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Preparation of palladium membrane over porous stainless steel tube modified with zirconium oxide

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Abstract

A palladium membrane has been prepared by electroless plating on the surface of a porous stainless steel tube. Since the large surface pores of the tube are obstacle for preparation of a defect-free palladium film on the surface, zirconium oxide particles were deposited inside the pores. The mean thickness of the resulting Pd membrane on the modified tube was ca. 10 μm. It is suggested that the permeability of hydrogen is partly governed by gas diffusion in the pores.

Keywords: Palladium membrane; Porous stainless steel tube; Zirconium oxide; Hydrogen separation

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1. Introduction

Palladium-based films are permeable for hydrogen and also catalytically active toward many hydrogen-involving reactions such as hydrogenation and dehydrogenation [1,2]. Owing to the combination of these functions, Pd-based catalytic membrane reactors have received much attention in recent years. The removal of hydrogen from a reaction medium is proved to be effective in shifting equilibrium-limited dehydrogenation reactions toward the product side [3–7]. For hydrogenation reactions, the controlled introduction of hydrogen often results in a high selectivity of target products [1,2]. Undoubtedly, the current development of palladium-based membranes aims to achieve high hydrogen permeability, good thermal stability, and good mechanical strength.

In general, massive palladium sheets are not suitable for the use in membrane reactors because economic considerations do not allow the industrial use of the expensive palladium metal in the massive form. Since hydrogen permeation flux is inversely proportional to the membrane thickness, membranes must be thin enough to ensure a reasonable permeation flux while such a thin membrane does not have enough mechanical strength to be self-standing. Composite palladium membranes meet to these criteria and are extensively employed in membrane reactors to separate hydrogen produced [2]. Porous ceramics such as alumina have often been employed as a support for Pd membrane for hydrogen separation, but connection of ceramics to metal is difficult and does not ensure the mechanical strength. Among various substrates studied, porous stainless steel is advantageous because of its thermal expansion coefficient being close to that of Pd-based films, ease to process, corrosion resistance, high thermal stability, high mechanical strength, etc. [2,8]. However, pores on its surface are considerably larger than those of ceramics, and preparation of defect-free thin Pd membranes is difficult. One of the solutions to solve this problem is the surface modification of the sintered stainless steel substrate aiming at reducing its surface pore size. In actual shot peening of iron particles on the surface of the metal support was proposed, but the material seemed to choke the surface pores and the hydrogen flux with 6 μm palladium film was similar to that of 20 μm palladium film on a porous alumina support without the treatment [8]. In this work, the large pores have been modified with zirconium oxide particles whose size can be controlled by changing the pH of its colloidal solution. On the modified surface, we prepared a thin palladium film in a dense form by electroless plating.

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2. Experimental

A stainless steel filter tube with nominal particle retention size of 0.2 µm (Mott Metallurgical) was employed as a support of a palladium membrane. The length of the filter was 70 mm with 7 mm ID and 9.5 mm OD. The porous tube was washed with carbon tetrachrolide for 1 h in ultrasonic vibration bath, then with ethanol for 0.5 h for removal of contaminants and dried at 120 °C for 1 h. The diameter of the major surface pores was 50–100 µm and the population of the pores was ca. 20 mm^{-2}.

Colloidal zirconium oxide (NSZ-30 A) was supplied from Nissan Chemical Industries. The pH value of the solution was controlled by addition of ammonia. The colloidal solution was sucked through the porous tube in an ultrasonic bath for 1 h at room temperature by evacuation from inside the tube for modification of the pores with zirconium oxide particles. The excessive zirconium oxide stuck on the support surface was removed with rinsing water; then, the tube was heated at 300 °C for 2 h. After repeating the procedure several times, palladium catalyst for electroless plating was given on the tube using a commercial activator (OPC-50 an OPC-150, Okuno Chemical Industries). Electroless palladium plating was carried out in a commercial palladium plating bath (Palatop A and Palatop C, Okuno) of which pH was 5–6 at 50–70 °C. After washed with water, the tube was dried at 120 °C for 2 h. The mean thickness of the palladium layer was calculated on the basis of the change in the palladium content of the plating bath determined by ICP spectrometry.

