

Extremely thin Pd-silica mixed-matrix membranes with nano-dispersion
for improved hydrogen permeability
Masakoto Kanezashi, Mitsunori Sano, Tomohisa Yoshioka, and Toshinori Tsuru
Department of Chemical Engineering, Hiroshima University
Higashi-Hiroshima, 739-8527, Japan
E-mail: kanezashi@hiroshima-u.ac.jp; tsuru@hiroshima-u.ac.jp

Supplementary Information

Experimental Methods

Preparation of silica-zirconia colloidal sols [1,2]

SiO₂-ZrO₂ composite colloidal sols with a molar ratio of 1/1 were prepared by the hydrolysis and condensation reaction of tetraethoxysilane (TEOS, > 99%, Kishida Chemical Co.) and zirconium butoxide (80 wt% solution in 1-butanol, ALDRICH). A specified amount of TEOS (3.52 g) was dissolved in 200 g of ethanol (> 99.5 wt %, SIGMA-ALDRICH) and water (0.23 g) and HCl (0.35 g, 35 wt %, SIGMA-ALDRICH) were added to the solution for a partial hydrolysis and condensation reaction for about 60 min. Then zirconium butoxide (6.48 g) was added to the solution at around 4 °C. After about 30 minutes of further hydrolysis and condensation, a large amount of water and a specified amount of HCl were added to the polymer solution to control the concentration of pH (<2). Then the solution was boiled for 12 hours, keeping the total amount constant at 500 g for colloidal formation. During the boiling, the organic solvent and organic chemicals formed by the hydrolysis reaction were removed.

Preparation of Pd-doped silica colloidal sols

Pd-doped silica colloidal sols with molar ratios of Si/Pd = 3/1, 3/7, 2/8, and 1/9 were prepared by the hydrolysis and condensation reaction of tetraethoxysilane (TEOS, > 99 %, Kishida Chemical Co.) in water with specific amounts of PdCl₂ (99 %, ALDRICH) and HCl (35 wt %, SIGMA-ALDRICH). The preparation procedures for Pd-doped silica colloidal sols of Si/Pd = 3/7, for example, were as follows. A specific amount of TEOS (0.75 g) was added to water (99.25 g) with PdCl₂ (1.49 g) and HCl (1 g), and the solution was stirred well for 12 h for hydrolysis and condensation reactions at 25 °C. Three kinds of sols (equivalent weight % of TEOS in sol: 0.75 wt%, 0.5 wt%, 0.25 wt%) were prepared.

Fabrication of Pd-silica mixed matrix membranes

Porous α -alumina tubes (porosity: 50 %, average pore size: 1 μm , outside diameter: 10 mm) were used as the supports for Pd-doped silica membranes. α -alumina particles (average particle diameter: 0.2-1.9 μm) were coated on the outer surface of a porous support using silica-zirconia colloidal sol as the binder (average colloidal diameter: 80 nm), and the module was fired at 550 $^{\circ}\text{C}$ for 30 minutes to make the surface smooth. These procedures were repeated several times to remove large pores that might result in pinholes in the final membrane. Then, the $\text{SiO}_2\text{-ZrO}_2$ (Si/Zr=1/1) sol was diluted to about 0.5 wt% and was coated onto the substrate using a hot coating method, in which the substrate (module) was heated to around 180 $^{\circ}\text{C}$ before coating with the colloidal sols by quickly contacting the module with a wet cloth containing the sols, to form an intermediate layer with pore sizes of several nm. This hot coating method, originally proposed by Asaeda *et al.* [3], dries the sol instantly, preventing the sol from penetrating deep into the pores. After coating, the membrane was fired at 550 $^{\circ}\text{C}$ for about 30 min in air atmosphere. Then, three kinds of Pd-doped silica colloidal sol were coated using the hot-coating method and were fired at 550 $^{\circ}\text{C}$ in hydrogen for 1 h. These procedures were repeated several times for each colloidal sol, ranging from sols with a large particle size to smaller ones. The morphology, thickness and location of the Pd particles were evaluated by TEM using an EDS analysis unit.

