science Inc.) for the analysis of organic compounds.

H₂ permeation tests were performed by introducing H₂ gas (100 mL/min) into the outer surface of the Pd membrane tube. The hydrogen pressure was changed from 0 kPa to 100 kPa using the back pressure regulator, while the permeate side of the membrane was kept below atmospheric pressure with He sweep gas (20 mL/min). The flux of hydrogen was measured using an automatic soap-film flow meter.

As the model reaction, hydrogenation of benzene was carried out by permeating hydrogen species through the Pd layer. The activities of both the inner and outer Pd surfaces were measured separately to compare the effect of contact with the FAU layer. The gas mixture of the hydrogen supply side was 0–10 mL/min of H₂ and 0–10 mL/min of He, while that of the permeate side was 2 mL/min for N₂ and 18 mL/min for He, including benzene vapor. Benzene was fed at a rate of 6.24 µL/h by using a microsyringe pump; and was converted into a gas at 0.03 mL/min. N₂ was used as an internal standard gas for calculation of the flow rate, because the total flow rate was not constant due to the permeation and reaction of hydrogen. By switching the 4-way valve (Fig. 2), the reaction site was varied for both the inside and outside of the Pd layer.

For comparison with the catalytic activity using the permeated hydrogen species, the reaction of a mixed gas was investigated. In this case, H₂, N₂, He and benzene were mixed and supplied to the inside of the membrane. The rate was the same as that used in the membrane reaction, except in the case of H₂. The H₂ flow rate corresponded to the hydrogen permeation rate used in the membrane reaction, at the same temperature. The outside of the membrane was sealed with Teflon tape to prevent H₂ permeation to the opposite side of the Pd layer.

For comparison with hydrogenation, the oxidation of benzene was performed by supplying a mixture of O₂ and benzene to react over the inner or outer membrane surfaces, respectively. The gas supply rate was 2 mL/min of O₂, 2 mL/min of N₂, and 16 mL/min of He, and benzene was supplied at the same rate as used in the hydrogenation.

3. Results and Discussion

3.1 Characterization of double-layer membrane

First, the synthesis condition of FAU zeolite layer was investigated. Figure 3 shows the XRD spectra of FAU zeolite membrane samples prepared under various synthesis conditions. Although the strong peaks were attributed to the α-Al₂O₃ support tube, the weak peaks observed for each condition corresponded to the standard diffraction pattern of FAU zeolite (Fig. 3 label (8)), suggesting the successful synthesis of the FAU zeolite membrane. The intensity of the FAU peaks increased with increasing synthesis temperature. The morphology of the samples labeled (2) and (5) in Fig. 3 are shown in Fig. 4. The SEM photographs clearly show the FAU crystals over the surface of the support tube (Fig. 4(a)). A dense layer of FAU zeolite of about 5 µm thickness completely covered the α-Al₂O₃ support (Fig. 4(b)). However, the large crystals of FAU zeolite were aggregated on a dense layer of ca. 30 µm thickness, which had large grain boundaries. Excessive crystal growth is not suitable for the Pd layer coating because of the difficulty in blocking of the grain boundary by deposition of Pd. The thick FAU layer might limit the efficient diffusion of gases. The SEM image of the FAU membrane prepared under milder synthesis conditions (temperature: 85°C, H₂O/Al = 4000) indicated a small crystal size (Fig. 4(c)) and a thin FAU layer of less than...
5 µm (Fig. 4(d)). Hence, the membrane prepared under these conditions was used for the subsequent CVD treatment.

The Pd layer was deposited by CVD treatment of the surface of the FAU zeolite membrane. After Pd coating by CVD, the surface color of the membrane changed from white to silver. The double layer structure was confirmed by SEM observation (Fig. 5). The α-Al2O3 support, FAU layer and Pd layer were individually observed in the cross-sectional image (Fig. 5(a)). A portion of the FAU layer was embedded in the pores of the α-Al2O3 support, suggesting a tight connection. The thicknesses of the FAU and Pd layers were ca. 5 µm and 1 µm, respectively. The morphology of the upper surface of the membrane (Fig. 5(b)) was similar to that of the zeolite (Fig. 4(c)). Pd was densely coated along the FAU zeolite crystal layer. To confirm the dense structure of the Pd layer, it was removed from the FAU layer by dissolving the FAU zeolite using hydrofluoric acid. The Pd layer was unglued as a thin metal sheet indicating that Pd completely covered the zeolite surface. Figure 5(c) shows the SEM photograph of the inner surface of the unglued Pd membrane, which made contact with the FAU layer. The imprint of the FAU layer was embossed on the inner surface of the Pd sheet, giving rise to a rough surface.

Figure 6 shows the permeation fluxes of hydrogen against the square root of the differential pressure at 200°C over the Pd-FAU double layer membrane. The permeation flux of H2 corresponded well with Sieverts’ law,14) which suggests that the Pd layer of the double layer membrane worked as a hydrogen separation membrane without defects. The permeation coefficient was 1.2 × 10⁻⁴ mol s⁻¹m⁻²Pa⁻¹ (200°C). The exterior of the membrane remained unchanged after the permeation test, which indicated that the connections between the α-Al2O3 support, and FAU zeolite layer and Pd layer were rigid as shown in Fig. 5.