Distribution of the pore size of the unmodified tube was measured by mercury porosimetry with a Micromeritics PORESIZER 9310. Particle sizes of the colloidal zirconium oxide were determined by dynamic light scattering with a Honeywell Microtrac UPA.

The surface morphology of the specimens was characterized using a Keyence VK8500 laser microscope.

Fluxes of helium and argon through the filter tube after the modification with zirconium oxide were measured at room temperature. A constant flow of the pressurized gas through a mass flow controller was fed to the outside of the tube by monitoring with a pressure gauge and the permeation side of the tube was kept at atmospheric pressure. Hydrogen flux through a palladium membrane was determined at 350–550 °C using the same equipment. A subtle flux was measured with a soap film meter connected to the exit of the permeation side.

3. Results and discussion

3.1. Modification of porous stainless steel tube with zirconium oxide

The aqueous chemistry of colloidal zirconium oxide is quite complex. In the solution both the monomeric and polymeric forms coexist, and the pH value is the most important factor that determines the size of the colloid. The properties of the colloids generally depend on the solution acidity, zirconium concentration and ionic background [9]. At low pH values, the monomeric form, $ZrO_2 \cdot 2H_2O$, predominates and no colloids are formed. Colloids could be found to start appearing at a pH from 3.0 to 3.5 [10]. The freshly precipitated amorphous gel is considered to be a network of zirconium tetramer unit. At higher pH values, hydrolysis and condensation of the hydroxides promote precipitation of a white gel-like colloid.

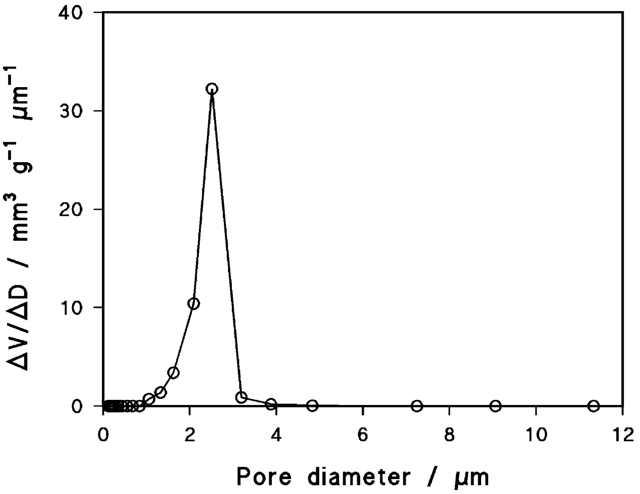


Fig. 1. Pore size distribution of porous stainless steel tube whose nominal particle retention size is 0.2 µm.

Since the pore size of the support tube was around 2 µm (Fig. 1), the particle size of ZrO_2 colloid should be close to the size or smaller for deposition of the particles in the pores. At first we employed a colloidal solution with the pH value of 7.6 for modification of the support tube with zirconium oxide, while the particle size distributed widely from 0.5 to 7 µm (Fig. 2). In the case of the solution with the lower pH

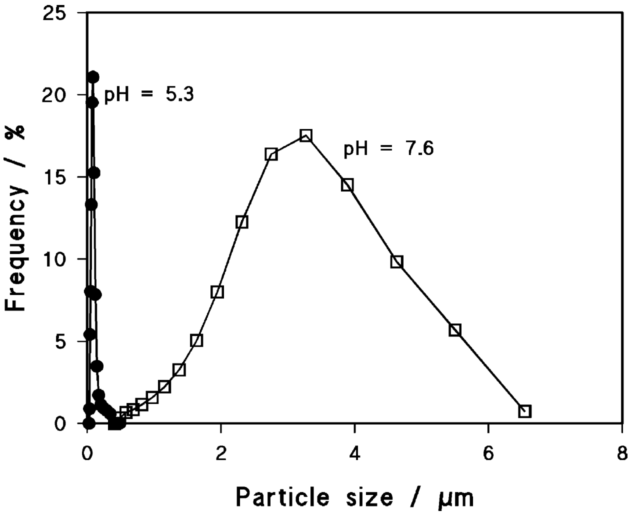


Fig. 2. Particle size distribution of colloidal zirconium oxide solution.

