Composite Membranes of Group VIII Metal Supported on Porous Alumina

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Asymmetric membranes consisting of palladium, ruthenium and platinum deposited on the surface or inside the pores (average size, 200 nm) of a tubular alumina membrane were prepared by the chemical vapor deposition (CVD) technique. Sublimation and decomposition temperatures of their acetylacetonato complexes used as metal sources for CVD were important factors in preparing the membranes selected for hydrogen separation. Among the membranes prepared by CVD, the palladium membrane gave the highest flux of hydrogen and was about 1.6 times higher than a dense palladium membrane with a thickness of 4.5 μm prepared by an electroless plating technique. The hydrogen permeation through the membranes prepared by CVD are related to the surface diffusion of spillover hydrogen.

Introduction

Palladium-based membranes have been applied to membrane reactors in which a variety of hydrogen-producing reactions such as the water gas shift reaction, steam reforming of methane, dehydrogenation of hydrocarbons, and decomposition of hydrogen sulfide and ammonia have been conducted (Armor, 1989; Hsieh, 1991; Shu et al., 1991; Saracco and Specchia, 1994; Zaman and Chakma, 1994; Kikuchi, 1995). In our previous studies (Uemiya et al., 1988, 1991; Kikuchi and Uemiya, 1991), we prepared a composite membrane consisting of a thin palladium film (4.5–13 μm) supported on a porous alumina tube with minute, controlled pores 200–300 nm in diameter by an electroless-plating technique. The composite membrane had an extremely high selectivity and exhibited a hydrogen flux at least 10 times greater than that of a commercial palladium-based membrane with a thickness of 150 μm. With the development of our composite membrane as a starting point, much effort has been devoted to the preparation of various excellent palladium-based composite membranes by electroless plating (Govind and Atnoor, 1991; Shu et al., 1993; Yeung et al., 1995; Jamaa et al., 1996) chemical vapor deposition (CVD) (Yan et al., 1994), the sol-gel method (Chai et al., 1994; Zhao et al., 1995), spray pyrolysis (Li et al., 1993), and sputtering (Athayde et al., 1994; Jayaraman et al., 1995).

In order to prepare efficient membranes providing higher hydrogen flux than any of the membranes developed so far, we proposed an asymmetric membrane consisting of palladium deposited inside the pores of an alumina membrane at atmospheric pressure by a CVD technique (Uemiya et al., 1994). A similar membrane was developed at the same time by Yan et al. (1994); however, the fabrication of their membrane required operation at a reduced pressure.

Serious disadvantages of palladium-based membranes are known to be not only their cost but also the lack of chemical resistance to sulfur compounds and carbon deposition. Ruthenium and platinum are expected to show properties better than those of palladium or its alloys under certain circumstances. For instance, the chemical resistance of a platinum membrane to hydrogen sulfide has been demonstrated by Edlund and Pledger (1994). They have also evaluated the possibility of the membrane as the hydrogen-permeable wall of a membrane reactor for thermal decomposition of hydrogen sulfide. It was also reported that ruthenium was hardly reacted with sulfur compounds (Ozaki et al., 1989). Chai et al. (1994) have developed and applied a ruthenium-dispersed alumina membrane to a membrane reactor for steam reforming of methane. However, the disadvantages of the low hydrogen permeability of the platinum membrane and the low selectivity of the ruthenium-dispersed alumina membrane have never been solved. Although membrane thickness must be reduced without any remaining pinholes in order to enlarge the hydrogen permeation rate while maintaining hydrogen selectivity, fabrication of dense thin membranes of ruthenium and platinum has never been established. Because there

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is limited information available on the fabrication, we focused on the fabrication of palladium, ruthenium, and platinum membranes by a CVD technique and their characterization in hydrogen permeation properties.

Experimental

Sublimination and decomposition behavior of CVD source

Acetylacetonato-complexes have been employed as CVD sources because of their relatively large temperature difference between sublimation and decomposition; however, the sublimation and decomposition behavior of acetylacetonato complexes of palladium, ruthenium and platinum have never reported as far as we know. The temperatures of sublimation and decomposition were experimentally determined as follows.

Their sublimation behavior was investigated by conventional electrobalance thermogravimetry to determine the starting temperature of sublimation for each complex.

Based on the results obtained by thermogravimetry, the amount of sublimated complex was quantitatively analyzed under atmospheric pressure using the apparatus shown in Figure 1, which is the same as the CVD apparatus. The complex, of which the initial amount was 25 mg, was placed on quartz wool in the cell. The temperature-controlled oven was heated from room temperature to a final sublimation temperature at a constant rate. The sublimated complex was trapped with quartz wool kept at room temperature outside the oven, and the amount of sublimated complex was measured quantitatively.

The decomposition temperature was determined from the morphology of the metallic film deposited on porous alumina and a nitrogen leak test. The details of the nitrogen leak test are explained later.

Membrane preparation

A porous alumina tube, manufactured by Toshiba Ceramics Co., was used as a support. This supporting tube was 7 mm ID, 10 mm OD, 250 mm long, and had an asymmetrical structure; a thin γ-alumina layer with a mean pore size of 200 nm was supported on the outer surface of the matrix with a pore size of 10 μm. Prior to metallic coating by CVD, the porous alumina tube was cleaned with trichloroethylene and ethanol in an ultrasonic bath for 15 min. The outer surface of the tube, except for the central part (20 mm) for metal deposition, was then covered with a sealing paste of glass powder (Nippon Electric Glass GA-4) mixed with α-terpineol and ethylcellulose, followed by drying at 393 K for 1 h and heat treatment in air atmosphere at 1,223 K for 1 h.

