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Hydrogen permeation properties through composite membranes of platinum supported on porous alumina

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Abstract

The hydrogen permeation mechanism through a supported platinum membrane prepared by chemical vapor deposition (CVD) was investigated and compared with an electroless-plating platinum membrane. A CVD membrane while maintaining an excellent hydrogen permselectivity provided a 10^3–10^4 times higher hydrogen permeation coefficient than an electroless-plating platinum membrane. This large difference in the hydrogen permeation coefficient resulted from the hydrogen transport phenomena, namely the surface diffusion mechanism for the CVD membrane and solution–diffusion mechanism for an electroless-plating membrane. Furthermore, the relationship between the structure of the metal layer and hydrogen permeance was also discussed for the CVD membrane. The membranes with smaller platinum grains gave higher hydrogen fluxes because the effective platinum area for the hydrogen surface diffusion increased with a decrease in grain size. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen permeation; Supported platinum membrane; Porous alumina; Chemical vapor deposition; Electroless-plating

1. Introduction

Realization of membrane reactors for hydrogen-producing reactions such as dehydrogenation and steam reforming requires thermally and mechanically stable membranes with both excellent hydrogen permeability and permselectivity [1,2]. Dense metal membranes, especially palladium-based membranes, do not perfectly satisfy these requirements. Hydrogen permeance of palladium-based membranes with a thickness larger than a micrometer is reported to be inversely proportional to their thickness [3]. Based on this relationship, fabrication of composite membranes consisting of a thin palladium film formed on a porous inorganic substrate has recently been investigated by many researchers. Electroless-plating [4–9], electroplating [10], chemical vapor deposition (CVD) [11–13], spray pyrolysis [14], and sputter-deposition [15–17] techniques have been successively applied for such a fabrication. These composite membranes showed excellent hydrogen permeance and mechanical stability for incorporation into membrane reactors. Supported pure palladium membranes as already reported, however, still have some drawbacks such as hydrogen embrittlement due to α–β phase transformation, rapid deactivation by impurities, e.g., sulfur compounds and carbon deposition, and high cost.

During practical use of conventional palladium-based membranes, sulfur compounds are removed to

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concentration levels lower than 5 ppm [18]. If there is another metal having both hydrogen permeability and chemical resistance to sulfur compounds, any pretreatment of the feed gas (reactant) in a hydrogen purification unit or membrane reactor will be omitted. From this point of view, Edlund and Pledger [19] proposed a platinum-coated vanadium membrane and demonstrated the chemical stability of platinum for hydrogen sulfide. Unfortunately, the hydrogen permeance of their vanadium membrane was too small to give sufficient reaction conversion in membrane reactors, due to the relatively thick platinum layer. In our previous study [12], composite membranes consisting of a group-VIII metal, such as palladium, ruthenium, or platinum, and a porous alumina tube used as a support were prepared by a CVD technique. Especially, the composite membranes consisting of a platinum layer formed on the surface or in the pores of a porous alumina tube with a pore size of 200 nm showed high hydrogen flux which was comparable to that of a palladium membrane prepared by the electroless-plating technique; typically, hydrogen permeance is 1000 times higher than that of dense platinum membranes. The hydrogen permeation behavior of these CVD membranes differed from that of a conventional, dense palladium membrane, in other words, the traditional solution–diffusion mechanism observed for dense metal membranes. A similar phenomenon was already observed by Chai et al. [20] for metal-dispersed, porous alumina membranes prepared using the sol–gel technique, and they advocated a hydrogen transport mechanism via the spillover or surface diffusion of hydrogen. Based on a comparison of the reported hydrogen permeation coefficient between the CVD membrane and dense metal membranes, we speculated that CVD composite membranes have a similar transport mechanism where hydrogen diffuses on the metal surface located between grain boundaries. Nevertheless, a detailed hydrogen permeation mechanism has not yet been clarified and information on hydrogen permeation through the composite CVD membranes, except for palladium and its alloys, is not currently of sufficient detail. In this work, the hydrogen permeation behavior through composite platinum membranes by CVD was investigated in a comparison with electroless-plating palladium membranes, and the relationship between the structure of the metal layer and hydrogen permeation performance was also discussed.