value, colloid particles were too small to stay inside the large pores of the tube. After heating at 300 °C the permeation rate of helium decreased to 0.019 from 0.05 mol s^{-1} m^{-2} kPa^{-1} for the parent porous tube at room temperature. The permeation rates of helium and argon were proportional to the pressures, and the ratio of the rates (He/Ar) was 2.05 (Fig. 3). When the pore size is sufficiently small, the gas flow in the pore is governed by the Knudsen diffusion in which region the flux of a gas is proportional to $w^{-0.5}$ where w is the molecular weight of the gas [11]. The separation ratio of He/Ar depends on the pore size in the region usually less than 0.1 μm while the theoretical ratio is 3.1. At the second step, a colloidal ZrO_2 solution at a lower pH value of 5.3 was used to modify smaller pores. After the modification, permeation rates of helium and argon decreased significantly and He/Ar separation ratio increased, showing reduction in the pore size by the modification with zirconium oxide (see Fig. 3). The modification with zirconium oxide was repeated and the permeation rates of helium and argon were stabilized at the fourth modification. The rough surface of sintered metal was observed in the laser micrographs of the unmodified tube (Fig. 4a). After the modification for five times, ZrO_2 small particles were observed on the surface (Fig. 4b); however, the metallic surface was not perfectly covered with the particles, showing that ZrO_2 particles mainly deposited in the pores.

3.2. Deposition of palladium on porous stainless steel tube modified with zirconium oxide

Palladium deposition was performed on the modified stainless steel tube by electroless plating. The surface of the tube was covered with a thin and bright palladium film after 1.2 h (Fig. 4c). The thickness of the palladium film obtained was estimated as 10 μm. No permeation of argon was detected for this sample under the studied pressure range at room temperature, indicating absence of pinholes or cracks on the film surface.

3.3. Hydrogen permeation through palladium membrane supported on the porous tube modified with zirconium oxide

It is known that hydrogen dissolves into palladium at low temperatures to form α-hydride and further β-hydride. Formation of a β-hydride phase induces a significant lattice expansion causing fracture of the membrane. Hence, hydrogen was introduced to the membrane at 300 °C or above. Permeation flux of hydrogen through the membrane prepared was proportional to $(p_1^{0.5} - p_2^{0.5})$ as shown in Fig. 5, where p_1 and p_2 are the partial pressures of hydrogen on pressurized and atmospheric sides, respectively. This essentially indicates atomic diffusion of hydrogen through the palladium membrane. The hydrogen flux, J, can be express as $J = Q(p_1^{0.5} - p_2^{0.5})/l$, where Q is the hydrogen permeation coefficient and l is the membrane thickness. Since the hydrogen transport through a non-porous palladium film is generally an activated process, the activation energy, E_A, can be obtained by the Arrhenius plot of Q (Fig. 6). That is, $Q = Q_0 \exp(-E_A/RT)$. The values of E_A and Q_0 were 7.1 kJ mol^{-1} and 0.60 μm mol s^{-1} m^{-2} $kPa^{-0.5}$, respectively. In the case of the palladium membrane supported on porous glass, these values were calculated as 10.7 kJ mol^{-1} and 1.8 μm mol s^{-1} m^{-2} $kPa^{-0.5}$ on the basis of the data in Ref. [12]. A large part of palladium membrane directly covered the surface of sintered metal. This portion should be less effective than the part covering the pores. Thus, the effective area of the membrane will be significantly smaller than the nominal area. Since the pores of the stainless filter

