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Rhodium- and iridium-dispersed porous alumina membranes and their hydrogen permeation properties

Masataka Kajiwara [a], Shigeyuki Uemiya [a,*], Toshinori Kojima [a], Eiichi Kikuchi [b]

[a] *Department of Industrial Chemistry, Faculty of Engineering, Seikei University, 3-3-1 Kichijoji-Kitamachi, Musashino-shi, Tokyo 180-8633, Japan*

[b] *Department of Applied Chemistry, School of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*

Abstract

Rhodium and iridium were used as novel membrane materials for hydrogen separation. The composite membranes consisting of these metals dispersed in the pores of an asymmetric porous alumina were prepared by the CVD technique. Rh(acac)$_3$ and Ir(acac)$_3$ complexes were selected as the CVD precursors. The hydrogen fluxes of the rhodium and iridium membranes were 0.155 and 0.178 $\mathrm{mol\,m^{-2}\,s^{-1}}$ at 773 K and the transmembrane pressure difference of 98 kPa, respectively, which were comparable to those of the palladium composite membranes prepared by electroless plating and CVD. The ideal permselectivities of hydrogen to nitrogen were 80 and 93 for rhodium and iridium, respectively. Hydrogen molecules adsorbed on metals dissociated into the atomic form and then the atoms diffused through the metal layer. The CVD membranes gave similar hydrogen permeation coefficients except for palladium. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium; Iridium; Hydrogen permeation properties

1. Introduction

Only the palladium-based membranes are commercialized to produce ultrapure hydrogen because they are permeable only to hydrogen. Commercially available, self-supporting dense palladium-based membranes with a thickness above 50–100 μm do not sound very attractive because of their drawbacks of high cost, low permeance, and low chemical stability. These drawbacks limited their industrial usage only to small-scale hydrogen purification equipment for the electronic, metallurgical, and fine chemical industries and the fusion fuel purification process to separate hydrogen isotopes.

In order to improve hydrogen permeance with maintaining the inherent excellent hydrogen permselectivity, Kikuchi and Uemiya's group developed composite membranes consisting of a thin dense film of pure palladium (4.5–20 μm) supported on an asymmetric porous glass or ceramic using an electroless-plating technique [1,2]. However, some drawbacks still exist; one is the embrittlement of palladium due to the formation of the hydrogen-rich β-PdH phase during the heating and cooling cycles, while the other is the high cost of the palladium metal. Uemiya et al. have recently developed CVD non-palladium membranes such as ruthenium and platinum supported on a porous alumina [3,4]. These membranes gave excellent hydrogen permeance, comparable to supported palladium membranes prepared by electroless plating. We speculate that the permeation of hydrogen through the CVD membranes is not based on the solution-diffusion

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* Corresponding author. Fax: +81-422-37-3871.
E-mail address: uemiya@ch.seikei.ac.jp (S. Uemiya).

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transport mechanism, but on the surface diffusion mechanism. Furthermore, their applicability to a membrane reactor system has also been investigated using the steam reforming of methane as a model reaction [5]. If hydrogen permselectivities of the CVD membranes are more improved than the present best value of $S_{H_2/N_2} = 280$, a breakthrough will be achieved using the CVD non-palladium membranes with advantages over the electroless-plating palladium membrane such as a lower amount of metal coating and a reduced tendency for hydrogen embrittlement.

Chai et al. [6] was also interested in non-palladium membrane for hydrogen separation and their incorporation into membrane reactor systems. They prepared metal-dispersed alumina membranes, such as ruthenium-, rhodium-, nickel- and platinum- as well as palladium-alumina membranes by the sol–gel technique. These metal-dispersed alumina membranes, however, gave a slightly higher H_2/N_2 selectivity than that predicted from the Knudsen diffusion mechanism. A platinum-coated vanadium membrane was developed by Edlund and Pledger [7]. A supported platinum membrane was prepared by Uemiya's group using an electroless-plating technique [8]. However, a systematic study of the supported precious membranes except for the palladium-based membranes has not yet been conducted, because precious metals except for palladium show too low a hydrogen diffusivity in their bulk to be used as a membrane material for hydrogen separation. With our development of the CVD non-palladium, platinum and ruthenium membranes as the starting point, other metals should be evaluated in order to prepare a variety of better supported metal membranes than the ones so far reported. In the present work, the precious metals, rhodium and iridium were used as membrane materials for hydrogen separation. The hydrogen permeance of the resulting membranes was evaluated and compared for the reported CVD membranes such as platinum, ruthenium, and palladium.