2. Experimental

2.1. Preparation of composite platinum membranes by CVD and electroless-plating techniques

Composite membranes consisting of platinum supported on commercially available porous alumina tubes with an average pore size of 200 nm were prepared by both the CVD and electroless-plating techniques. Details of the preparation procedures of the composite platinum membranes were reported in [21] for electroless-plating and in [12] for CVD. The preparation procedures are now briefly described. Commercially available, asymmetric porous alumina tubes (outer diameter, 10 mm; inner diameter, 7 mm; length, 250 mm; effective average pore size, 200 nm) were used as the supports. Prior to the formation of the platinum layer, the porous alumina tube was ultrasonically washed with trichloroethylene for 15 min and successively with ethanol for 15 min. In the case of CVD, bis(acetylacetonato)platinum(II), supplied from Tanaka Kikinzoku, Japan, was used as the CVD source because its difference between sublimation and decomposition temperatures is large enough for the CVD operation. The metal deposition was limited within the central part of the support having an area of 6.28 cm^2 to obtain an approximate uniform thickness of the metal deposited layer. The CVD was conducted under the condition where particle formation in the gas phase hardly occurred and the pressure on the inside of the support was reduced for the deposition of platinum mainly in the pores.

The platinum electroless-plating procedures were as follows. Aiming at the initialization of electroless-plating, a traditional activation treatment was adopted; catalytic palladium nuclei were deposited on the outer surface of the support by successive immersion in 1 kg/m^3 tin chloride and 0.1 kg/m^3 palladium chloride solutions. The fundamental plating bath composition and conditions are listed in Table 1.

Table 1
Plating bath composition

$Pt(NO_2)_2(NH_3)_2$	3.89 mol/m^3
NH_3	1.91 mol/m^3
$HONH_3Cl$	0.06 mol/m^3
$H_2NNH_2\cdot H_2O$	0.26 mol/m^3
Temperature	323 K

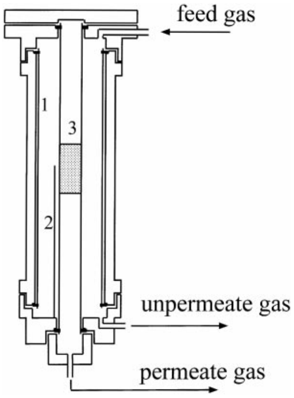


Fig. 1. Schematic diagram of stainless-steel test cell for gas separation.

The activated support was dipped in the bath and platinum was then uniformly deposited on the surface. The morphology was observed using scanning electron microscopy (SEM). The thickness of the membrane was measured using X-ray fluorescence coating thickness gauge (Seiko Instrument). In the case of the electroless-plating, platinum was mainly deposited on the outer surface of the porous alumina supports.

2.2. Permeation experiments

The permeation measurements of the platinum composite membranes were carried out using a stainless-steel test cell for the gas separation. The experimental setup is shown in Fig. 1. The composite platinum membrane installed in the separation test cell was heated in a nitrogen atmosphere. Pure grade hydrogen, helium, methane, nitrogen or oxygen were fed into the outside of the membranes, and the flow rate of the permeating gas was measured using a soap-film meter under the condition that the permeation side was kept at atmospheric pressure. The transmembrane pressure difference was varied from 49 to 196 kPa in the temperature range of 298–773 K.

2.3. Characterization of composite platinum membranes

The surface morphology and cross-section of the resulting composite membranes were observed using SEM. The distribution of the platinum deposited in the pores of the porous alumina supports was analyzed using an electron probe micro analyzer (EPMA).