Gas permeation measurement and hydrothermal stability test

Figure S1 is a schematic diagram of an experimental apparatus for gas permeation measurement and hydrothermal stability testing. A single gas of industrial grade (He, H_2 , N_2) was fed on the membrane surface at atmospheric pressure, while the permeate side (downstream) was evacuated by a vacuum pump. The temperature of the permeation cell was kept at a given temperature between 300 and 500 $^{\circ}\text{C}$. The permeances were calculated from the observed pressure difference across the membrane and the permeation rate, which was obtained by a calibrated critical nozzle placed between the permeation cell and the vacuum pump. A hydrothermal stability test was performed at 500 $^{\circ}\text{C}$ in a gas mixture of N_2 and H_2O . The mixture was fed on the outside (upstream) of a cylindrical membrane module under atmospheric pressure, while the permeate side (downstream) was evacuated. The partial pressure of H_2O was keeping at 70 kPa. After exposing the membrane to steam at 500 $^{\circ}\text{C}$ for a specified

time interval, the membrane was dried completely in a N_2 stream at the same temperature. The permeance changes during this hydrothermal test were observed in the specified time intervals by repeating the procedures mentioned above.

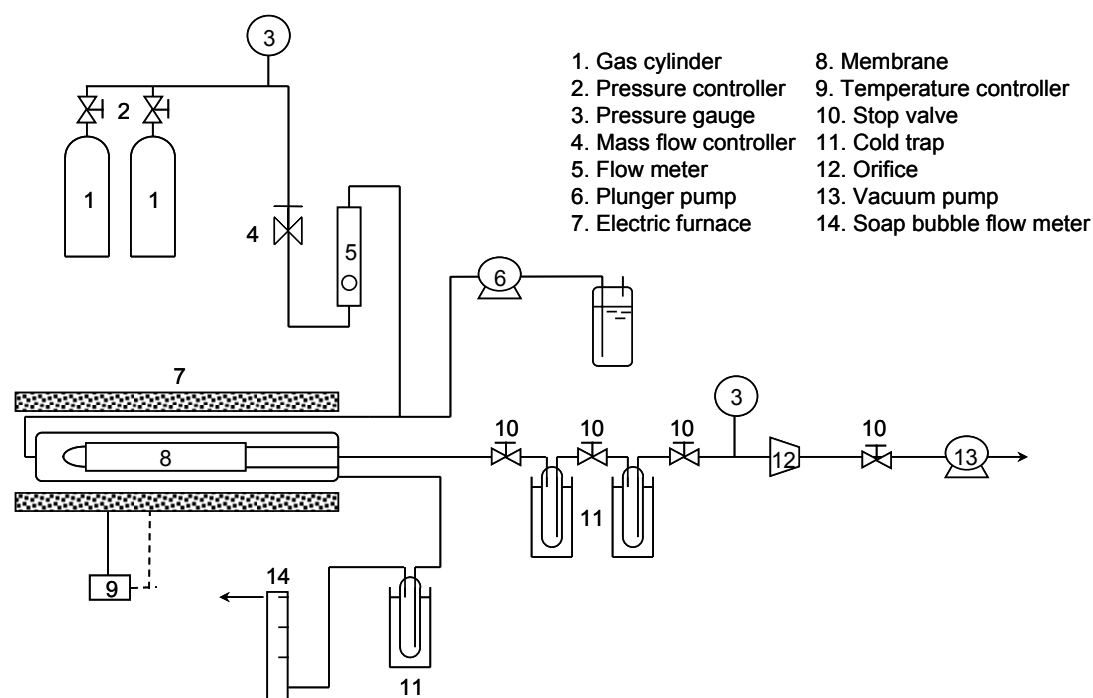


Figure S1 Schematic diagram of the experimental apparatus for gas permeation measurement and hydrothermal stability testing