2. Experimental

The composite membranes consisting of rhodium or iridium dispersed in the pores of asymmetric porous alumina tubes were prepared by the CVD technique. The porous alumina tube (outside diameter, 10 mm; inside diameter, 7 mm; length, 250 mm; effective average pore size, 200 nm), purchased from NGK Insulator, Japan, was used as the support. Prior to the CVD of the metal layer, the support was ultrasonically washed with trichloroethylene for 15 min and then with ethanol for 15 min. The $Rh(acac)_3$ or $Ir(acac)_3$ complex, purchased from Tanaka Kikinzoku, Japan, was used as the CVD precursor. The metal deposition was restricted within the central part of the support having an area of 6.28 cm^2 with the aim of making the metal layer approximately uniform. The metal layer was intended to be mainly formed at the inside of the pores by thermal decomposition of the precursor under the condition where the inside of the support was evacuated using an electric vacuum pump. The sublimation and decomposition temperatures of the precursor significantly affected the structure of the resulting membranes and consequently their hydrogen permeance. The CVD preparation conditions were selected to avoid the nucleation of metal particles in the gas phase, as summarized in Table 1. The preparation conditions of the CVD platinum, palladium, and ruthenium membranes are also listed in Table 1. A detailed procedure for the membrane preparation using the CVD technique is referred to in our previous papers [3,4].

The resulting membranes were installed in a separation test cell and heated up to a definite test temperature in a nitrogen atmosphere. Pure grade hydrogen and nitrogen were fed to the outside of the membranes (high pressure side), and the amount of gas permeating through the membranes was measured by a conventional soap-film meter. The hydrogen and nitrogen fluxes were measured at the temperatures of 573–773 K and the transmembrane pressure differences of 49–196 kPa with maintaining the permeation side (low pressure side) at atmospheric pressure. The hydrogen permselectivity is defined as the molar ratio of fluxes of hydrogen to nitrogen.

3. Results and discussion

Fig. 1 shows the variation in the CVD time in nitrogen leakage under the conditions listed in Table 1. Rhodium or iridium was selectively deposited mainly on the inside of the support pores under the condition listed in Table 1. A decreased flux of nitrogen leakage

Table 1
Summary of CVD conditions

Metal	Sublimation temp. (K)	Deposition temp. (K)	CVD rate (μm h^{-1})	CVD time (h)	Thickness (μm)	(S_{H_2/N_2})[a]	Heat of adsorption (kJ mol^{-1})
Rhodium	473	513	1.24	14	17.3	80	117
Iridium	483	513	1.04	8	8.3	93	109
Palladium[b]	433	543	0.13	24	3.3	240	117
Ruthenium[b]	473	543	0.24	14	3.2	120	118
Platinum[b]	473	493	0.29	20	5.8	210	109

[a] Ideal permselectivity for H_2 over N_2 at 773 K.

[b] Quoted from [3].

resulted from plugging of the pores, being proportional to the amount of deposited metal. For rhodium and iridium, CVD times of 14 and 8 h were totally required, respectively, until the nitrogen flux was unchanged or reduced to below 10 cm^3(STP) min^{-1} at 773 K and a transmembrane pressure difference of 98 kPa. The resulting CVD membranes gave high ideal hydrogen permselectivities (S_{H_2/N_2}), compared with the value based on the assumption of the Knudsen diffusion, typically 80 for rhodium and 93 for iridium at 773 K.

Fig. 2 shows a comparison of the hydrogen fluxes for a variety of CVD precious metal membranes. The hydrogen fluxes of the CVD rhodium and iridium membranes were 0.155 and 0.178 mol m^{-2} s^{-1} at 773 K and a transmembrane pressure difference of 98 kPa, respectively. These hydrogen permeances are comparable to those of supported palladium membranes prepared by electroless plating and CVD.

