Performance Under Thermal and Hydrothermal Condition of Amorphous Silica Membrane Prepared by Chemical Vapor Deposition

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Introduction

Silica membranes, which are often prepared by chemical vapor deposition (CVD)[1] or sol–gel[2] methods, have hydrogen-permselective characteristics and have been studied by many researchers. In addition, many applications of hydrogen-selective membranes have been proposed.[3–5] Generally, hydrogen permeance and its selectivity through silica membranes are inferior to those of palladium membranes and palladium alloys. However, palladium is an expensive, rare metal, and so it is desirable to prepare a hydrogen-selective membrane that has a comparable performance using a cheaper material, such as silica. In fact, there exist some reports on silica membranes that match palladium membranes in performance.

From the viewpoint of practical use, a severe problem remains unsolved. Silica membranes are not thermally or hydrothermally stable. Exposure to moisture, in particular, quickly leads to deterioration of the membrane performance. It is often pointed out that this probably results from ‘‘densification’’ of the silica.[6,7] Under thermal or hydrothermal conditions, the structure of the silica membrane changes by rearrangement of siloxane bonds or dehydration of silanol groups into siloxane groups. To overcome this lack of stability, several kinds of metal-doped silica membranes have been proposed and investigated. Kanezashi et al.[8,9] have reported numerous excellent silica membranes. One of them was a nickel-doped silica membrane, prepared by the sol–gel method, which exhibited high hydrogen permeance, of the order of 10^{-7} mol m^{-2} s^{-1} Pa^{-1}, and high hydrogen/nitrogen selectivity of 400, even after exposure to steam at 873 K.[10] Oyama and coworkers[11,12] also reported many fruitful articles on silica membranes. Recently, this group reported a silica-alumina composite membrane prepared by dual-element CVD and elucidated that the membrane showed high hydrogen permeance, of the order of 10^{-7} mol m^{-2} s^{-1} Pa^{-1}, even after exposure to 16 mol % water vapor for 520 h at 873 K[7]. Our group has also been developing silica membranes with excellent performance and stability. A membrane prepared by counter-diffusion CVD using tetramethoxysilane (TMOS) and oxygen maintained hydrogen permeance of the order of 10^{-8} mol m^{-2} s^{-1} Pa^{-1} to 10^{-7} and high hydrogen/nitrogen selectivity of around 1000 under 76 kPa of steam at 773 K for 21 h.[13] In addition, we recently developed a silica membrane, prepared by one-sided diffusion CVD using dimethoxydiphenylsilane and oxygen, that showed higher hydrogen permeance, nearly 10^{-6} mol m^{-2} s^{-1} Pa^{-1}, under humid conditions containing 3.4 kPa of steam at 573 K.[14] However, almost all of these studies were conducted below 873 K, and silica membrane performance under higher temperature conditions above 873 K has hardly been reported.

In this study, we prepared silica membranes by counter-diffusion CVD at 873 K using TMOS and oxygen, and we investigated their performance, especially under higher temperature and humidity conditions from 873 K to 1073 K. This research broadens the possible applications of silica membranes, for example, as hydrogen-selective membranes in a membrane reactor used to decompose hydrogen sulfide.

Experimental

Silica membranes, which consisted of α-alumina with 100 nm diameter pores as a substrate, a γ-alumina layer to reduce the pore size to 4 nm, and a silica layer for gas separation with around 0.3 nm of pores, were prepared by CVD at 873 K using TMOS and oxygen, according to the previous reports.[13–15] Silica membrane was synthesized at the center

