Journal of Membrane Science 421–422 (2012) 124–130

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Organic–inorganic layered membrane for selective hydrogen permeation together with dehydration

Keita Miyajima [a,b,*], Tomokazu Eda [b], Balagopal N. Nair [b], Yuji Iwamoto [a]

[a] Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
[b] Research and Development Center, Noritake Co. Limited, 300 Higashiyama, Miyoshi-cho, Miyoshi 470-0293, Japan

ARTICLE INFO

Article history:
Received 5 March 2012
Received in revised form
26 June 2012
Accepted 2 July 2012
Available online 8 July 2012

Keywords:
Amorphous silica
Membrane
Polysilazane
Polytetrafluoroethylene (PTFE)
Plasma oxidation
Hydrogen
Gas separation
Dehydration
Hydrophobisity

ABSTRACT

Gas and vapor permeations of microporous amorphous silica membranes derived from commercial perhydropolysilazanes (PHPS) were investigated. Amorphous silica membranes were synthesized by a conventional heat treatment at 650 °C in air, and by a novel method using irradiation of air plasma. In the synthetic study of amorphous silica membranes by the conventional heat treatment, the membrane was formed on a porous silicon nitride tubular support. Two types of PHPS, with and without methyl ($-CH_3$) groups at the ends of the silicon–nitrogen backbone were used, and the amorphous silica membrane derived from the PHPS having $-CH_3$ end groups was found to exhibit higher hydrogen permeance and hydrogen/nitrogen perm-selectivity compared to those of the membrane derived from the end group-free PHPS. Then, by using a novel air plasma irradiation technique, low temperature conversion of PHPS into amorphous silica was investigated. The results of Fourier-transform infra-red spectroscopic analysis showed that the PHPS having $-CH_3$ end groups was fully oxidized to yield amorphous silica after the irradiation for 60 min. By this novel technique, an amorphous silica membrane was successfully formed on a polytetrafluoroethylene (PTFE) film attached on a porous alumina substrate. The layered membrane exhibited simultaneous functions of hydrogen separation together with dehydration as designed. By comparing the activation energies measured for the hydrogen permeation through the membranes synthesized in this study, it was estimated that the amorphous silica membranes synthesized by using the plasma irradiation were composed of the microporous random silicate network similar to those of the conventionally synthesized membranes.

1. Introduction

The separation process using gas and vapor separation membranes has been paid great attention because it can decrease the enormous energy consumption in chemical engineering processes such as condensation, purification and recovery. Various materials including metal [1], organic [2], inorganic and their compounds [3,4] are studied to fabricate the membrane with high perm-selectivity and permeance. Inorganic gas separation membranes having nano-pores are expected to apply to the separation process that organic membranes cannot use, because they indicate high permeance in wide temperature range and have high chemical stability in the atmosphere containing vapor of organic solvents which can cause swelling and elution of organic membranes. Especially, it is well known that microporous amorphous silica membranes synthesized by the sol–gel or the CVD method have a suitable pore-size (approximately 0.3 nm) for hydrogen (H_2) separation, and many studies have been carried out to apply the membranes to industrial uses such as a well-known hydrogen production by methane steam reforming, and a novel hydrogen storage system using chemical hydrides [5–9]. Moreover, the study on the pore-size tuning of the amorphous silica membranes [10,11], and the related composite membranes such as SiO_2–TiO_2 [12] and SiO_2–Al_2O_3 [13] have been in progress.

Among the inorganic membranes, zeolite and metal-organic framework (MOF) membranes are also actively studied. Especially, the applications for vapor permeation (VP) or pervaporation (PV) process to dehydrate and purify alcohol, ester or organic acid are focused on the studies, and zeolite NaA type membranes have been already put into practical use [14,15]. Remarkable improvements have been reported in the studies of inorganic membranes for gas and vapor separation, however, there are few reports about the membranes which have the functions of gas separation and dehydration simultaneously, for example the membrane which can separate only H_2 from mixture gases containing water vapor. In many cases of industrial gas separation process, the mixture gases often contains water vapor, and it is

* Corresponding author at: Research and Development Center, Noritake Co. Limited, 300 Higashiyama, Miyoshi-cho, Miyoshi 470-0293, Japan.
Tel.: +81 561 34 6215; fax: +81 561 34 4997.
E-mail address: keita-miyajima@n.noritake.co.jp (K. Miyajima).

0376-7388/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2012.07.002

needed for purification process to operate gas separation and dehydration separately because the kinetic diameter of water vapor (H_2O, 0.265 nm) is smaller than that of H_2 (0.289 nm) [16]. Thus, water vapor can be permeable together with H_2. Therefore the membrane having the function of gas separation together with dehydration is expected to achieve simplification of the separation process and contribute saving of energy consumption.

Porous organic membranes made of a hydrophobic compound such as polytetrafluoroethylene (PTFE) have been already utilized as gas diffusion layers of the air batteries [17–19]. In air batteries, oxygen as the cathode active material has to be supplied to the liquid electrolyte without leakage of the liquid. In addition, it is necessary to supply oxygen without incorporation of water because water causes dilution of liquid electrolyte and decreasing the performance of the batteries. For that purpose, porous PTFE layer shows suitable simultaneous properties of the gas diffusion and the water vapor barrier.

As mentioned above, we considered that the membrane which has the properties of molecular sieve and water vapor barrier can be expected by combining the inorganic membrane and the organic membrane. In order to combine them, the inorganic membrane such as amorphous silica membrane must be synthesized at lower temperatures, for example below 200 °C.