As discussed in detail elsewhere [3,4], we reported that the hydrogen permeation mechanism of the CVD membranes is surface diffusion with a slight contribution of the Knudsen diffusion and the solution diffusion. In the following discussion, hydrogen fluxes excluded contribution of the Knudsen diffusion were calculated using Eqs. (1) and (2).

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

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

where J_{M,H_2} is the hydrogen flux excluded the contribution of the Knudsen diffusion, J_{T,H_2} is the total hydrogen flux, J_{K,H_2} and J_{K,N_2} are the hydrogen and nitrogen fluxes via the Knudsen diffusion, and M_{H_2} and M_{N_2} are the molecular weights of hydrogen and nitrogen, respectively. J_{K,N_2} can be obtained by measuring the nitrogen fluxes through the membrane.

The influence of the transmembrane pressure difference on the hydrogen fluxes of the CVD rhodium and iridium membranes is shown in Fig. 3. Hydrogen permeance of both CVD membranes showed a square-root pressure dependency. This result reveals

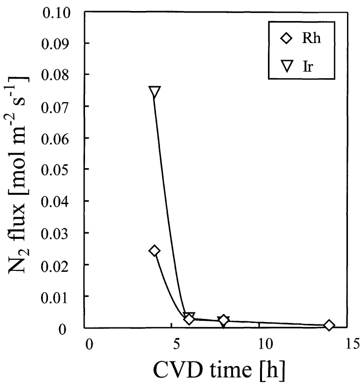

Fig. 1. Variation of CVD time in flux of nitrogen leakage.

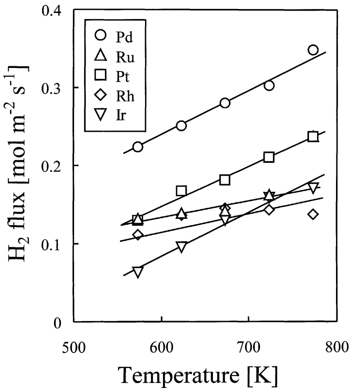

Fig. 2. Comparison in hydrogen flux among various CVD precious metal membranes.

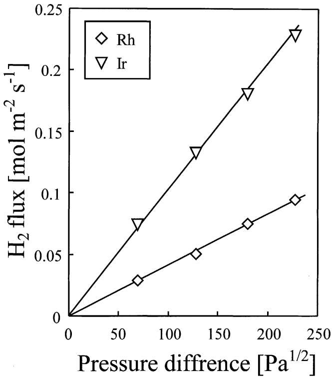

Fig. 3. Influence of transmembrane pressure difference on the hydrogen fluxes of the CVD rhodium and iridium membranes.

that hydrogen molecules adsorbed on metals dissociate into an atomic form and the produced hydrogen atoms then diffuse through the metal layer. Fig. 4 shows the hydrogen flux through the CVD iridium membrane as a function of CVD time. The hydrogen flux was almost inversely proportional to the CVD time. Assuming that the thickness of the metal layer is proportional to CVD time, it may be considered that hydrogen flux was inversely proportional to the thickness. These findings derived from Figs. 3 and 4 indicate that the rate-determining step of the hydrogen permeation is hydrogen diffusion through the metallic layer.

The temperature dependence of the hydrogen permeabilities of the composite membranes is illustrated in Fig. 5, where the reported values of dense palladium and platinum are also shown for comparison [9]. It can be seen that the hydrogen permeabilities through bulk layers of palladium and platinum are completely different. The present results indicate that permeability by bulk diffusion strongly depends on metal kind. On the other hand, the CVD membranes gave the same order of hydrogen permeabilities of 10^{-8} mol m^{-1} s^{-1} Pa$^{-1/2}$, irrespective of the metal. Unfortunately, it is impossible to directly compare hydrogen permeabilities between the CVD and dense membranes, due to lack of hydrogen permeability data for the dense rhodium and iridium. We have reported that the hydrogen permeation mechanism through the CVD platinum membrane is mainly surface diffusion with a slight contribution of the Knudsen diffusion and the solution diffusion. In the case of CVD rhodium and iridium membranes, we speculate that dominant diffusion mechanism is surface diffusion.

