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Fumio Shibao[a]; Byeong-Heon Jeong[a]; Yasuhisa Hasegawa[a]; Ken-Ichiro Sotowa[a]; Katsuki Kusakabe[a]
[a] Department of Applied Chemistry, Kyushu University, Fukuoka, Japan

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Gas Permeation Through Metal-Loaded Yttrium Doped Zirconia Membranes

Fumio Shibao, Byeong-Heon Jeong, Yasuhisa Hasegawa, Ken-Ichiro Sotowa, and Katsuki Kusakabe*

Department of Applied Chemistry, Kyushu University, Fukuoka, Japan

ABSTRACT

Yttria stabilized zirconia (YSZ) powders comprised of Y/Zr in molar ratios of 0.01, 0.04, and 0.08, were prepared by a sol–gel method and their crystal structures and pore size distributions were determined. The 8-mol% Y-doped zirconia (8YSZ) powder restrained the crystallization and had the smallest pores. Porous 8YSZ membranes, prepared on a porous α-alumina support tube by a sol–gel method, showed a low permselectivity of 5.1 for H_2 to CO_2. The membranes were modified by impregnation with Pt or Ni to improve the H_2 permselectivity. The permselectivities of H_2 to CO_2 at 500°C through the Pt–YSZ and Ni–YSZ membranes were increased to 22 and 29, respectively.

Key Words: Yttria stabilized zirconia; Membrane; Gas permeation; Sol–gel method; Hydrogen separation.

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*Correspondence: Katsuki Kusakabe, Department of Applied Chemistry, Kyushu University, Fukuoka 812-8581, Japan; Fax: +81-92-651-5606; E-mail: kusaktcf@mbox.nc.kyushu-u.ac.jp.

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INTRODUCTION

The removal of CO and CO_2 in hydrogen-rich gas, produced by the reforming of hydrocarbons, has attracted considerable interest because of its applications in polymer electrolyte fuel cells. The separation of hydrogen separation through a porous ceramic membrane at working temperature is one of the feasible operations needed for this process. Amorphous silica membranes prepared on porous supports by sol–gel techniques showed high selective permeation properties for H_2.[1–4] However, the silica membrane was found to be unstable at temperatures higher than 600°C[4] and especially in a steam atmosphere due to the formation of defects in the membrane. Zirconia is a thermally stable ceramic as compared with silica. The permeation properties of zirconia and yttria stabilized zirconia (YSZ) membranes, prepared by the sol–gel method, were reported to be controlled by the Knudsen diffusion mechanism.[5–7]

This paper reports on the preparation of zirconia powders doped by yttrium (hereafter, referred to as YSZ) using a sol–gel technique in order to control the crystallization of the zirconia. The effects of yttrium-doping on the crystallinity and pore structure were examined. Nickel and platinum were loaded into the YSZ membranes in order to control the pore size. The gas permeation properties of the membranes were investigated in the temperature range of 100–500°C.

EXPERIMENTAL

A zirconia sol was synthesized in a glove box in an atmosphere of dry nitrogen at room temperature. A mixture of zirconium *n*-propoxide (70 wt% in 1-propanol, 8.8 mL), 1-propanol (14.4 mL), 1,5-diamino pentane (0.6 mL), and yttrium nitrate was prepared. The mixture was stirred for 30 min and glacial acetic acid (4.3 mL) was added. The stirring was continued for 40 hr, and concentrated nitric acid (1.5 mL) was then added dropwise to complete the hydrolysis. The molar ratios of yttrium to zirconium in the zirconia sols were 0, 0.01, 0.04, and 0.08 (hereafter, referred to as ZrO_2, 1YSZ, 4YSZ, and 8YSZ, respectively). Each sol was cast on a glass plate and dried in air at room temperature. Dried flakes were then recovered and ground finely with a mortar. The prepared powder was then calcined at 500°C for 1 hr. The crystal structures of the calcinated zirconia powders were determined by x-ray diffraction (XRD, Rigaku, RINT 2500). The pore size distribution, surface area, and pore volume were calculated from a nitrogen sorption isotherm with an adsorption porosimeter (Micrometrics, ASAP 2000). Zirconia membranes were prepared on a porous α-Al_2O_3 support tube (NOK Corp., Japan, outer diameter = 2.1 mm, inner diameter = 1.7 mm, length = 200 mm, void fraction = 39%, average pore size = 150 nm). The outer surface, except for