Characterization of Pd-silica mixed-matrix powder by XRD

Figure S2 shows the XRD patterns of PdO-silica composite gel (a) and those of a simple mixture of PdO powder and SiO_2 powder (b), with a Pd molar composition of 25 mol% fired at 550 °C in air. The PdO-silica composite gel, which was prepared by the sol-gel method, showed broad peaks of PdO, which were quite different from those for a simple mixture of SiO_2 and PdO. The peak intensity of PdO for PdO-silica composite gel was less than that of a simple mixture of SiO_2 and PdO, although in the same molar ratio. This result suggests that the Pd of the PdO-silica composite gel consists of not only crystalline PdO, but also noncrystalline Pd-compounds, such as extremely fine particles that are undetectable by XRD or only as Pd composites with silica.

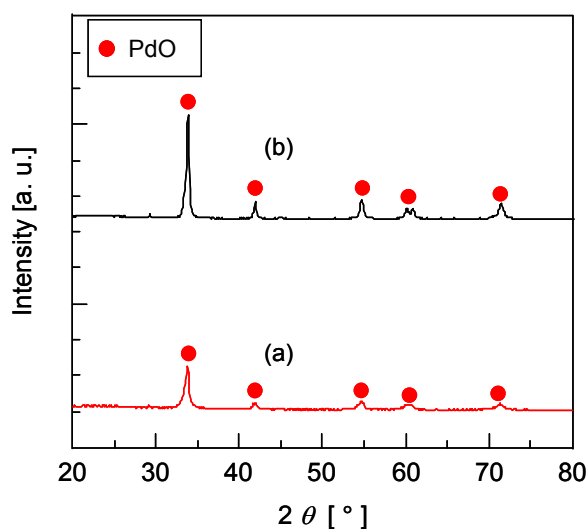
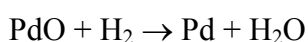


Figure S2 XRD patterns (Pd concentration 25 mol%, Si/Pd=3/1) of PdO-silica composite gel (a) and a simple mixture of PdO and SiO₂ powders (b)

Figure S3 shows XRD patterns of Pd-silica composite powder (Si/Pd molar ratio: 3/1) under different calcination conditions. After calcination at 550 °C in a hydrogen atmosphere for Pd-SiO₂ powder, similar to the conditions of the membrane fabrication, only Pd peaks can be detected in the XRD patterns, suggesting no residual organic groups and Cl in the Pd-SiO₂ composite powder. Pd peaks for sample (d), which were prepared by calcination of sample (a) at 550 °C in H₂, showed quite smaller than that prepared by calcination in H₂ after calcination in air (sample (c)), suggesting that aggregation of Pd particles can be prevented by direct calcination in H₂. This can be explained as follows. The sample (a) prepared by gelation at 180 °C showed an amorphous structure and a small peak of PdCl₂, suggesting a very small Pd and/or a PdO that can be incorporated into silica networks. By firing sample (a) directly in an H₂ atmosphere, the following reaction can occur.



Amorphous silica networks with incorporated Pd particles can be densified by generated HCl and H₂O at 550 °C, thus Pd particles incorporated in silica networks cannot move and aggregate since silica networks can work something like a cage. These results suggest that calcination of a gelated sample under a hydrogen atmosphere can prevent the aggregation of Pd particles at high temperatures.