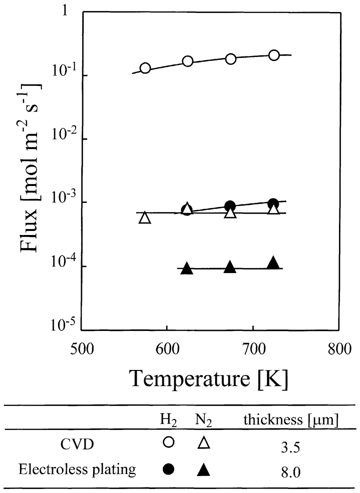


Fig. 2. Temperature dependence of hydrogen permeabilities of CVD and electroless-plating platinum membranes.

3. Results and discussion

Fig. 2 shows the temperature dependence of hydrogen permeabilities of the CVD and electroless-plating membranes, which were obtained by 12 and 16 h preparation times, respectively. The CVD membrane gave about 200-times higher hydrogen flux than the electroless-plating membrane. Since the nitrogen fluxes of both membranes were about 10^{-4} mol/m^2 s, the ideal selectivity of hydrogen over nitrogen (S_{H_2/N_2}), defined as the flux ratio of hydrogen to nitrogen, is mainly dependent on the difference in the hydrogen flux; typically, 198 and 4 at 773 K for the CVD and electroless-plating membranes, respectively.

Fig. 3 shows a comparison of the surface morphology between the CVD and electroless-plating membranes. The resulting membranes had a similar surface morphology such that the metallic grains entirely covered the surface of the support, but a different probability exists as pinholes. In the electroless-plating, although a dense platinum layer was formed on the support, there were some pinholes that still existed in the platinum layer so that an appreciable amount of leakage nitrogen as well as hydrogen could permeate

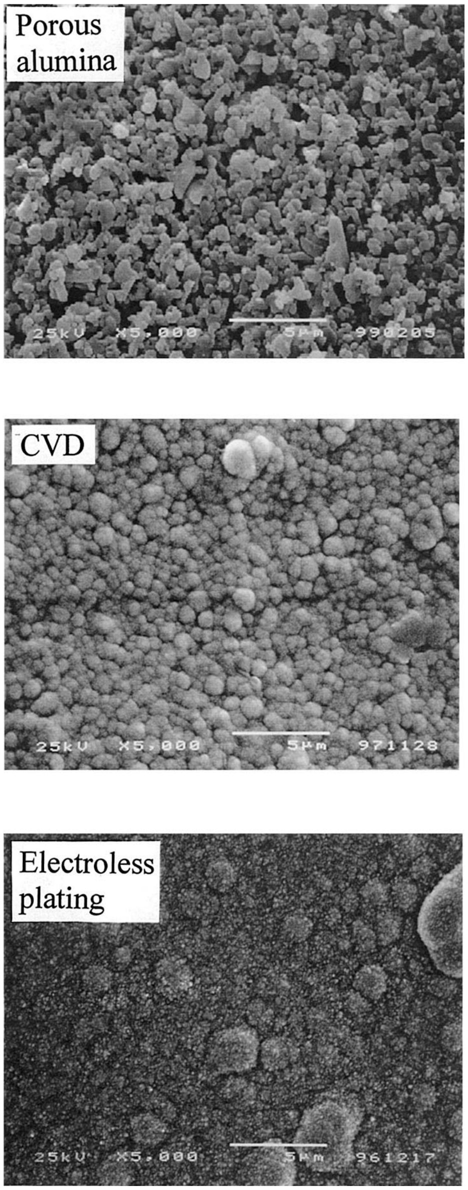


Fig. 3. Comparison of surface morphology between CVD and electroless-plating platinum membranes.

through these pinholes. On the other hand, no pinhole was found using SEM observations in the CVD membrane.