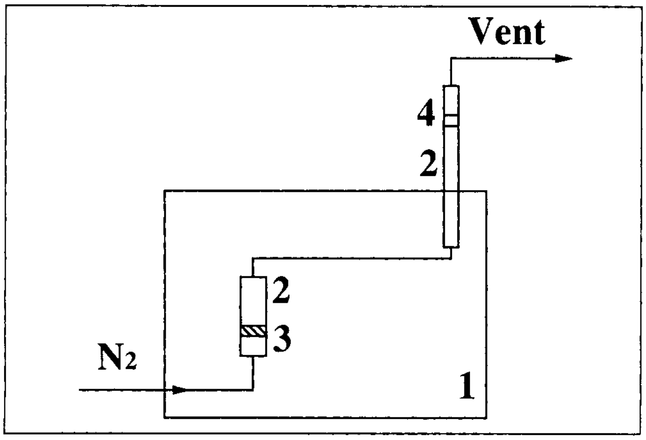


Figure 1. Apparatus for quantitative analysis of amount of sublimated complex.

1, Temperature-controlled oven; 2, quartz tube; 3, CVD metal source (complex); 4, quartz wool.

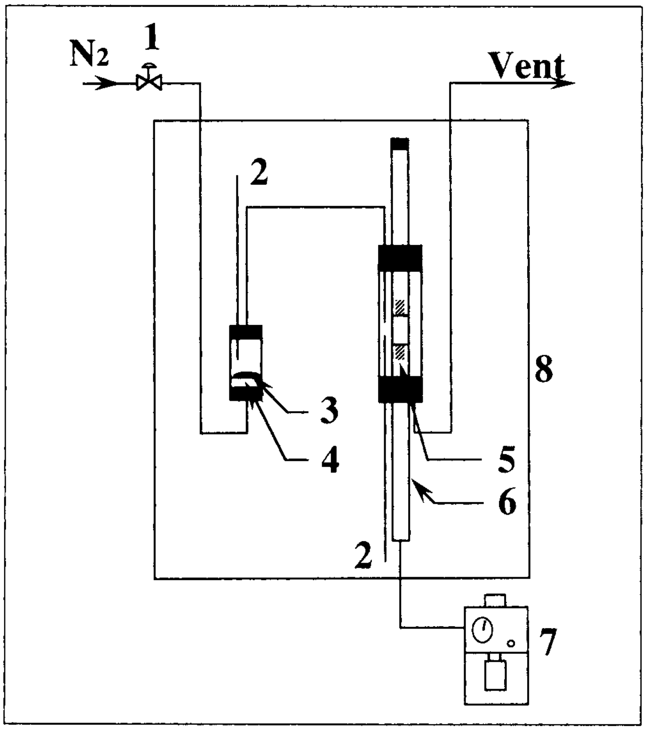


Figure 2. Experimental CVD apparatus.

1, Mass-flow controller; 2, thermocouple; 3, metal source (complex); 4, silicawool; 5, heater; 6, porous alumina tube; 7, aspirator; 8, temperature-controlled oven.

Figure 2 shows the apparatus for membrane preparation. The temperature of the oven was maintained at the sublimation temperature of each complex to prevent condensation in the tube connecting the complex-placed quartz cell (ID, 34 mm; length, 110 mm) and the reactor (ID, 34 mm; length, 190 mm). The complex was sublimated and then introduced into the CVD reactor with nitrogen as a carrier gas. The rate of the carrier gas was 100 cm^3 (STP) min^{-1}. The complex introduced into the reactor was thermally decomposed by a heater inserted inside the porous alumina tube. During CVD, the pressures outside and inside the membrane were maintained at 101 kPa and 60 kPa, respectively, to deposit the metal mainly inside the pores of the supporting tube. The deposition temperature was measured by a chromel-alumel (CA) thermocouple placed near the deposition area. A leak test using pure-grade nitrogen (99.99%) was conducted in the temperature ranges of 298 K and 473–773 K at a feed-side pressure range of 150–300 kPa while maintaining at an atmospheric pressure (101 kPa) on the permeation side—at regular 2-h intervals. The results were compared with those using helium to clarify the permeation mechanism through the pores still remaining. The CVD and leak test were repeated until most of the pores were plugged with metal, and the permeation of nitrogen was unchanged and ignored. The complex was recharged after every leak test.

Membrane characterization

Hydrogen permeation tests were conducted with pure-grade hydrogen (99.99%). The detailed structure of the separator used in this study is shown in Figure 3. Hydrogen was fed to the outside of the membrane at a rate of 1,000 cm^3 (STP)·min^{-1}, and the volumetric flow rate permeating through the membrane was measured with a wet gas meter. Hydrogen permeability was investigated over the temperature range of 473–773 K at a feed-side pressure range of 150–300 kPa while maintaining atmospheric pressure (101 kPa) on the permeation side. Here, a sweep gas was not introduced to the inside of the membrane. The selectivity for hydrogen was defined as the ratio of the molar fluxes of hydrogen to leak nitrogen.

Morphological analysis of membrane surface

Surface morphology of the composite membranes prepared at different decomposition temperatures was observed by scanning electron microscopy, and the depth profile of the metal across the membrane, especially near its outer surface, was analyzed by an electron probe microanalyzer.

Results and Discussion

Sublimation behavior of acetylacetonato complexes

Thermogravimetric results on the sublimation behavior of acetylacetonato complexes at a heating rate of 10 K·min^{-1} are shown in Figure 4. Palladium, ruthenium, and platinum complexes began sublimating at 413, 433, and 433 K, respectively, and their sublimation rates were increased with increasing temperature.