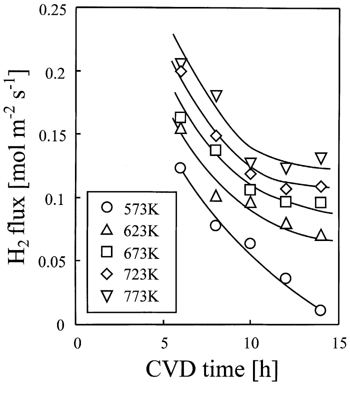

Fig. 4. Hydrogen flux through CVD iridium membrane as a function of CVD time.

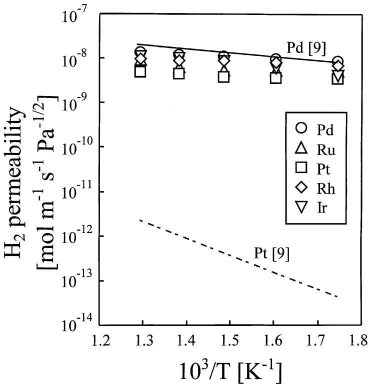

Fig. 5. Temperature dependence of hydrogen permeabilities of various supported metal membranes.

The surface diffusion phenomenon is of great importance during catalysis, the transport in porous media and so on [10]. Recently, inorganic membranes for carbon dioxide separation have been designed using this phenomenon [11]. Surface diffusion can be divided into two types; the diffusion of physically adsorbed species and chemically adsorbed species. Hydrogen chemically adsorbs on precious metals. Gilliland et al. [13] measured the surface diffusivity of hydrogen on platinum. His group extended their study from the surface diffusion of chemically adsorbed species to physically adsorbed ones, and suggested that the surface diffusivity was correlated as a function of the heat of adsorption for a coverage up to 0.49 [12,13]. Namely, surface mobility of strongly adsorbed species is slow as compared to that of weakly adsorbed species.

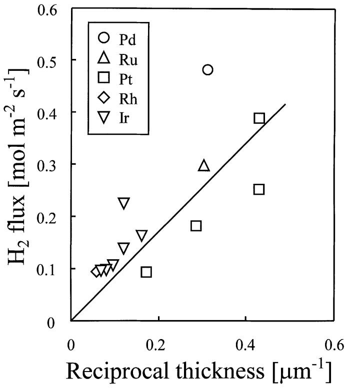

Fig. 6. Hydrogen fluxes of various CVD membranes as a function of their reciprocal thickness.

The heat values of hydrogen adsorption for the precious metals used in this study are almost the same, being in the range of 109–118 kJ mol^{-1} [14], as listed in Table 1. This indicates that the precious metals gave similar hydrogen surface diffusivities. If there is little difference in the surface area among the metals used, the precious metals have similar hydrogen permeabilities. From this point of view, the relationship between hydrogen flux and thickness of the metal layer was investigated, anticipating that it reveals the effect of metal type on the hydrogen permeance of the CVD membranes. In Fig. 6, the hydrogen fluxes for the CVD membranes are plotted as a function of the reciprocal thickness calculated on the assumption that the entire sublimated precursor was completely decomposed in the central area of the support, and the metal gave a similar distribution along with the cross-sectional depth. The plots have a slight scatter, maybe due to the difference in the surface area, but most metals except for palladium obey the relation indicated by the line in Fig. 6. On the other hand, the palladium membrane gave a higher flux than the one predicted by this relation, probably due to the contribution of the solution diffusion through the bulk of the agglomerated grains. Further study on hydrogen permeation mechanism concerning the CVD membranes is required.

4. Conclusions

CVD rhodium and iridium membranes produced a hydrogen permeance comparable to an electroless-plating dense palladium membrane as well as a CVD platinum membrane. Hydrogen molecules adsorbed on metals dissociated into the atomic form and then the hydrogen atoms diffused through the metal layer. The rate-determining step for the hydrogen permeation was hydrogen diffusion through the metal layer. The CVD membranes gave a similar hydrogen permeation coefficient except for palladium.

Acknowledgements

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