An X-ray line mapping of platinum and aluminum are also drawn on the SEM photographs of the cross-section of the resulting membranes, as shown in Fig. 4. In the CVD, the X-ray intensity of platinum gives a shape similar to that of aluminum. This result indicates that an effective platinum layer for selective hydrogen separation was mainly formed inside the pores of the support. In fact, however, platinum was also deposited on the surface because agglomerated platinum grains can be observed in the SEM photograph, and furthermore, the evacuation efficiency inside the support got worse with preparation time. Typically, only a slight amount of nitrogen as the carrier gas for the platinum precursor permeated through the support after the CVD time of 8–10 h. The thickness of the effective platinum layer for hydrogen separation, which cannot be determined from the SEM photograph, was estimated to be about 3.5 μm, calculated from the amount of the precursor complex vaporized and fed into the CVD reactor. On the other hand, a distinct film can be observed on the outside of a support from the SEM observation for the electroless-plating membrane, and furthermore, the platinum intensity can be detected on the film. It is obvious from these results that a dense platinum film was formed on the top layer surface of the support. The thickness of about 8 μm predicted from the deposition rate measured separately and plating time coincides with that observed in the SEM photograph. It is realized from these results that the CVD platinum membrane has an effective layer in the pores of the support and shows greater hydrogen permeance than an electroless-plating membrane, in spite of slight difference in thickness of the platinum layer between the CVD and electroless-plating membranes. Though the diffusivity of hydrogen is small in the bulk of the dense platinum like an electroless-plating film, the CVD platinum membrane produced an excellent hydrogen permeance.

For the purpose of revealing the permeation mechanism not only for hydrogen but also for other gases including nitrogen through the CVD platinum membrane, the relationship between molecular weight and flux was investigated for the various gases. These results are shown in Fig. 5. Helium, methane, nitrogen and oxygen could permeate via a Knudsen diffusion mechanism because the fluxes of these gases were inversely proportional to the square root of their molecular weight. On the other hand, the hydrogen flux was much higher than those of the other gases tested and deviated from the tendency predicted by the Knudsen diffusion mechanism.

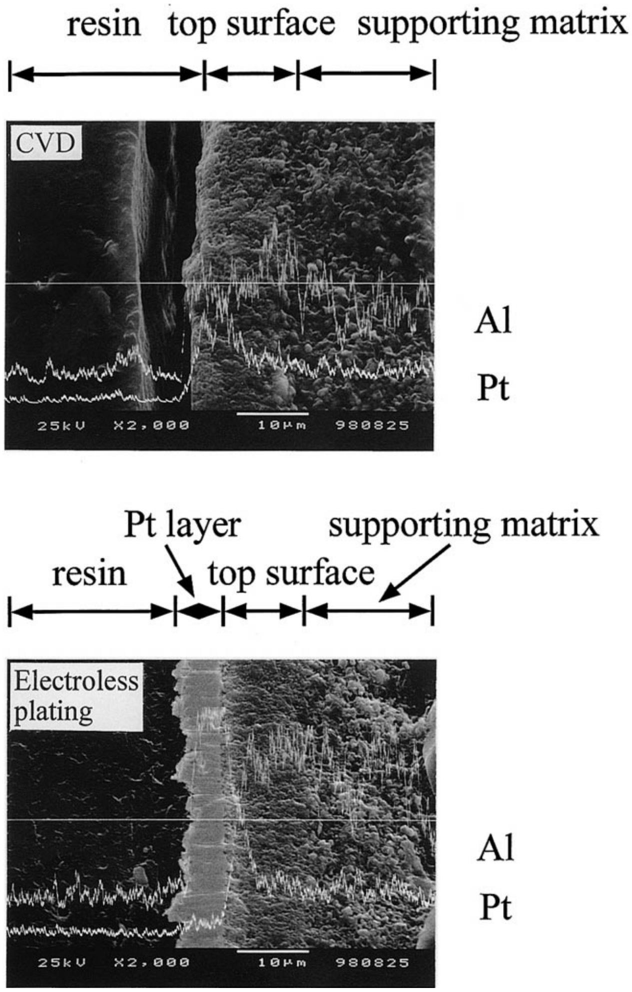


Fig. 4. X-ray line mapping of platinum and aluminum shown on SEM photographs of a cross-section of CVD and electroless-plating platinum membranes.