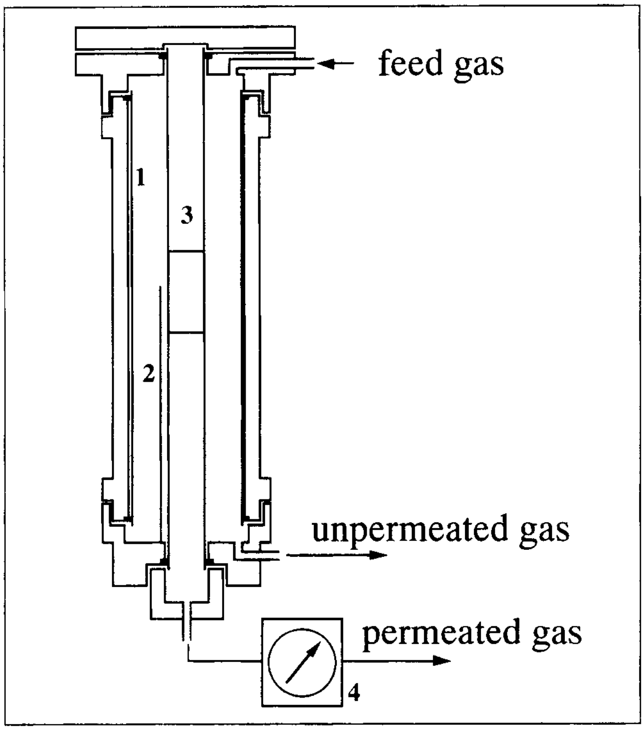


Figure 3. Detailed structure of hydrogen separator.

1, Quartz tube; 2, thermocouple; 3, membrane; 4, flow meter.

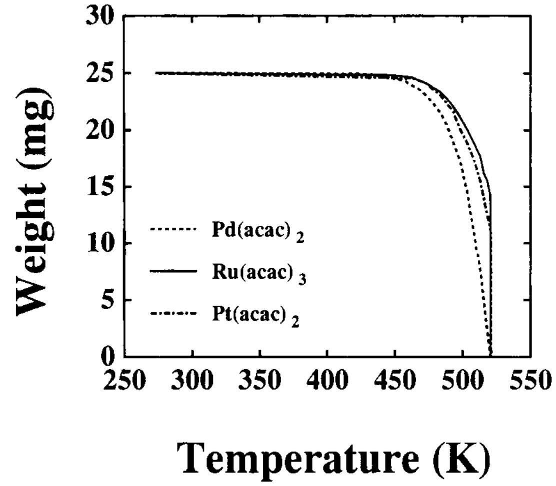


Figure 4. Sublimation behavior of acetylacetonato complexes.

Based on the results given earlier, the amount of complex introduced into the CVD reactor from the sublimation cell was evaluated at temperature ranging from 413 to 493 K for 2 h under conditions such as a flow rate of carrier gas and packing of the complex similar to those for the preparation of the composite membranes. The results are shown in Figure 5. The amount of complex introduced was increased with increasing temperature to reach maximum at 453 K for palladium and at 473 K for ruthenium or platinum. Above these temperatures, a decrease in the amount of complex intro-

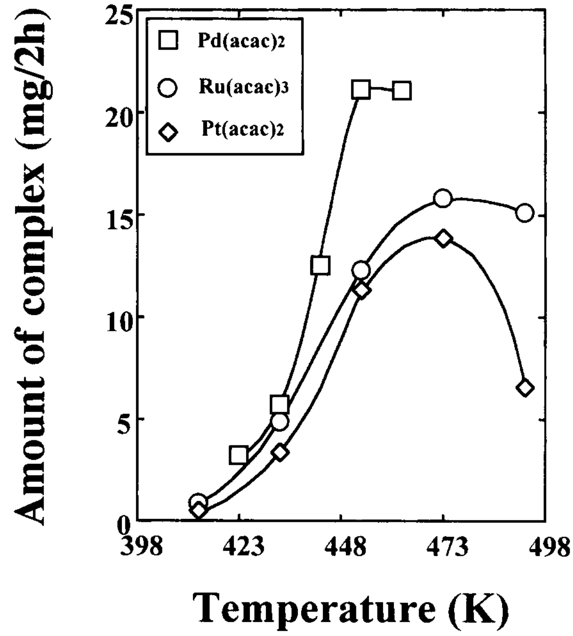
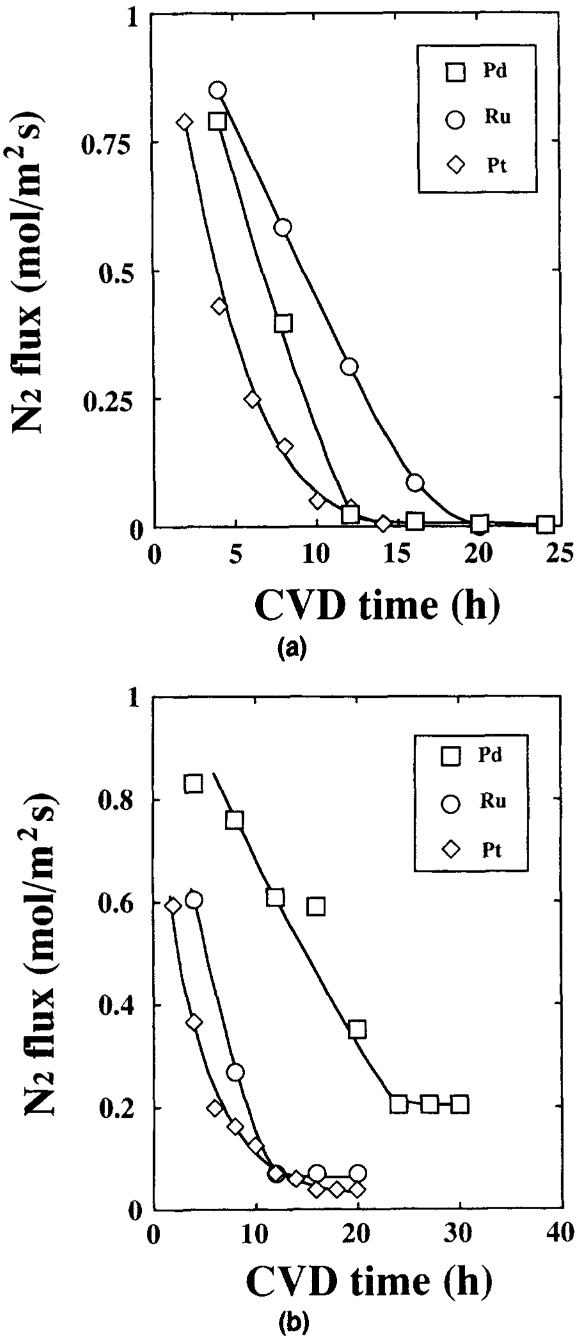


Figure 5. Amounts of acetylacetonato complexes introduced into CVD reactor.

duced was observed, because of the simultaneous decomposition of the complexes. It can be concluded from these results that the sublimation temperatures at 453 K, 473 K, and 473 K are suitable for CVD of palladium, ruthenium, and platinum, respectively.