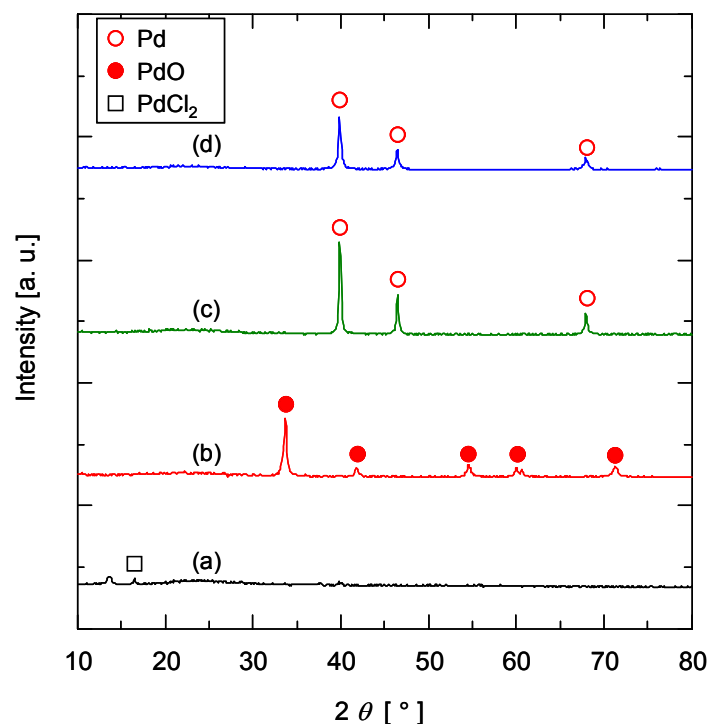


Figure S3 XRD patterns of Pd-silica composite powder (Si/Pd=3/1) under different calcination conditions; (a) gelation at 180 °C, (b) calcination of the sample (a) at 550 °C in air, (c) calcination of the sample (b) at 550 °C in H₂, (d) calcination of the sample (a) at 550 °C in H₂ [4]

Depth profile of Pd-silica mixed-matrix membrane (Si/Pd=3/1) by XPS

The depth profile by XPS is shown in Figure S4. The concentration of Si that is attributed to both Pd-silica and the SiO₂-ZrO₂ layer was constant from 0 to 70 nm in depth and decreased with an increase in depth when approaching the α -alumina support. The concentration of Pd atoms, which is attributed to the Pd in Pd-silica mixed-matrix membrane, showed a trend similar to that of the detection curve of Si. To the contrary, the concentration of Al atoms, which was obtained from the alumina support, was 0 from 0 to 100 nm in depth and increased at 100 nm from the membrane surface. The concentration of Zr that is attributed to the SiO₂-ZrO₂ layer increased at 70 nm from the membrane surface and decreased with an increase in depth. No residual organic groups or Cl was detected in the Pd-silica mixed-matrix membrane.

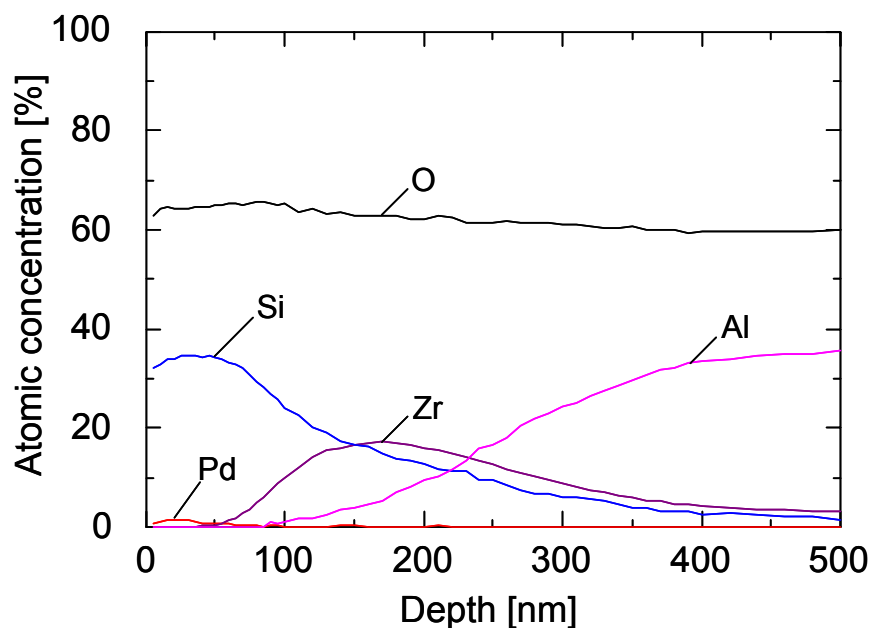


Figure S4 Depth profile of Pd-silica mixed-matrix membrane (Fig. 2 in manuscript) by XPS