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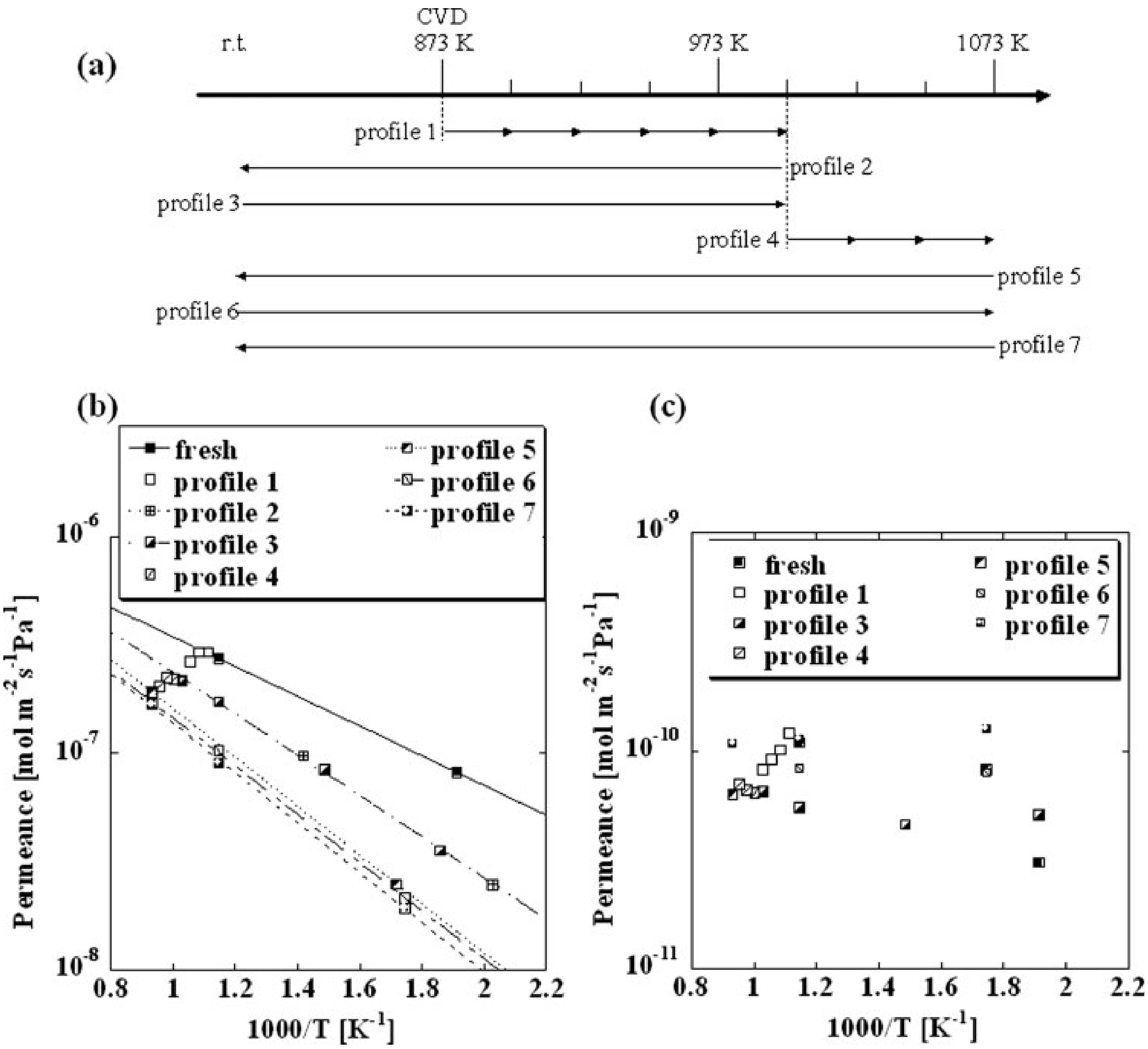

Figure 1. (a) Temperature profiles during membrane performance tests from 873 K to 1073 K, and Arrhenius plots of (b) hydrogen and (c) nitrogen permeance through the TMOS-derived membrane during the temperature profiles.

of the substrate (50 mm), and the other parts were glazed with a sealant. The permeation test using hydrogen and nitrogen was conducted to investigate the performance of the prepared membrane. The performance from 873 K to 1073 K was investigated using the temperature profiles as shown in Figure 1a. A high-temperature stability test at 1073 K and steam stability tests at 973 K and 1073 K were also performed using the same apparatus. In the steam stability test, nitrogen was bubbled at 200 mL/min through pure water kept at 318 K and fed to the membrane.

Results and Discussion

Membrane performance above 873 K

After preparation, the fresh membrane showed hydrogen permeance of 2.7×10^{-7} mol m^{-2} s^{-1} Pa^{-1} at 873 K and 1.1×10^{-10} mol m^{-2} s^{-1} Pa^{-1} nitrogen permeance. The separation factor of hydrogen or nitrogen was over 2×10^3. These values are reasonable, compared with our previous study.[13,14] Figure 1b, c show Arrhenius plots of hydrogen and nitrogen permeance, respectively, through the membrane. These permeances were measured 1 h after the temperature was raised and stabilized. During the hydrogen permeance experiments shown in Figure 1b, in the first temperature profile, hydrogen permeance increased according to the Arrhenius law as temperature increased to around 923 K, and it slowly decreased above this temperature. During the second and third temperature profiles, all permeance data fell on the same line in the Arrhenius plot. During the fourth temperature profile, hydrogen permeance decreased slowly with increasing temperature. Finally, during the fifth, sixth, and seventh temperature profiles, each data fell on a line nearly overlapping the other two. Conversely, the nitrogen permeance shown in Figure 1c was observed not to depend on the temperature during each temperature profile. In addition, the separation factor of hydrogen or nitrogen was above 2000 during every temperature profile. It should be noted that after the membrane was exposed to a