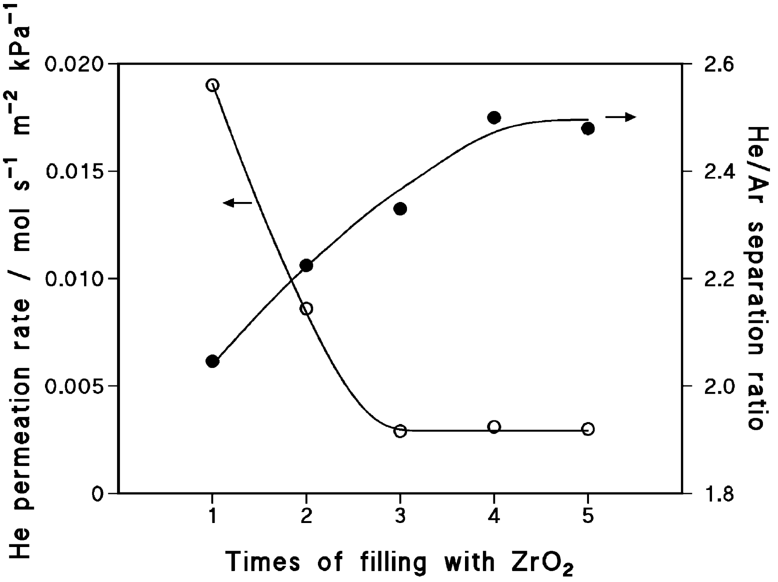
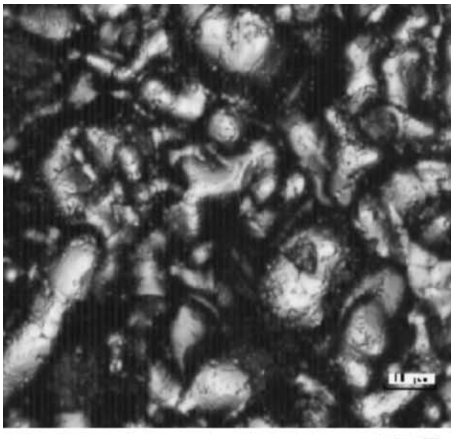
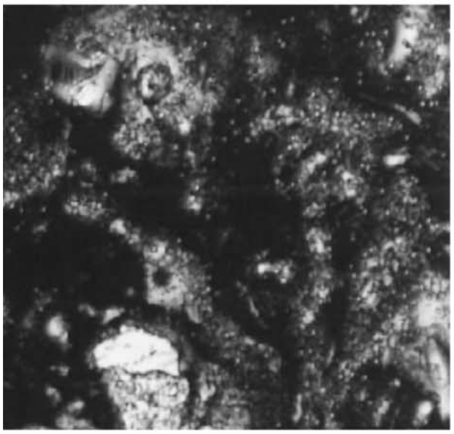


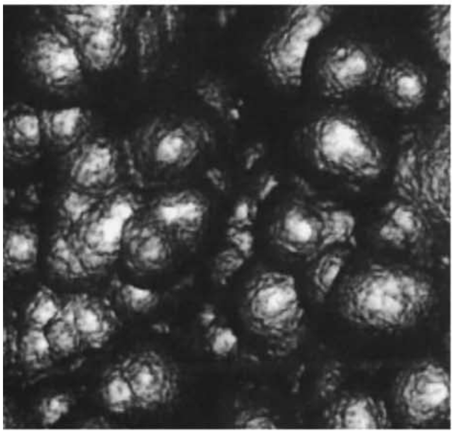
Fig. 3. Change in fluxes of helium and argon through porous stainless steel filter by modification with zirconium oxide particles.



(a) without modification



(b) after modification with ZrO_2



(c) after palladium plating

Fig. 4. Laser microscope images of the tube surface. The solid line below the image (a) shows the length of 10 μm.