Platinum was easily sulfided by the reaction with hydrogen sulfide, which is contradictory to Edlund and Edlund's results [19]. After contact with hydrogen sulfide (6200 ppm), the hydrogen flux deteriorated rapidly, and then the ideal selectivity of hydrogen over nitrogen diminished to 3.7. This value is the same as that predicted based on the assumption of the Knudsen diffusion mechanism. In other words, in the case of a sulfur-poisoned platinum membrane, hydrogen could permeate only by the Knudsen diffusion mechanism like all of the other gases. In usual cases, hydrogen could permeate via a complicated permeation mechanism consisting of Knudsen diffusion and platinum-promoted diffusion. It is obvious that a chemical interaction between hydrogen and the aggregated platinum grains in the pores governs most of the hydrogen permeation through the CVD membranes because most of the hydrogen permeability of the CVD membranes was lost by sulfurization using hydrogen sulfide.

Fig. 6 demonstrates our proposed model of gas permeation through the CVD membranes. In a CVD membrane, nitrogen permeates through micropores, probably formed between the boundaries of the platinum grains, based on the Knudsen diffusion mechanism. On the other hand, hydrogen permeates

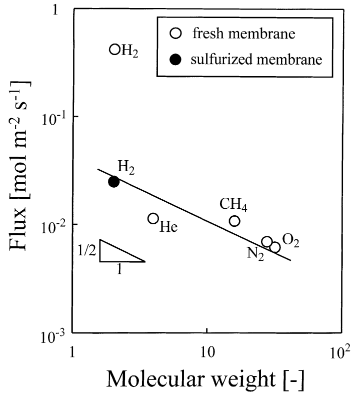


Fig. 5. Relationship between molecular weight and flux for various gases for CVD platinum membrane.

by the Knudsen diffusion mechanism as well as by a platinum-promoted diffusion mechanism, i.e., surface diffusion mechanism or solution–diffusion mechanism. Thus, the possible permeation routes for hydrogen are as follows:

1. Hydrogen permeates through the pores of the deposited platinum layer based on the Knudsen diffusion mechanism.
2. Hydrogen permeates in the bulk of the deposited platinum layer via a solution–diffusion mechanism.
3. Hydrogen permeates on the surface of the platinum grains via a surface diffusion mechanism.

In the following discussion, the rate of hydrogen permeation dominated by platinum-promoted diffusion was calculated using Eqs. (1) and (2):

$$J_{\mathrm{M,H_2}} = J_{\mathrm{T,H_2}} - J_{\mathrm{K,H_2}} \tag{1}$$

$$J_{\mathrm{K,H_2}} = J_{\mathrm{K,N_2}} \left(\frac{M_{\mathrm{N_2}}}{M_{\mathrm{H_2}}}\right)^{1/2} \tag{2}$$

where $J_{\mathrm{M,H_2}}$ is the hydrogen flux of platinum-promoted diffusion, $J_{\mathrm{T,H_2}}$ is the total hydrogen flux, and $J_{\mathrm{K,H_2}}$ and $J_{\mathrm{K,N_2}}$ are the Knudsen diffusive fluxes of hydrogen and nitrogen, respectively. $M_{\mathrm{N_2}}$ and $M_{\mathrm{H_2}}$ are the molecular weight of nitrogen and hydrogen, respectively. $J_{\mathrm{K,N_2}}$ can be obtained by measuring the nitrogen flux through the membranes.

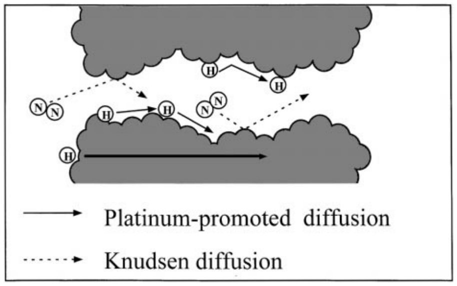


Fig. 6. Proposed model of gas permeation through CVD platinum membrane.