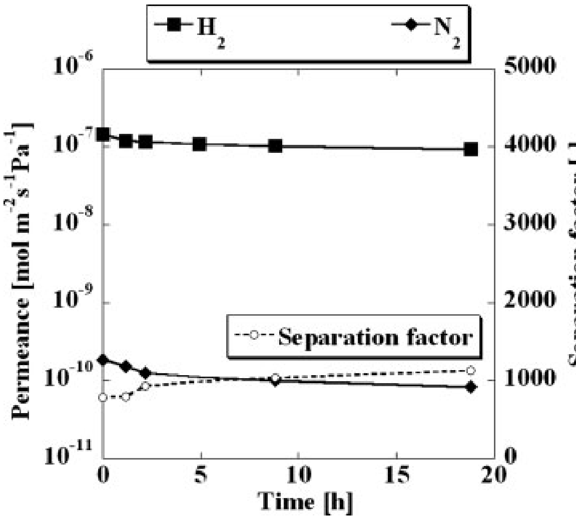

Figure 2. Time course of the permeance of hydrogen and nitrogen through the membrane at 1073 K.

temperature higher than the membrane synthesis temperature, hydrogen permeance did not change after cooling and raising the temperature again. Meanwhile, in our previous study,[13] we reported the possibility that the silica membrane was damaged by exposure to temperatures higher than the CVD temperature. However, the CVD temperature was 573 K or 673 K in that case.[13] There would be significant differences between membranes prepared at 573 K or 673 K and the membranes prepared at 873 K, in terms of surface and structure. The membrane deposited at low temperature may change its structure easily at higher temperature, whereas the membrane deposited at high temperature, such as 873 K, may have a more stable structure or surface even at higher temperature. Currently, this scheme is a speculation and needs more quantitative investigation, but the fact that our silica membrane prepared by CVD at 873 K can be used at 973 K or 1073 K is valuable and promising for some applications.

Membrane performance with time at 1073 K under dry condition

For industrial application of hydrogen-selective silica membranes, stable performance with time is one of the important factors. The permeance of hydrogen and nitrogen through the membrane at 1073 K and its separation factor over time are shown in Figure 2. The permeance of hydrogen and nitrogen decreased slightly over about 18 h, but the values remained almost constant around 10^{-7} mol m^{-2} s^{-1}