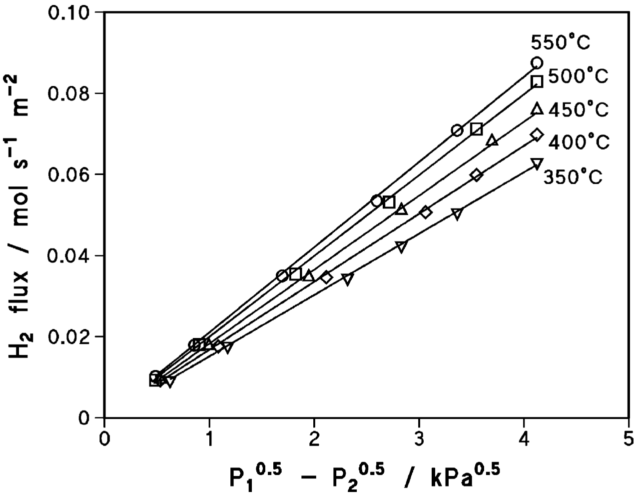


Fig. 5. Hydrogen flux through palladium membrane of ca. 10 μm on porous stainless steel support modified with zirconium oxide particles.

were filled with ZrO_2 particles, the surface porosity may be small in comparison with the porous glass. Presence of ZrO_2 particles in the pores reduces gas permeation (see Fig. 3). The flux of helium just after the ZrO_2 modification was 0.2 mol s^{-1} m^{-2} at room temperature (pressure difference, 100 kPa) and that of hydrogen through the palladium membrane at 500 °C was 0.083 mol s^{-1} m^{-2} at the same pressure difference, suggesting that the diffusion of hydrogen in the pores is a possible resistance of hydrogen permeation through the tube. Since the gas flux in the Knudsen diffusion region is proportional to $(RT)^{-0.5}$ [11], the flux at 550 °C is 87.5% of that at 350 °C. When the diffusion in the micropores contributes to the hydrogen flux, the apparent activation energy of hydrogen permeation should be lower than the activation energy through palladium foils. This accounts for the low activation energy determined from the Arrhenius plots (see Fig. 6), while the value for thin palladium membrane is usually 10–12 kJ mol^{-1} [2,12–14].

When argon was introduced to the membrane, leak of argon was detected with the rate of 5.3×10^{-6} mol s^{-1} m^{-2} kPa at 500 °C. Since no flow of argon was detected before applying a high temperature, defects are formed during the heating process, while purity of hydrogen is another important issue.

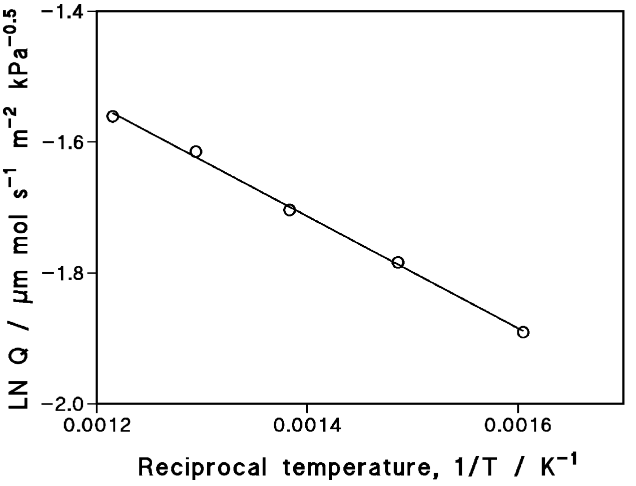


Fig. 6. Arrhenius plots of hydrogen permeation coefficient in the range of 350–550 °C.

4. Conclusions

A palladium membrane of ca. 10 μm in thickness can be prepared on the surface of a porous stainless steel tube modified with zirconium oxide particles. After the deposition of zirconium oxide on the porous tube, the permeation rate of helium decreased considerably, appearing that the oxide particles are successfully introduced into the large surface pores which are an obstacle for preparation of a defect-free palladium film on the tube surface. The hydrogen flux is lower than that for a palladium membrane prepared on a porous glass. The lower activation energy shows that zirconium oxide particles are resistance of hydrogen diffusion inside the pores.

Acknowledgements

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