Polysilazane is one of the polymer precursors for silicon nitride (Si_3N_4) ceramics, and used for high temperature structural materials after pyrolysis and subsequent heat treatment at high-temperatures under the inert gas atmosphere of nitrogen (N_2). The polysilazane can be also converted into amorphous silica by heat treatment in an oxidative atmosphere at low temperature [20]. In the synthetic studies of gas separation membranes, amorphous silica membranes having H_2 perm-selectivity were synthesized by the conventional thermal conversion at 650 °C of perhydropolysilazane (PHPS) in air [21]. Amorphous silicon nitride-based H_2 separation membranes have been also successfully synthesized by pyrolysis of organo-polysilazane in an ammonia atmosphere at 650 °C, and it was found that the H_2 permeance and perm-selectivity were remarkably influenced by the molecular structure of the organo-polysilazane [22].

In this study, a main objective has been focused on the synthesis of a H_2-permselective amorphous silica membrane at low-temperatures to combine with a hydrophobic porous PTFE membrane. It is expected to be essential to achieve simultaneous membrane properties, H_2 separation and dehydration.

Prior to the study of the low-temperature synthesis, amorphous silica membranes were synthesized by the conventional heat treatment of PHPS at 650 °C in air. The gas permeances through the PHPS-derived membranes were evaluated, and the activation energy for the H_2 permeation was examined to study the influence of chemical structure of PHPS on the gas permeation properties. Then, a suitable PHPS was selected, and successfully converted into amorphous silica by a novel method using a plasma oxidation at low temperature. The polymer/amorphous silica conversion was monitored by the Fourier-transform infrared (FT-IR) spectroscopy. Finally, the amorphous silica-PTFE layered membrane was synthesized by the novel plasma oxidation process. The gas and water vapor permeances through the organic–inorganic layered membrane were evaluated and discussed from a view point to develop novel membranes for selective hydrogen permeation together with dehydration.

2. Experimental

2.1. Synthesis of silica membrane at high temperature

Two types of commercially available PHPS (AZ Electronic Materials, Japan) were used for synthesizing amorphous silica membranes: type NN310 having $-CH_3$ groups at the ends of the silicon–nitrogen backbone, and end group-free type NN110. The average molecular weights of the NN110 and NN310 were 500 g/mol and 1500 g/mol, respectively. Hereafter, NN110- and NN310-derived membranes are named as PHPS1 and PHPS2, respectively.

The PHPS-derived amorphous silica membrane was synthesized on a tubular-type Si_3N_4 porous support (outer diameter:13 mm, inner diameter:11 mm, length:100 mm) developed by Noritake Co. Lid. [23,24]. The porous support was asymmetric and composed of the inner layer (mean pore diameter:1.0 μm, porosity: 35%) and the outer surface layer (mean pore diameter: 0.1 μm, porosity: 50%). The outer surface layer was further modified with polyorganosilazane according to the published procedure [22], and converted as a fine intermediate layer to minimize the formation of defects in the membrane. The thickness of the intermediate layer was determined to be approximately 3 μm by microstructure analysis.

The xylene solution of PHPS was dip-coated on the porous Si_3N_4 support and pyrolyzed at 650 °C in air. The process of the coating and the subsequent pyrolysis was repeated twice. The concentrations of the PHPS xylene solution were 5 wt% and 2.5 wt%. It should be noted that the previously developed conventional asymmetric Al_2O_3 support composed of a mesoporous γ-Al_2O_3 surface thin layer and multi-layered porous α-Al_2O_3 [25] was not useful for this polymer route. Formation of defects such as delamination or crack often occurred at the interface between the mesoporous γ-Al_2O_3 layer and the porous α-Al_2O_3, which could be caused by the relatively large volume expansion of PHPS during the oxidative thermal conversion from polymer to amorphous silica. On the other hand, as one of the authors successfully synthesized a PHPS-derived microporous amorphous silica membrane on a macroporous Si_3N_4 support [21], the asymmetric Si_3N_4 porous support was successfully used for fabricating the amorphous silica membrane in this study. This could be due to that the tensile strength of Si_3N_4 is superior to that of Al_2O_3.

Microstructure of the PHPS1 was observed by a field emission scanning electron microscope (FE-SEM, Model S-4700, Hitachi, Japan). H_2 and N_2 permeances through the PHPS-derived amorphous silica membranes were measured at 50–600 °C, and the activation energy for the H_2 permeation was calculated from Arrhenius plots of all the measured H_2 permeances.

2.2. Low temperature synthesis of silica from PHPS

Low temperature synthesis of silica was performed by an air plasma oxidation using PHPS (Type NN310) as the precursor. PHPS xylene solution was put into an alumina crucible, and dried at 100 °C for 1 h. The dried residue was crushed and introduced into the chamber of a plasma reactor (Model PR-41, Yamato Scientific, Japan) and air plasma was irradiated on the sample. In order to oxidize the dried PHPS bulk efficiently, it was better to use oxygen as plasma source, however synthetic air (O_2: 22 vol%, N_2: 78 vol%) was used as the plasma source for the safety of the experiment. The pressure of the air and the applied power were set up 100 Pa and 500 W, respectively. The FT-IR spectra were recorded for the samples before and after the plasma irradiation for 5, 20 and 60 min.

2.3. Synthesis of organic–inorganic layered membrane

The organic–inorganic layered membrane was synthesized by coating PHPS (NN310) on a hydrophobic porous PTFE film. The PTFE film (Valflon Adhesive Tape: Nippon Valqua Industries, Japan) with adhesive compound was attached on a planar type of porous alumina support (disk diameter: 6.5 mm, thickness: 1.0 mm, mean pore diameter: 0.7 μm, porosity: 35%) to keep the