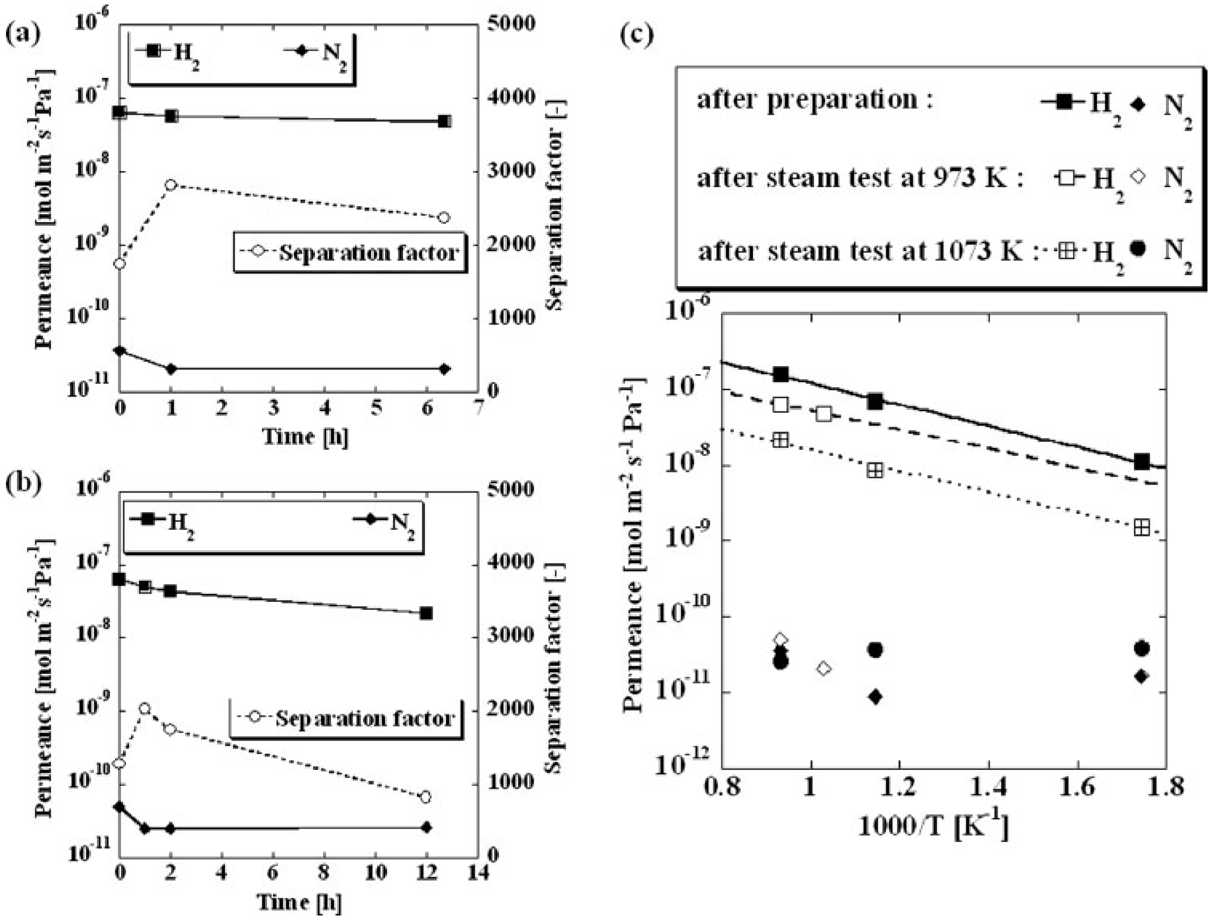

Figure 3. Time course of the permeance of hydrogen and nitrogen through the membrane at (a) 973 K and (b) 1073 K under humid conditions, and (c) Arrhenius plots of hydrogen and nitrogen permeance through the membrane after preparation, after the steam stability test at 973 K and after the steam stability test at 1073 K.

Pa^{-1} and 10^{-10} mol m^{-2} s^{-1} Pa^{-1}, respectively. Conversely, the separation factor increased to some degree because a slight decrease in nitrogen permeance had a large effect on the selectivity value. Neither permeance nor separation factor decreased drastically, meaning that severe deterioration of the membrane structure did not occur. In general, when a silica membrane deteriorates, permeance of hydrogen decreases drastically in around 1 h, and permeance of nitrogen increases as a result of densification and pinhole generation. Thus, we can say that our silica membrane was thermally stable at 1073 K for 18 h under dry condition.

Membrane performance with time at 973 K and 1073 K under moist condition

Our silica membranes prepared with TMOS and oxygen by our method at 873 K were stable under steam, as reported elsewhere,[13] but the steam stability test was conducted at 773 K. In this study, we investigated the steam test at higher temperatures, such as 973 K and 1073 K. The permeance of hydrogen and nitrogen over time under humid conditions at 973 K and 1073 K is shown in Figure 3a, b, respectively. At 973 K, permeance of hydrogen and nitrogen dropped slightly in the first 1 h and then remained nearly constant for around 6 h. The selectivity remained high at over 1000. Conversely, at 1073 K, hydrogen permeance decreased gradually over 12 h, whereas nitrogen permeance decreased slightly in the first 1 h and remained almost constant up to 12 h. The separation factor was around 1000. Compared with Figure 3a, b, the performance decrement under the condition of 1073 K was recognized slightly. Figure 3c shows the Arrhenius plots of hydrogen and nitrogen through the fresh membrane, after the steam test at 973 K and after the steam test at 1073 K. The permeance of nitrogen was almost the same in all three cases, but the hydrogen permeance was affected by steam treatment. The fresh membrane had the highest permeance, followed by the membrane treated at 973 K, and finally the membrane treated at 1073 K. However, the activation energy for hydrogen permeance through the membranes was 26 kJ/mol in all the three cases. One of the reasons of this decreasing permeance was probably deterioration of the γ-alumina layer or change in the interfacial structure between the γ-alumina layer and the silica layer, because γ-alumina is a metastable phase that transforms into α-alumina with increasing temperature.[16] However at this stage, this is just an assumption. We should continue studying about this issue for practical applications.

Conclusions

Hydrogen-selective amorphous silica membrane was prepared by CVD using TMOS and oxygen at 873 K, and the performance under thermal and hydrothermal conditions was investigated under various conditions from 873 K to 1073 K using the permeation tests of hydrogen and nitrogen. Under dry conditions, hydrogen permeance decreased slightly at temperatures above the fabrication temperature; however, once the membrane went through the higher temperature, hydrogen permeance did not change even when it was exposed to high temperature again. In humid conditions, hydrogen permeance through the TMOS-derived silica membrane was comparatively stable at 973 K, but slight performance deterioration was observed at 1073 K. These characteristics in performance are probably attributed to the microporous structure of the membrane prepared at such higher temperature as 873 K. We are now working for elucidation of the relationship between membrane structure and membrane performance quantitatively.

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