CVD experiment results

Time variation in the fluxes of leak nitrogen during membrane preparation is shown in Figure 6. A decrease in the flux indicates the pore plugging process as CVD progresses. Every metal was deposited mainly on the support, and the pores of the support were gradually plugged by metal layers that resisted nitrogen permeation. Finally, nitrogen fluxes through these membranes, prepared at 543, 543, and 493 K, were reduced to below 10 cm^3 (STP)$\cdot min^{-1}$ by continuing CVD for 24, 14, and 20 h, respectively, for palladium, ruthenium and platinum. On the other hand, metal deposition above temperatures 30 K higher than the aforementioned temperatures hardly yielded membranes with nitrogen permeation resistance.



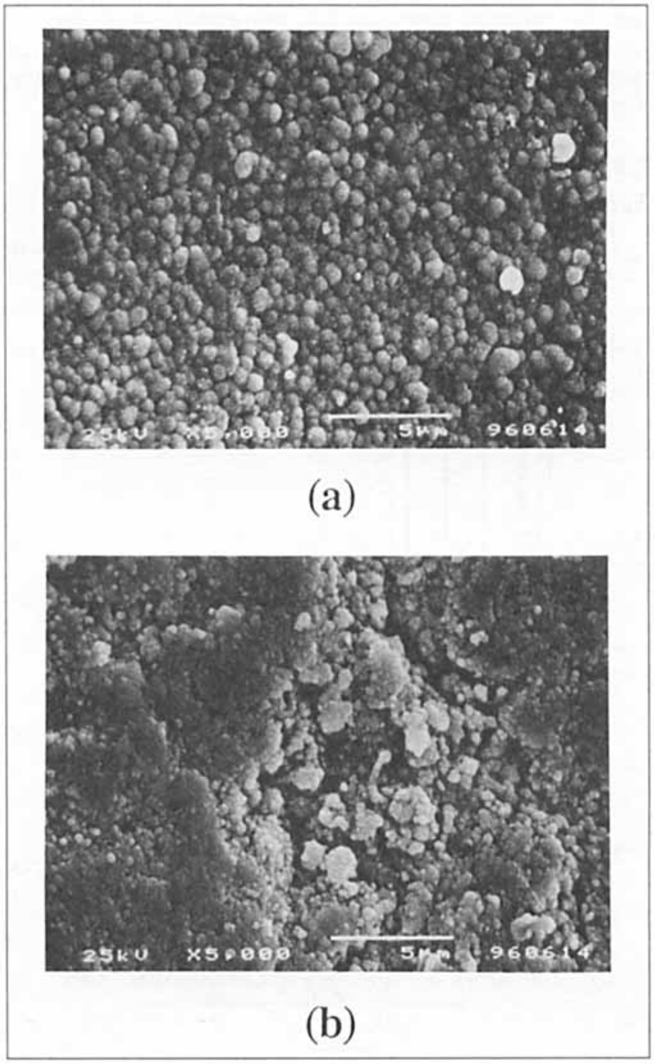
(a)

(b)

Figure 6. Time variation of nitrogen flux though metal membranes.

Deposition temperature: (a) Pd, 543 K; Ru, 543 K; Pt, 493 K; (b) Pd, 573 K, Ru, 573 K; Pt, 523 K.

Figures 7–9 show SEM photographs of the outer surface of the composite membranes formed at different decomposition temperatures. The surface morphology of composite membranes deposited at 543 K, 543 K, and 493 K for palladium, ruthenium, and platinum, respectively, was similar to the surface morphology of a dense palladium film deposited by electroless plating, and any pores in the support, pinholes, or cracks were hardly observed at the surface. In the case of metal deposition at temperatures 30 K higher than the afore-



(a)

(b)

Figure 7. Surface morphology of palladium membranes deposited by CVD; deposition temperature: (a) 543 K; (b) 573 K.

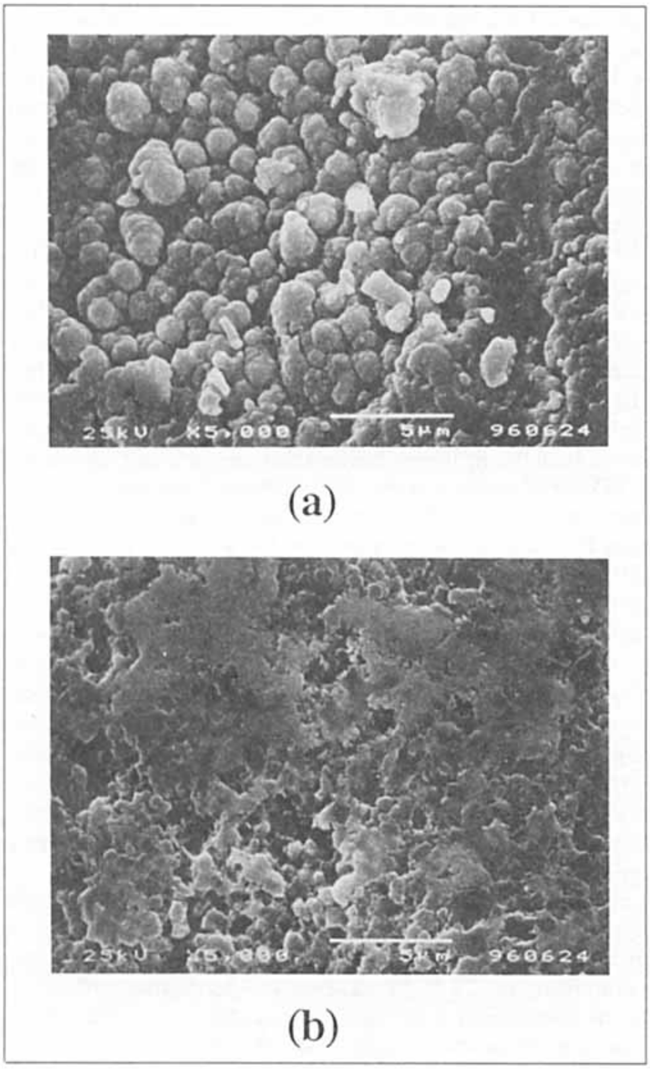


Figure 8. Surface morphology of ruthenium membranes deposited by CVD; deposition temperature: (a) 543 K; (b) 573 K.