### 3.2 Catalytic activity of model reactions

To evaluate the catalytic activity of the double-layer membrane, the hydrogenation of benzene was performed by various reaction modes (Fig. 7). The hydrogenation occurred at the surface of the Pd layer. The sole product was cyclohexane. When the reaction was carried out over the inner membrane by using permeated hydrogen species, the conversion of benzene was 2% at 120°C and increased with temperature (Fig. 7, ◇). The conversion reached ca. 9% at 180°C, and that was almost same at 200°C. The phenomenon has been reported by many researchers.15-17) It is attributed to the competitive adsorption of the benzene and hydrogen molecules. At the high temperature, the surface coverage of benzene decreased.18) In contrast, the activity was relatively low when the reaction was carried out over the outer surface (Fig. 7, ■). The activity of the inner surface was higher than that of the outer surface. In the reaction using mixed hydrogen, the activity of the inside surface was poor (Fig. 7, ○) in contrast to the reaction employing permeated hydrogen species. The results of these reactions suggest that the inner surface of the Pd layer, which made contact with the FAU layer, exhibited high activity with the permeated active hydrogen species.

To compare the reactivity of permeated hydrogen and mixed hydrogen, the effect of the hydrogen concentration
was investigated at 160°C (Fig. 8). By using mixed hydrogen, the conversion increased linearly with increasing hydrogen flow rate, whereas high conversion was observed by using the permeated hydrogen species. In particular, at a low hydrogen supply rate (< 2 mL/min), a significant difference was observed using the mixed hydrogen and permeated hydrogen species. In general, permeated hydrogen species were combined and desorbed as hydrogen molecules over the surface of Pd. Under this condition, however, most of the permeated hydrogen was consumed by reaction with benzene. The dissociatively activated hydrogen species were directly supplied to the surface of membrane from the inside of the Pd layer. Hence, the reactivity was high at the low hydrogen supply rate. This corresponds to control of the surface concentration of hydrogen and the reactivity by the permeation rate.

The catalytic activity of the inner and outer surfaces was also confirmed by the oxidation of benzene using mixed oxygen gas as shown in Fig. 9. The products were CO₂ and H₂O for the reaction over both surfaces. Although, the conversion of benzene increased with increasing temperature, the activity of the reaction carried out over the inner membrane was higher than that over the outer membrane. The reasons for the high activity over the inner Pd membrane which was close to the FAU layer are as follows. (i) the surface roughness of Pd surface caused by the contact with FAU zeolite layer as shown in Fig. 5(c), (ii) the effect for concentrating benzene in the intrinsic micropores of FAU zeolite layer, and (iii) high reactivity of active hydrogen species at the interface of Pd and FAU zeolite layer. FAU zeolite is superior to the surface hydrogen transfer. Hence, the active hydrogen species might be sufficiently supplied at the interface of Pd and FAU zeolite layer.

### 3.3 Catalytic activity over ion-exchanged Pd-FAU membrane

The inner surface of the Pd layer of the double layer membrane exhibited high activity for hydrogenation with the permeated hydrogen species. As the next step, Pd particles were loaded into the micropores of the FAU zeolite by ion exchange of Na with Pd. The loading amount of Pd was ca. 4 mass% by ICP analysis. The FAU zeolite has relatively numerous ion-exchange sites compared with other types of zeolites such as ZSM-5 and mordenite, owing to the Si/Al ratio. ZSM-5 and mordenite are synthesized with a high Si/Al ratio over 15.

The hydrogenation of benzene was performed over the Pd ion-exchanged (IE-FAU-Pd) membrane (Fig. 10). The conversion of benzene with the permeated hydrogen species reached 17% at 200°C, which was almost double the conversion over FAU-Pd (Fig. 7). In contrast, the catalytic activity with mixed hydrogen was under 3% at all temperature range, suggesting that the combination of the IE-FAU-Pd membrane and the permeated hydrogen species from the Pd layer exhibited high catalytic performance. As mentioned in section 3.2, FAU zeolite is superior to the surface hydrogen transfer. It might effect for the catalytic performance by the supply of active hydrogen species from Pd layer to the Pd particles through the surface of FAU zeolite.

Note that the hydrogen permeation rate of IE-FAU-Pd membrane was smaller than that of FAU-Pd membrane.
shown in section 3.2. It is mainly due to the difference of the thickness of Pd layer. The permeation rates under the reaction condition were 1.6 mL/min and 0.5 mL/min for FAU-Pd and IE-FAU-Pd membrane, respectively. Under 160°C, the conversion of benzene over IE-FAU-Pd membrane (Fig. 10) was smaller than that over FAU-Pd (Fig. 7). It is responsible for the insufficient supply of hydrogen species owing to the low hydrogen permeation rate. Under the sufficient supply of active hydrogen species over 160°C, the advantage of ion-exchange treatment clearly appeared.

The ion exchange is not limited to Pd but other metals may be used to produce a bi-functional catalytic effect. The FAU layer works well as the support of metal particles.

4. Conclusion

The preparation of a double-layer membrane by the combination of FAU zeolite and Pd metal was attempted as a first step in the preparation of structured membrane catalysts with enhanced membrane catalytic activity.

A double layer membrane was successfully synthesized on an α-Al2O3 support tube by the hydrothermal synthesis of FAU zeolite and successive CVD treatment with Pd. The thicknesses of the FAU and Pd layers were ca. 5 μm and 1 μm, respectively. The double layer membrane functioned as a hydrogen separation membrane. The permeation flux of H2 corresponded well with Sieverts’ law. No change in the morphology of the membrane was observed during the permeation test, due to the rigid connection of the α-Al2O3 support and both the FAU and Pd layer.

The inner surface of the Pd layer, which made contact with the FAU layer, exhibited a high hydrogenation activity using the permeated active hydrogen species. The outer surface of the Pd layer had poor catalytic activity. The high activity may be attributed in part to the roughness of the inner Pd surface.

The FAU layer has a high surface area due to the intrinsic micropores. Metal particles can be loaded into the pores by ion-exchange treatment. Loading of dispersed Pd particles into the micropores of the FAU layer by ion exchange enhanced the hydrogenation activity. The double layer membrane has the potential for the acceleration of catalytic membrane reactions.

REFERENCES