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Design of Silica Networks for Development of Highly Permeable Hydrogen Separation Membranes with Hydrothermal Stability

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Much attention has been devoted to inorganic materials such as zeolite, silica, zirconia, and titania for development of gas- and liquid-separation membranes because they can be utilized under harsh conditions where organic polymer membranes cannot be applied.[1−3] Silica membranes have been studied most extensively for the preparation of various kinds of separation membranes: hydrogen, carbon dioxide, and C3 isomers. Sol−gel and chemical vapor deposition (CVD) methods have been applied in the preparation of silica membranes.[4−6] In general, CVD-derived silica membranes show high permselectivity for hydrogen to nitrogen with low hydrogen permeance ($\sim 10^{-8}$ mol m^{-2} s^{-1} Pa^{-1}) because of the dense silica layer on porous substrates.[4] The sol−gel method is much more flexible for the fabrication of porous and dense membranes. The main advantage of the sol−gel method is a strong possibility of controlling the pore size of the silica membranes, which can be done in two ways: the polymeric sol−gel route and the colloidal sol−gel route, where spaces between colloidal particles are assumed to be pores in a membrane.[5] The polymeric route for control of pore sizes is preferable in the preparation of small gas-separation membranes, especially for hydrogen-separation membranes, since pore sizes by the polymeric route are considered to be made up of spaces within amorphous silica networks.

Tetraethoxysilane (TEOS) is a commonly used precursor for preparation of sol−gel-derived silica membranes. In the process of the hydrolysis and polymerization reaction of TEOS, the Si−O−Si unit can be a minimum unit for amorphous silica networks. Recently, the amorphous silica structure prepared by molecular dynamics simulation was reported to have a pore volume with a pore size of less than 0.25 nm, through which He atoms (with a kinetic diameter of 0.26 nm) and H_2 molecules (0.289 nm) cannot permeate.[7] The improvement of hydrogen permeability is a breakthrough for the practical application of silica membranes.

The use of an organic−inorganic hybrid alkoxide that contains at least one organic group that cannot be hydrolyzed, such as methyltriethoxysilane (MTES), has been proposed by several research groups for the control of pore size.[8−13] The organic-template approach has been applied in the design of the pore size for silica membranes.[8−10] The inorganic network prepared using amorphous silica with pyrolysis of methyl groups gave a high CO_2 permeance on the order of 10^{-7} mol m^{-2} s^{-1} Pa^{-1} and a CO_2/CH_4 selectivity of more than 70.[8] Here we propose the use of a new type of organic−inorganic hybrid alkoxide that contains the organic groups between two silicon atoms, such as bis(triethoxysilyl)ethane (BTESE), for the development of a highly permeable hydrogen separation membrane. The concept for improvement of hydrogen permeability of a silica membrane is to design a loose organic−inorganic hybrid silica network using BTESE, i.e., to shift the silica networks to a larger pore size for an increase in H_2 permeability.

Only a few successes have been reported in the development of microporous membranes using BTESE as a silica precursor for improvement of the hydrothermal stability of silica membranes.[12,13] Hybrid silica membranes derived by copolymerization of MTES and BTESE showed high hydrothermal stability because of the incorporation of organic linking groups into the silica networks.[12,13] However, no progress has been made in the use of BTESE in the design of silica networks. The objective of this communication is to report on the strategy of designing silica networks using BTESE in the development of a highly permeable hydrogen-separation membrane with hydrothermal stability.

A hybrid silica layer was prepared by coating a silica−zirconia intermediate layer with a BTESE polymer sol followed by drying and calcination at 300 °C in nitrogen. A thin, continuous separation layer (thickness < 0.5 μm) of hybrid silica for selective H_2 permeation can be observed on top of the SiO_2-ZrO_2 intermediate layer, as shown in Figure 1.

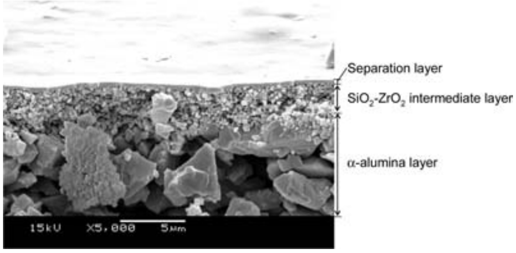

Figure 1. SEM image of a cross section of a hybrid silica membrane.

It is quite difficult to obtain an exact pore size distribution of porous membranes for gas separation. The only way to estimate the pore size distribution is to measure several gas permeances as a function of the kinetic diameter of the gas molecules. Figure 2 shows the kinetic diameter dependence of gas permeances for hybrid silica (BTESE) and previously reported sol−gel-derived silica

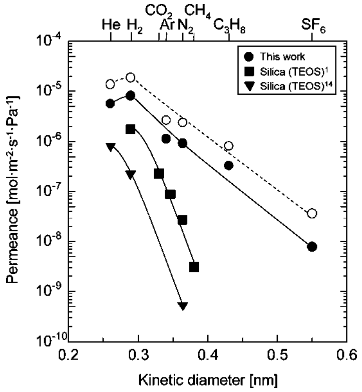

Figure 2. Kinetic diameter dependence of gas permeances for hybrid silica and previously reported sol−gel-derived silica membranes[1,14] at 200 °C (closed symbols, without heat treatment; open symbols, with heat treatment at 400 °C in air for 3 h).