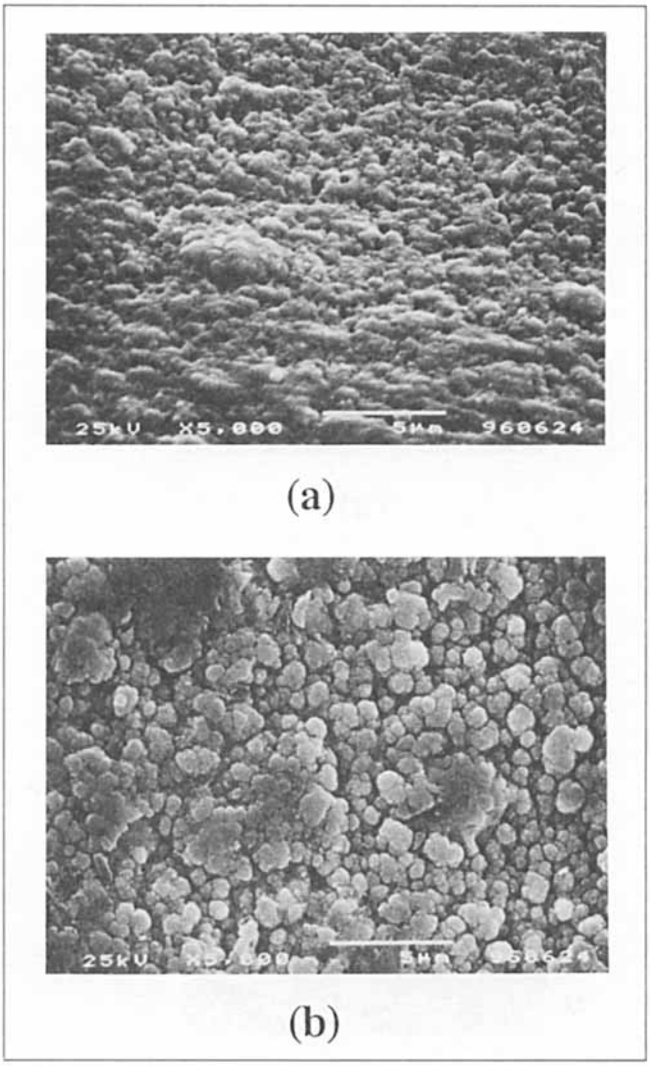


Figure 9. Surface morphology of platinum membranes deposited by CVD; deposition temperature: (a) 493 K; (b) 523 K.

mentioned decomposition temperatures of 543, 543 and 493 K, the pores of the support partly remained even after more than 20 h deposition, because the complex was mainly consumed in metal particle nucleation occurring in the vapor phase, but not in the pores. From the SEM observation, the formed particles are thought to accumulate on the support because the surface morphology is not completely different from the surface of the support. Although the surface of the support was not clearly seen, the pores appeared not to be completely plugged, so that nitrogen permeation was not completely prevented. These results indicate that the deposition temperature should be controlled at around the optimum where the metal was selectively deposited on the surface or pores near the surface of the support tube. Optimum CVD conditions are summarized in Table 1. Here, the palladium composite membrane was prepared at 433 K, which is below the optimum decomposition temperature for CVD of palladium.

The depth profile of each metal prepared near the surface of the composite membranes under the conditions in Table 1 is shown in Figure 10. The aluminum profiles corresponding to the alumina support and each metal peak had their peaks in the same region. It is suggested that metal was deposited not only on the surface but also in the pores of the support, which is different from the structure of the metal film prepared by other techniques such as electroless plating and sputter deposition forming only on the surface of the support. The thickness of the deposited metal layer in the pores, which will be somewhat different from the true thickness of the effective layer for hydrogen separation, was 10, 3, and 10 μm for palladium, ruthenium, and platinum, respectively, as

Table 1. Summary of CVD Conditions

Metal	Sublimation Temp. (K)	Decompositon Temp. (K)	Selectivity* (H_2/N_2)
Palladium	433	543	240
Ruthenium	473	543	120
Platinum	473	493	210

*Flux ratio of hydrogen to leak nitrogen at 773 K.