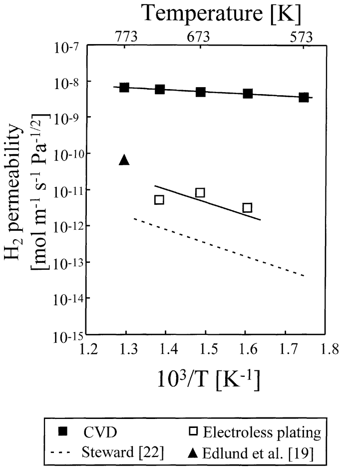


Fig. 7. Temperature dependence of hydrogen permeabilities of various platinum-based membranes.

Hydrogen permeabilities contributed by platinum-promoted diffusion for the CVD membranes are represented in Fig. 7, where the reported values for dense platinum membranes are also plotted for comparison [22]. The CVD membranes showed a higher hydrogen permeability than the corresponding dense platinum membranes, of course, including metal–ceramics composite membranes prepared by an electroless-plating technique; for instance, a platinum CVD membrane gave about a 1000-times greater hydrogen permeation coefficient than the reported values, which are regarded to be on the same order as the data obtained for the platinum electroless-plating membranes [21]. These results lead us to conclude that hydrogen permeates not in the bulk of the deposited metal via the traditional solution–diffusion mechanism but on the pore surface of the deposited platinum layer via a surface diffusion mechanism.

Fig. 8 illustrates the variations in the hydrogen fluxes during membrane preparation. The hydrogen

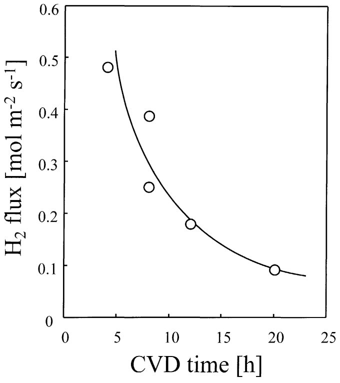


Fig. 8. Variations in hydrogen fluxes during CVD membrane preparation.

flux was almost inversely proportional to the CVD time. Assuming that the thickness of the platinum layer is proportional to the CVD time, it may be considered that the hydrogen flux was inversely proportional to the thickness of the platinum layer. This finding indicates that the rate-determining step of the hydrogen permeation at the relatively high temperature of 673 K is hydrogen diffusion through the platinum layer.

The temperature dependency of the hydrogen, helium and nitrogen fluxes through the CVD membrane are plotted in Fig. 9, including a series of permeation data at the low temperatures of 298–773 K. Note that non-palladium, platinum membranes may endure hydrogen embrittlement even at ambient temperature. As shown in Fig. 9, the helium and nitrogen fluxes increased with decreasing temperature, as predicted from the Knudsen diffusion mechanism. On the other hand, the hydrogen flux decreased steadily with a decrease in the temperature from 773 to 573 K, and then decreased dramatically with a decreasing temperature from 578 to 298 K. As mentioned in Fig. 8, the rate of hydrogen permeation was determined by hydrogen diffusion through the platinum layer at the relatively high temperatures of 573–773 K. Below 573 K, the rate-determining step was shifted to hydrogen adsorption, i.e., a hydrogen dissociative adsorption on the platinum surface. In general, the hydrogen dissociation on a platinum surface is strongly dependent on temperature. According to the published report of Chai et al. [20], the chemisorption of hydrogen was apparently observed at temperatures higher than 473 K, but not at ambient temperature. These findings will support our speculation that the rate-determining step was shifted to hydrogen dissociative adsorption on the platinum surface below 573 K.