Hydrothermal stability of Pd-silica mixed-matrix membrane (Si/Pd=3/7)

Figure S5 shows the time course of gas permeances at 500 °C for a Pd-silica mixed-matrix membrane (Si/Pd=3/7) under steam (steam: 70 kPa) and a hydrogen atmosphere. After a slight decrease, the permeances of He, H₂ and N₂ for a Pd-silica mixed-matrix membrane (Si/Pd=3/7) approached constant values. The activation energy of He permeation showed little change after exposure to steam and hydrogen for 12 hours. These results suggest that Pd-silica mixed-matrix membrane (Si/Pd=3/7) was also relatively stable in a steam and hydrogen atmosphere at high temperatures, showing a similar trend to Pd-silica mixed-matrix membranes (Si/Pd=3/1) (as shown in Fig. 3).

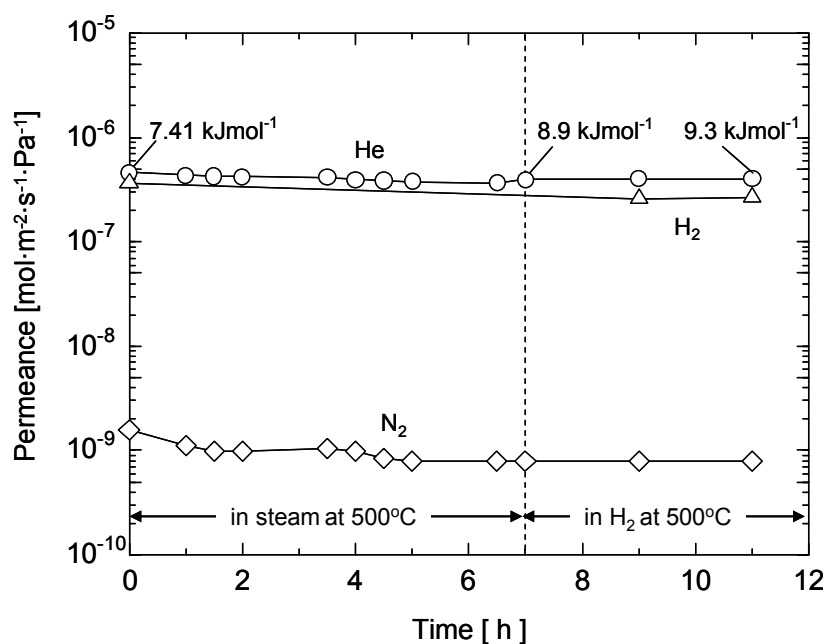


Figure S5 Time course of gas permeances at 500 °C for a Pd-silica mixed-matrix membrane (Si/Pd=3/7) under a steam (steam: 70 kPa) and hydrogen atmosphere

Pd particle size distribution for Pd-silica mixed-matrix membranes

Figure S6 shows particle diameter distribution (number-based) for Pd-silica mixed-matrix membranes (Si/Pd=3/1 (a), Si/Pd=3/7 (b)). As mentioned in Figure S2, a Pd-silica composite gel consists of not only crystalline Pd, but also noncrystalline Pd-compounds, such as extremely fine particles that are undetectable by XRD or as Pd composites with silica. Thus, it should be noted that a Pd particle diameter of less than 2 nm, which was not detected in these figures, may exist in Pd-silica mixed-matrix membranes. Judging from the particle diameter distribution of the Pd-silica mixed-matrix membrane (Si/Pd=3/7), the aggregation of Pd particles were comparatively prevented by the calcination in a hydrogen atmosphere — even in the case of a high Pd concentration in silica.