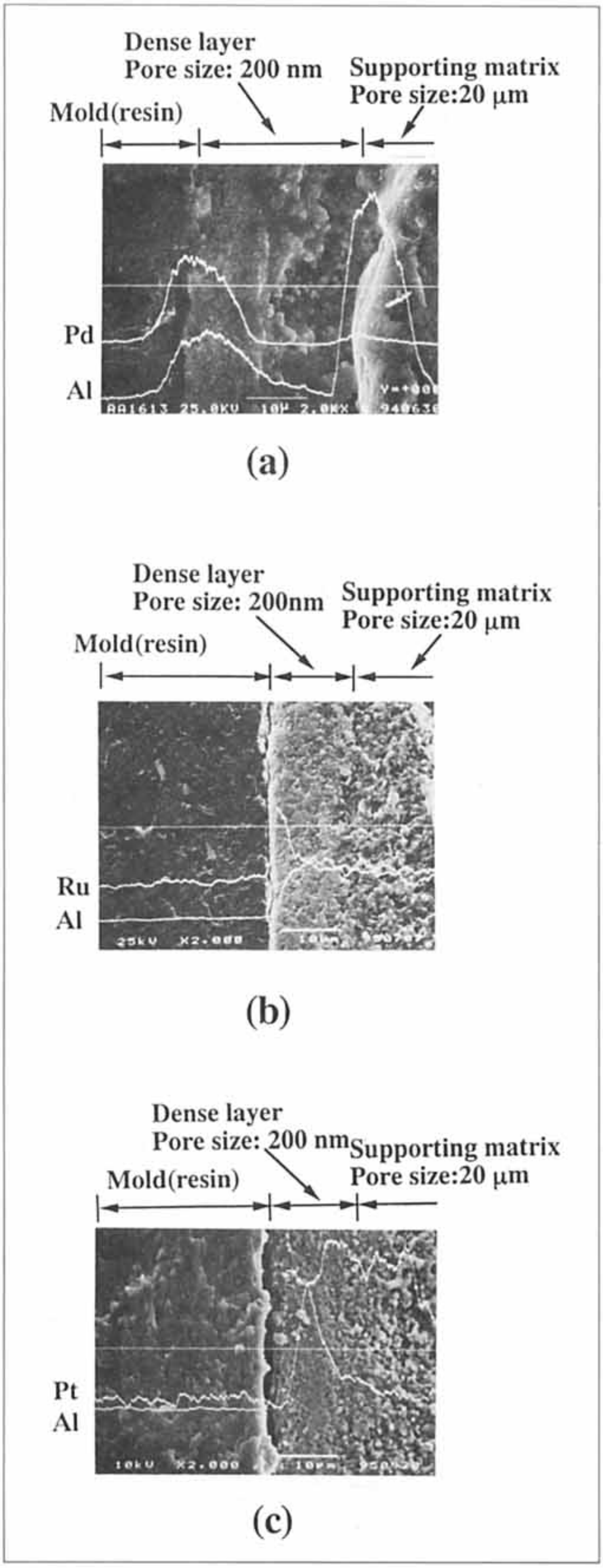


Figure 10. Depth profiles of deposited metals in porous alumina tube; (a) palladium; (b) ruthenium; (c) platinum.

estimated from the SEM observation. The film thickness can be generally estimated by SEM observation. The thickness of a dense hydrogen-permeable metal membrane, such as a palladium membrane, can also be calculated or estimated by comparing the rate of hydrogen permeation, because the rate is inversely proportional to the membrane thickness. In the case of palladium, ruthenium, and platinum membranes prepared by the CVD technique, metal was deposited both on the surface of the support and in the pores. The pores of the support were not completely plugged with metal, and the CVD membranes, especially the platinum membrane, exhibited still higher hydrogen permeability than that of the dense and thick metal membranes previously reported, even when the difference in the apparent metal membrane thickness observed by SEM was considered. From these results, we conclude that the hydrogen permeation mechanism through the CVD membranes is somewhat different from that of dense metal membranes. Thus, it was difficult to use SEM observation to estimate the thickness of the effective layer of the CVD membranes for gas separation and to compare the rate of hydrogen permeation. Taking the aforementioned results into consideration, the approximate film thickness calculated on the basis of the amount of sublimated complex is shown in this article, assuming that the entire sublimated complex was completely decomposed in the central part (20 mm) of the support. The thickness of the CVD membranes was calculated to be 3.2, 3.3, and 5.8 μm for palladium, ruthenium, and platinum, respectively. From these results, we estimated the effective thickness at around 5 μm for the composite membranes prepared by the CVD technique. From SEM observation, any defect (cracking or peeling off of the film from the support) was not observed, and the morphology of our membranes was not changed after exposure at elevated temperature up to 773 K. In addition, the permeation properties of the membranes were also unchanged before and after the exposure. Thus, we consider that palladium, ruthenium, and platinum membranes are thermally stable up to 773 K. Taking their application to membrane reactors into consideration, their resistance to thermal and mechanical stress induced by pore plugging by CVD as well as surface coating was one of the most important membrane properties relating to lifetime.

Hydrogen selectivity

The hydrogen selectivities of our composite membranes, defined as the ratio of the molar fluxes of hydrogen to leak nitrogen at 773 K, are also summarized in Table 1. The selectivities were high values of 240, 120, and 210 for palladium, ruthenium, and platinum, respectively, compared with any of the porous ceramic membranes. The flux of leak nitrogen decreased with increasing temperature. Furthermore, a linear relation between the fluxes of nitrogen and helium and an inverse relation of the square roots of their molecular weights were observed. These results indicate that, governed by the Knudsen diffusion mechanism (Saracco and Specchia, 1994), nitrogen and helium permeates through the narrow pores still remaining. In addition, as for hydrogen, other mechanisms such as "surface diffusion mechanism" and "solution diffusion mechanism" contribute to hydrogen permeation. The rate of hydrogen permeation governed by these mechanisms is much higher than that of nitrogen of helium governed only by Knudsen diffusion, and consequently, the CVD membranes exhibit higher hydrogen selectivity.

Hydrogen permeability

Hydrogen fluxes through the membranes prepared under the conditions in Table 1 are shown in Figure 11, as a function of pressure difference or square-root pressure difference between the high- and low-pressure sides of the membrane. We can see in Figure 11 that the hydrogen fluxes through any membrane were proportional to the difference in the square root of pressure. The present result indicates that the rate-determining step is the permeation of the dissociated hydrogen through the membrane, though we did not show where the main resistance exists in the membrane.