Recently, the effect of crystal grain size on the hydrogen permeance of a supported palladium membrane has received a considerable amount of attention [13,23]. In order to study the effect of platinum grain size on hydrogen diffusion, another CVD platinum membrane was prepared under different sublimation conditions. It has been reported that the grain size of

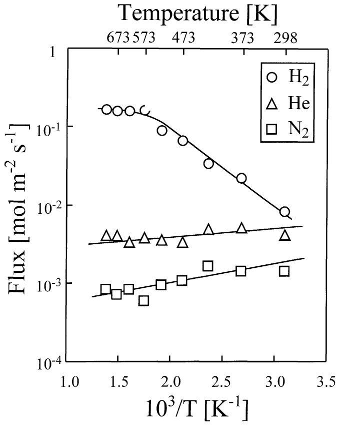


Fig. 9. Temperature dependency of hydrogen, helium and nitrogen fluxes through CVD platinum membrane.

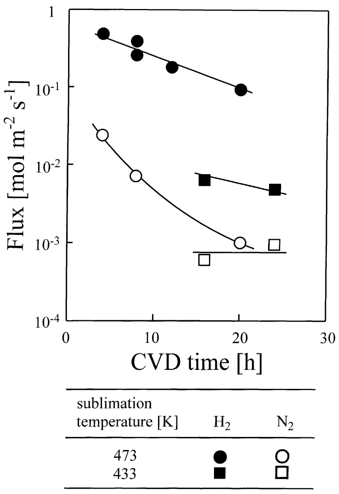
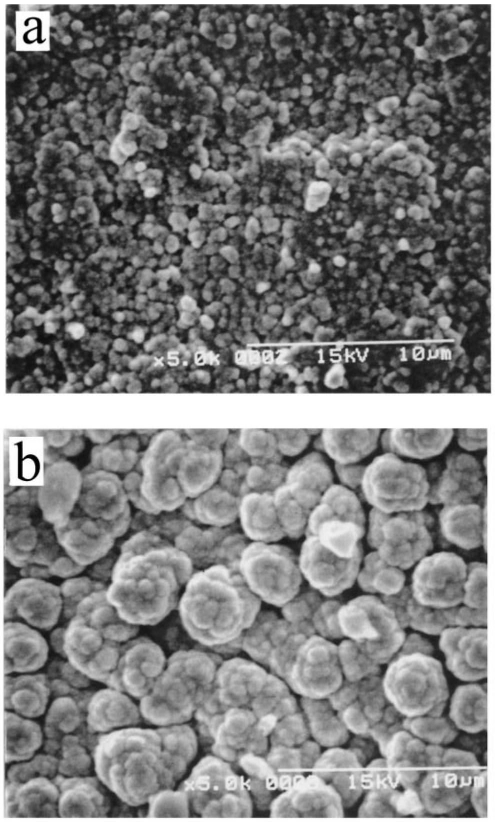


Fig. 10. Effect of sublimation temperature of platinum precursor on hydrogen flux through CVD platinum membrane.



Membrane	Temperature [K]	
	Sublimation	Deposition
a	473	493
b	433	493

Fig. 11. SEM photographs of CVD platinum membranes prepared at different sublimation temperatures.

deposited metal increases with decreased feed concentration of the CVD precursor [15]. These results are shown in Fig. 10. In this study, larger platinum grains were prepared by lowering the sublimation temperature of the CVD. A high hydrogen permeance was obtained for the membrane at 473 K. The SEM photographs shown in Fig. 11 indicate that the sizes of platinum grains prepared at a sublimation temperature of 433 K were large compared to that at 473 K. The surface area of the platinum effective for the surface diffusion of hydrogen is considered to have decreased for large grains, and the amount of adsorbed hydrogen on platinum surface decreased with a decrease in the surface area. Therefore, the hydrogen permeance of CVD platinum membrane decreased with increased platinum grain size.