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membranes[1,14] at 200 °C, where the effect of the surface flow is negligible. A hybrid silica membrane shows ~1 order of magnitude higher H_2 permeance (~10^{-5} mol m^{-2} s^{-1} Pa^{-1}) than previously reported silica membranes using TEOS[1,14] and a high H_2-to-SF_6 permeance ratio of ~1,000 with a low H_2-to-N_2 selectivity (~10). On the other hand, silica membranes using TEOS[1,14] are highly selective for H_2 over N_2 (with H_2/N_2 permeance ratios of ~1,000), indicating a much smaller pore size distribution than that of a hybrid silica membrane. The difference of these pore size distributions can be attributed to the spaces between the two silicon atoms in the alkoxide. In the process of hydrolysis and polymerization of BTESE, the Si−C−C−Si unit is expected to be the minimum one for organic−inorganic hybrid silica networks, resulting in the formation of a much looser structure than that derived using TEOS, which contains one silicon atom. The increase in gas permeances for the hybrid silica membrane during heat treatment at 400 °C in air should be due to the partial pyrolysis of the Si−C bonds, since the pore size distribution shows little change. The pyrolysis of the $-(CH_2)_2-$ groups between pairs of silicon atoms started gradually above 315 °C in an air atmosphere.[12,13] The permeance of H_2 for the heat-treated hybrid membrane was 2×10^{-5} mol m^{-2} s^{-1} Pa^{-1} with an H_2/SF_6 permeance ratio of 500.

The evaluation of membrane quality for amorphous silica membranes is not simple because the pore size distributions include both pores in the silica networks and interparticle pores (grain boundaries). The H_2/SF_6 permeance ratio (kinetic diameters: H_2, 0.289 nm; SF_6, 0.55 nm) has been used as an indicator for estimation of the quality of zeolite membranes having defined (zeolite channel) pore sizes, such as MFI-type (~0.56 nm) and DDR-type (~0.45 nm) zeolites. The H_2/SF_6 permeance ratios as a function of H_2 permeance for inorganic membranes are shown in Figure 3. In general, the H_2/SF_6 permeance ratio decreases with increasing H_2 permeance as a result of the presence of defects and/or interparticle pores in a membrane. High-quality DDR-type zeolite membranes[22] show a high H_2/SF_6 permeance ratio (>10,000); however, the permeance of H_2 is not as high because of the thick zeolite layer (~10 μm). The variation of the H_2/SF_6 permeance ratio for MFI-type zeolite membranes[17−21] probably depends on the presence of intercrystalline gaps. Hybrid silica membranes clearly show a high H_2 permeance with a high H_2/SF_6 permeance ratio. The H_2 permeance of hybrid silica membranes, showing values of ~10^{-5} mol m^{-2} s^{-1} Pa^{-1}, is much higher than that for thin palladium membranes at 200 °C, since H_2 permeability for palladium membranes drastically decreases with decreasing temperature.[23] A reproducible H_2/SF_6 permeance ratio (700−10000) suggests that the presence of few grain boundaries larger than 0.55 nm can be expected. The permeance of H_2 corrected for support resistance using the resistance model[11] ($0.36-2 \times 10^{-5}$ mol m^{-2} s^{-1} Pa^{-1}) is about twice the original permeance. It should be noted that the result of multicomponent (He, SF_6) gas separation showed a swelling effect caused by SF_6 molecules, which has been suggested for a zeolite membrane[24] but was not observed in amorphous silica networks (Figure S2 in the Supporting Information).

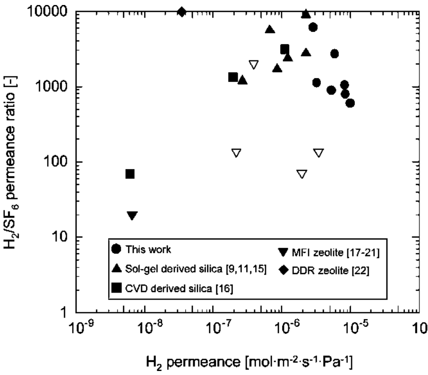

Figure 3. H_2/SF_6 permeance ratios as a function of H_2 permeance at 200 °C (closed symbols) and 25 °C (open symbols) for hybrid silica, silica,[9,11,15,16] and zeolite (MFI-type[17−21] and DDR-type[22]) membranes.

The hydrothermal stability of a hybrid silica membrane was examined by measuring the time course of gas permeance before and after exposure to steam at 300 °C. The hybrid silica membrane showed high hydrothermal stability, on the basis of the fact that there was no significant difference between its permeance before and after exposure to the steam (Figure S3 in the Supporting Information). The improvement in hydrothermal stability for hybrid silica membranes can be explained by the presence of Si−C−C−Si bonds in the silica networks,[12,13] which result in an increase in hydrophobicity, leading to a decrease in the formation of Si−OH groups in a hydrothermal atmosphere.[25]

In conclusion, the design of silica networks using an organic−inorganic hybrid structure for improvement of H_2 permeability could be successfully conducted using BTESE as a silica precursor. Hybrid silica membranes showed a very high H_2 permeance with high H_2-to-SF_6 selectivity. The hydrothermal stability of the hybrid silica membranes due to the presence of Si−C−C−Si bonds in the silica networks was also confirmed.

Supporting Information Available: Experimental procedures and the results of multicomponent gas separation and hydrothermal stability tests. This material is available free of charge via the Internet at http://pubs.acs.org.

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