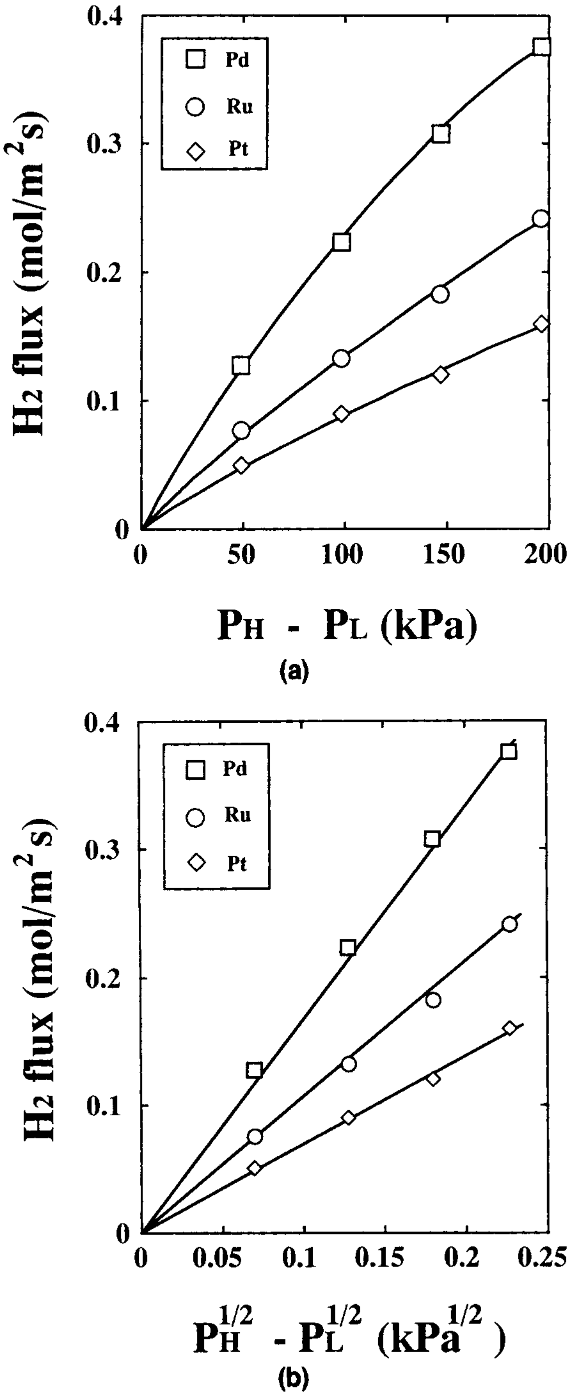


Figure 11. Dependency of hydrogen flux on (a) pressure difference and (b) square root pressure difference between high and low pressure sides of the membrane.

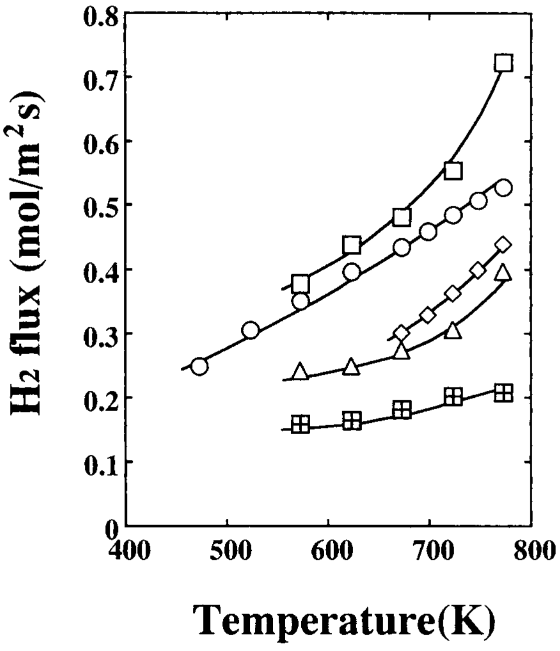


Figure 12. Comparison among hydrogen fluxes through various membranes.

□, Palladium (CVD); △, ruthenium (CVD); □, platinum (CVD); ○, palladium-silver (electroless plating); ◇, palladium (electroless plating).

Figure 12 shows hydrogen fluxes through the various composite membranes. The performance for hydrogen permeation of the membranes is compared with that of the palladium-based composite membranes, prepared by an electroless-plating technique (Uemiya, 1991; Kikuchi and Uemiya, 1991), where the dense metal layer thickness ranges from 4.5 μm to 5.8 μm. The palladium membrane prepared by the CVD technique showed the highest flux among the membranes tested, namely, at 673 K, which is 1.6 times higher than that of the dense palladium membrane with a thickness of 4.5 μm, prepared by the electroless-plating technique. In the cases of polymeric membranes, hydrogen is dissolved in the membrane and diffuses without the dissociation of hydrogen molecules to atoms. On the other hand, however, the hydrogen permeation mechanism of dense metal membranes is generally characterized as a solution-diffusion mechanism involving three processes: (1) dissociative chemisorption of hydrogen on the membrane surface, followed by dissolution of atomic hydrogen into the structural lattice of the metal; (2) diffusion of the hydrogen atom through the membrane; and (3) a combination of hydrogen atoms dissociating into molecules and desorption (Barrer, 1951). Assuming that the mechanism of hydrogen permeation occurred in the same manner between electroless-plated and CVD membranes, the thickness of the effective palladium layer relative to hydrogen

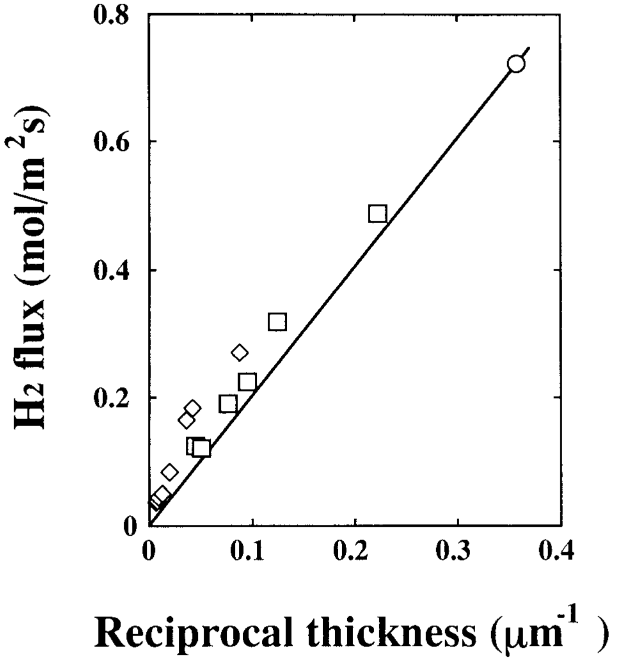


Figure 13. Relationship between the hydrogen flux and the thickness of palladium film.