4. Conclusions

A CVD membrane had a higher hydrogen permselectivity than that predicted by Knudsen diffusion and a 1000-times higher hydrogen permeability than a dense electroless-plating platinum membrane. It can be speculated that hydrogen diffuses on the surface of the platinum rather than inside the bulk. The hydrogen flux was inversely proportional to the thickness of the platinum layer, indicating that the rate determining step of hydrogen permeation was hydrogen diffusion through the platinum layer. The CVD membranes with smaller metal grains gave a higher hydrogen flux because the effective area for the hydrogen surface diffusion was increased. Application of this CVD technique to the fabrication of hydrogen-permselective supported metal membranes will make it possible to adopt other novel metals that have never been considered as hydrogen separating medium. These supported metal membranes may give unique characteristics for hydrogen separation.

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References

[1] H.P. Hsieh, Inorganic Membranes for Separation and Reaction, Elsevier, Amsterdam, 1996.
[2] E. Kikuchi, CATTECH 1 (1997) 67.
[3] J. Shu, B.P.A. Grandjean, A. Van Neste, S. Kaliaguine, Can. J. Chem. Eng. 69 (1991) 1036.
[4] S. Uemiya, Y. Kude, K. Sugino, N. Sato, T. Matsuda, E. Kikuchi, Chem. Lett. (1988) 1687.

[5] E. Kikuchi, S. Uemiya, Gas Sep. Purification 5 (1991) 261.
[6] J.P. Collins, J.D. Way, Ind. Eng. Chem. Res. 32 (1993) 3006.
[7] K.L. Yeung, A. Varma, AIChE J. 41 (1995) 2131.
[8] J. Shu, B.P.A. Grandjean, S. Kaliaguine, P. Ciavarella, A. Giroir-Fendler, J.-A. Dalmon, Can. J. Chem. Eng. 75 (1997) 712.
[9] P.P. Mardilovich, Y. She, Y.H. Ma, M.H. Rei, AIChE J. 44 (1998) 310.
[10] L. Yang, O. Sakai, S. Kosaka, T. Kawae, T. Takahashi, in: Proc. 5th Int. Conf. Inorg. Membr., Nagoya, Japan, 1998, P-139.
[11] S.C. Yan, H. Maeda, K. Kusakabe, S. Morooka, Ind. Eng. Chem. Res. 33 (1994) 616.
[12] S. Uemiya, M. Kajiwara, T. Kojima, AIChE J. 43 (1997) 2715.
[13] G. Xomeritakis, Y.S. Lin, AIChE J. 44 (1998) 174.
[14] Z.Y. Li, H. Maeda, K. Kusakabe, S. Morooka, H. Anzai, S. Akiyama, J. Membr. Sci. 78 (1993) 247.
[15] T. Kodas, H. Hampden-Smith, The Chemistry of Metal CVD, VCH, Weinheim, Germany, 1994.
[16] A.L. Athayde, R.W. Baker, P. Nguyen, J. Membr. Sci. 94 (1994) 299.
[17] G. Xomeritakis, Y.S. Lin, J. Membr. Sci. 133 (1997) 217.
[18] S. Yamauchi, Kagaku to Kogyo 21 (1968) 1364 (in Japanese).
[19] D.J. Edlund, W.A. Pledger, J. Membr. Sci. 77 (1993) 255.
[20] M. Chai, Y. Yamashita, M. Machida, K. Eguchi, H. Arai, J. Membr. Sci. 97 (1994) 199.
[21] S. Uemiya, N. Hatakeyama, M. Kajiwara, T. Kojima, K. Mizumoto, T. Doi, Preparation of platinum-porous alumina composite membrane by electroless-plating, J. Surf. Finish. Soc. Jpn. 48 (1997) 98 (in Japanese).
[22] S.A. Steward, Review of Hydrogen Isotope Permeability Through Materials, US National Laboratory Report, UCRL-53441, 1983.
[23] K.J. Bryden, T.J.Y. Ying, Nanostructured Mater. 9 (1997) 485.