20 mm area in the central region, was coated with a glass sealant. The support tube was dipped into the 8YSZ sol for 1 min, dried in air at ambient temperature for 12 hr, and calcined in air at 500°C for 1 hr at a heating rate of 1 K min^{-1}. The dipping-firing process was repeated for a total of five times. The 8YSZ membranes were modified by dipping in a solution of 0.10 mol L^{-1} H_2PtCl_6 or $Ni(NO_3)_2$ for 30 min. The membranes were then dried in air at room temperature for 12 hr and calcined in air. The metal loading procedure was repeated for a total of three times. The morphology of the membrane was observed by scanning electron microscopy (Hitachi, FE-SEM S-5200). The amount of Pt and Ni loading was determined by EDX (Kevex, Delta Class). The permeation properties of the membrane were determined through the use of H_2, CO_2, N_2, CH_4, and n-C_4H_{10} at 100–500°C. The single-component gases with argon as the sweep gas were fed into the feed and permeate side, respectively. The total pressure on the both sides of the membrane was maintained at atmospheric pressure. The flow rates were determined with soap-film flow meters, and the gas compositions were determined by a gas chromatograph equipped with a TCD (Shimadzu, GC-8A). The permeance was calculated from the following equation:

$$\text{Permeance} = \frac{\text{(moles of transferred per unit time)}}{\text{(membrane area)(partial pressure difference)}} \qquad (1)$$

The permselectivity is defined by the ratio of permeances.

RESULTS AND DISCUSSION

Figure 1 shows x-ray diffraction patterns of YSZ powders. Peaks corresponding to a tetragonal phase were detected from each powder. When zirconia is produced by a sol–gel method, the tetragonal nanophases can be stabilized by the hydrolysis involved in the synthesis.[7,8] YSZ powder also possesses a tetragonal crystal structure because of the stabilization as the result of doping the zirconia with yttrium.[9] The peak intensities at $2\theta = 30^\circ$ became small with increasing amounts of doped yttrium. This indicates that yttrium-doping prevents crystallization of the amorphous to the tetragonal phase. The crystallite size of 8YSZ as calculated from Sherrer's equation was determined to be 12.6 nm. Kim and Lin prepared 8YSZ membranes by a sol–gel method.[5] The crystallite size of YSZ calcinated at 450°C was 20.8 nm, which is larger than the value found in this work. The pore size distributions of the ZrO_2 and YSZ powders are shown in Fig. 2. Although the pore size distribution of ZrO_2 powder is broad, it became narrow as the result of doping with yttrium. The pore size distribution of the 8YSZ powder broadened again because of the development of a micropore structure.

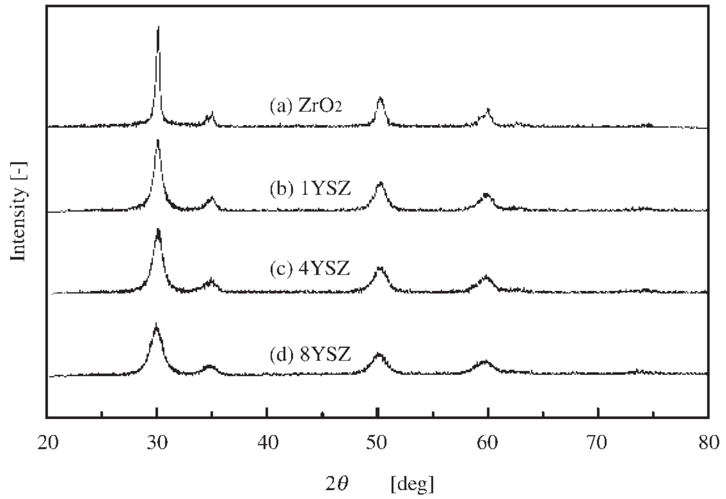

Figure 1. XRD patterns of Y doped ZrO_2 powders. (a) Non-doped ZrO_2 (crystalline size = 47 nm), (b) 1YSZ powder (crystalline size = 17.6 nm), (c) 4YSZ powder (crystalline size = 14.1 nm), and (d) 8YSZ powder (crystalline size = 12.6 nm).

From the results of the pore size distribution, 8YSZ membranes were prepared and the gas permeances to H_2, CO_2, N_2, CH_4 and n-C_4H_{10} at 100°C were determined. The permeances to H_2 and CO_2 were 4.2×10^{-6} and $8.3 \times 10^{-7}\,\mathrm{mol\,m^{-2}\,sec^{-1}\,Pa^{-1}}$, respectively, and the permselectivity

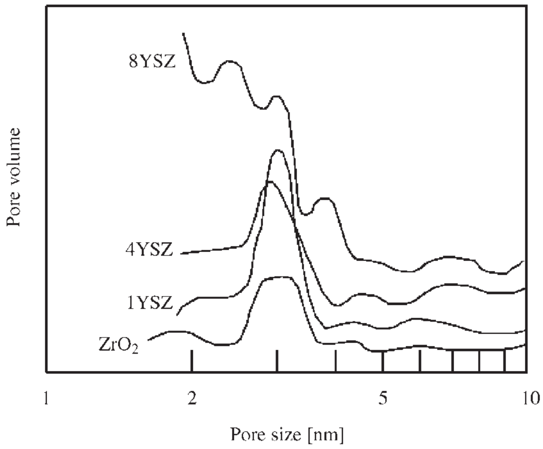

Figure 2. Effect of Y doping on pore size distributions of ZrO_2 powders.