○, Experimental value; ◇, reported value (Hurlbert et al., 1961); □, reported value (Kikuchi et al., 1991).

selective permeation was estimated to be 2.8 μm, as shown in Figure 13. Moreover, the palladium membrane showed a 1.8 and 2.7 times higher flux than that of ruthenium and platinum membranes, respectively. The thickness of the palladium, ruthenium, and platinum membranes was in the same order, considering that the total amount of deposited metal was almost the same as given earlier.

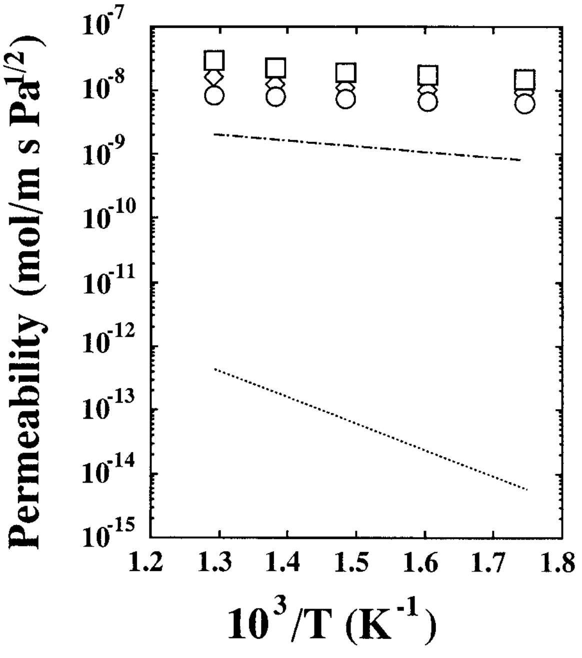


Figure 14. Comparison of hydrogen permeability of various membranes.

□, Pd; ○, Ru; ◇, Pt; –·–·– Pd (Steward, 1983); ····, Pt (Steward, 1983).

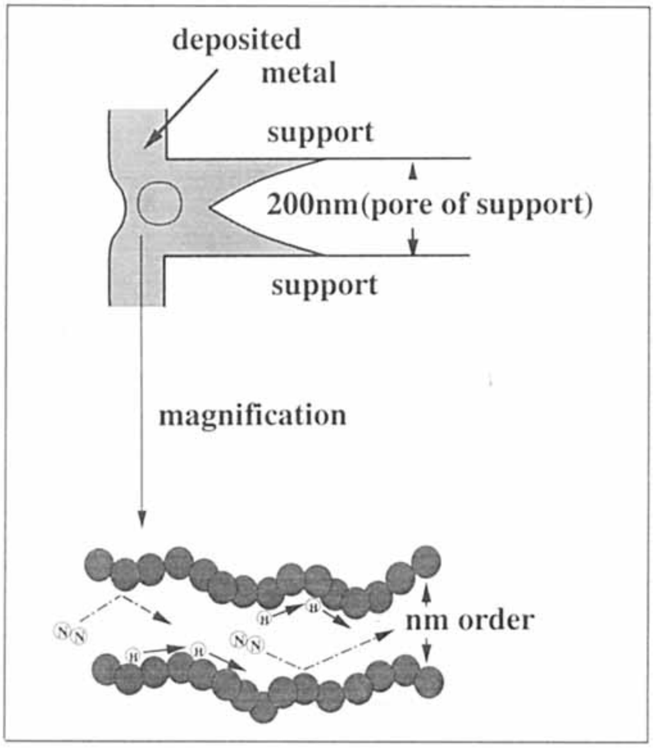


Figure 15. Mechanism of hydrogen permeation through metal membranes.

——, Surface diffusion; –·–·–, Knudsen diffusion.

Comparison of hydrogen permeability through various membranes is shown in Figure 14. Hydrogen permeability of a palladium membrane prepared by CVD was approximately the same value as previously reported (Hurlbert and Konecny, 1961; Uemiya et al., 1991; Kikuchi and Uemiya, 1991), while the permeability of a platinum membrane was 1,000 times higher than that of a previous study (Steward, 1983). As shown earlier, hydrogen permeates through dense palladium membranes by a solution and diffusion mechanism. On the other hand, Chai et al. (1994) reported that hydrogen diffusion through the metal-dispersed alumina membranes is related to hydrogen chemisorption and desorption of spillover hydrogen on the surface and surface diffusion in the micropores. In this case, the hydrogen flux can also be proportional to the difference in the square roots of hydrogen pressures between both sides of the membrane. The hydrogen selectivities of our membranes were high compared with those of any of their metal-dispersed membranes. At present, the mechanism of hydrogen permeation through our membrane is not clear; that is, the hydrogen diffusion can be explained by surface diffusion of spillover hydrogen on metals or a combined mechanism of surface diffusion and solution and diffusion, as shown in Figure 15. Further study of the mechanism of the hydrogen permeation is necessary.

Conclusions

Composite membranes of palladium, ruthenium, and platinum formed on a porous alumina support using the CVD technique were prepared and their characteristics for hydrogen-selective permeation were investigated. The effective thickness of the metal layer for hydrogen permeation was obtained under the conditions summarized in Table 1. Hydrogen fluxes through these membranes were proportional to the difference in the square roots of hydrogen pressures between both sides of the membrane. This result indicates that the rate-determining step is the diffusion of the disssociated hydrogen through the membrane.

Acknowledgment

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