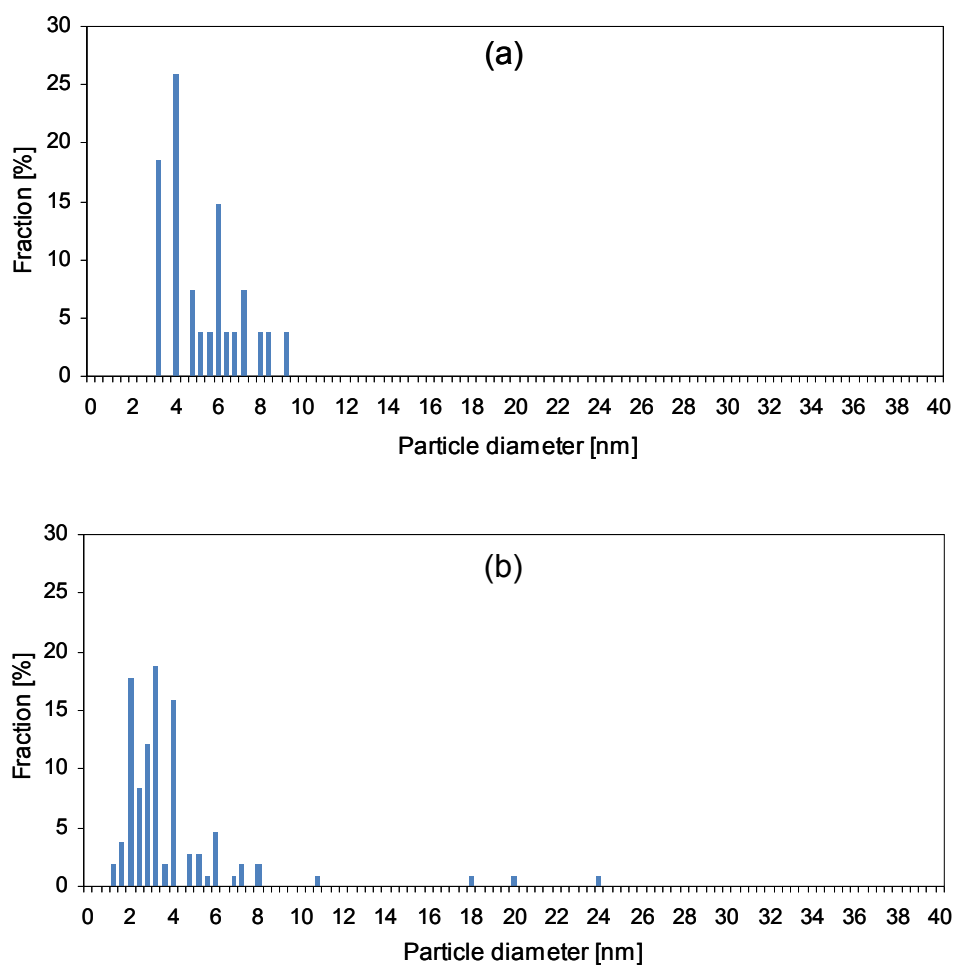


Figure S6 Particle diameter distribution (number-based) for Pd-silica mixed-matrix membranes; Si/Pd=3/1 (a), Si/Pd=3/7 (b)

References

- [1] M. Asaeda, J. Yang and Y. Sakou, *J. Chem. Eng. Jpn.*, 2002, **35**, 365.
- [2] M. Asaeda, Y. Sakou, J. Yang and K. Shimasaki, *J. Membr. Sci.*, 2002, **209**, 163.
- [3] M. Asaeda, K. Okazaki and A. Nakatani, *Ceramic Transactions*, 1992, **31**, 411.
- [4] M. Kanezashi, C. Shimada, M. Sano, T. Yoshioka and T. Tsuru, *Kagaku Kogaku Ronbunshu* (in Japanese), in Press