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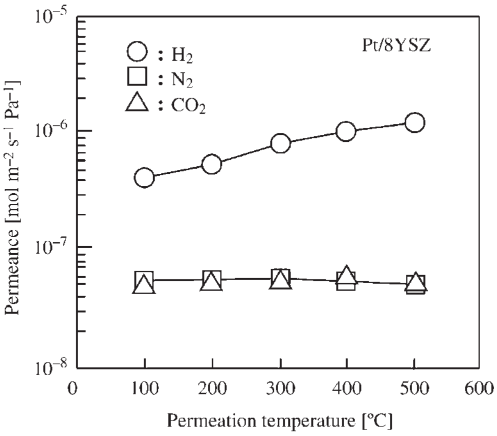

Figure 3. Permeances to H_2, CO_2, and N_2 through the Pt–8YSZ membrane as a function of temperature in the range of 100–500°C.

of H_2 to CO_2 was calculated to be 5.1, which is a slightly high value compared to the theoretical Knudsen value of 4.7.

The 8YSZ membrane was then loaded with either Pt or Ni using an impregnation method in order to improve the preferential H_2 permeation. The thickness of the membranes was 0.7 μm, and the amounts of loaded-Pt and -Ni were 13.7 and 8.2 wt%, respectively. Figure 3 shows the permeances to H_2, N_2, and CO_2 through the Pt-loaded 8YSZ (Pt–8YSZ) membranes in the temperature range of 100–500°C after the hydrogen reduction treatment. The H_2 permeance of the Pt–8YSZ membrane increased with increasing temperature. The N_2 and CO_2 permeances were nearly constant against the permeation temperature. As a result, the H_2 permeance increased to $1.07 \times 10^{-6}\,\mathrm{mol\,m^{-2}\,sec^{-1}\,Pa^{-1}}$ at 500°C and the permselectivity of H_2 to CO_2 was 22. The preferential permeation of hydrogen as the result of Pt-loading was observed in the case of the Pt–ZrO_2 membrane.[10]

When Ni was impregnated into the ZrO_2 membrane using the same procedures as for the Ni–8YSZ membrane, the H_2 permeance of the Ni–ZrO_2 membrane was found to be independent of the permeation temperature and the permselectivity of H_2 to CO_2 was nearly the same as those for ZrO_2 membranes as shown in Fig. 4(a). Effective pore plugging to improve the separation properties did not occur for the Ni–ZrO_2 membrane because of large pore size distribution in ZrO_2 membrane. As shown in Fig. 4(b), the H_2 permeance of Ni–8YSZ membrane increased with increasing temperature, similar to that for the Pt–8YSZ membrane. The H_2 permeance of the Ni–8YSZ membranes at 500°C was found to be $1.95 \times 10^{-6}\,\mathrm{mol\,m^{-2}\,sec^{-1}}$

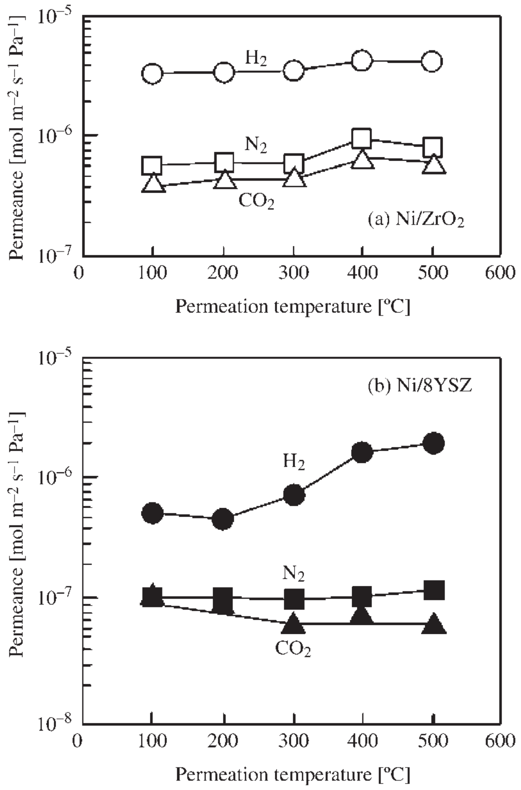

Figure 4. Permeances to H_2, CO_2, and N_2 through (a) a Ni–ZrO_2 membrane and (b) a Ni–8YSZ membrane as a function of temperature in the range of 100–500°C.

Pa^{-1} and the permselectivity of H_2 to CO_2 was 29. However, the permeances to CO_2 and N_2 were not greatly dependent on the permeation temperature.

CONCLUSIONS

The crystallization and pore diameter of sol–gel derived zirconia powders are influenced by yttrium-doping. Crystallization was inhibited and the pore size became smaller with increasing amounts of yttrium. The permselectivity of H_2 to CO_2 is close to the theoretical Knudsen diffusion value. Pt–8YSZ and Ni–8YSZ membranes showed H_2 selective permeation and the permselectivities of H_2 to CO_2 at 500°C were improved to 22 and 29, respectively.

This improvement in selective H_2 permeation indicates that the mesopores of the 8YSZ membranes were plugged with loaded metals.

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