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Preparation of organic–inorganic hybrid silica membranes using organoalkoxysilanes: The effect of pendant groups

Gang Li, Masakoto Kanezashi, Toshinori Tsuru*

Department of Chemical Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

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ABSTRACT

Organic–inorganic hybrid silica membranes were prepared via a sol–gel process using organoalkoxysilanes with pendant groups. Two kinds of organoalkoxysilanes, methyltriethoxysilane (MTES) and phenyltriethoxysilane (PhTES), were used to investigate the effect of the pendant groups on the gas permeation properties and micropore structures of hybrid silica membranes. The hybrid silica membranes showed relatively low H_2 permeance, and the H_2 permeance decreased with the pendant group size. Moreover, based on pore sizes determined by normalized Knudsen-based permeance (NKP), the hybrid silica membranes showed large pore sizes that increased with the size of the pendant groups. Compared with silica membranes prepared from tetraethoxysilane (TEOS) and 1,2-bis(triethoxysilyl)ethane (BTESE), which have no pendant groups, the large pore sizes of silica membranes derived from MTES and PhTES were not associated with high H_2 permeance. This could be ascribed to the different membrane structures of MTES- and PhTES-derived silica membranes, due to the presence of pendant groups in the silica matrix.

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1. Introduction

A great deal of attention has been paid to silica membranes, which can accomplish separation tasks even under harsh conditions due to their high separation performance, chemical inertness, and thermal stability [1–3]. Two strategies have been proposed to prepare amorphous molecular sieving silica membranes, the sol–gel process and the chemical vapor deposition (CVD) method. Tetraethoxysilane (TEOS), which is a common Si precursor, has been widely adopted in both approaches, and the resultant membranes have been extensively investigated for gas separation [1,4,5], pervaporation [6,7] and membrane reaction [8–11]. However, traditional TEOS-derived silica membranes suffer from poor hydrothermal stability, which greatly hampers their practical application. Inspired by the distinctive features of organic–inorganic hybrid silica materials with respect to flexibility, hydrothermal stability and tunable pore sizes [12], researchers have concentrated on the preparation of hybrid silica membranes with improved hydrothermal stability and controlled pore sizes, using organoalkoxysilanes instead of TEOS [13–23]. As a result of the unique properties of hybrid silica materials, the preparation, characterization and application of hybrid silica membranes has become a very interesting area of membrane science and technology over the past decade.

Two typical kinds of organoalkoxysilanes have been used as Si precursors to prepare silica membranes via a sol–gel process. One is a di-silicon alkoxide with a bridged group between the two silicon atoms, such as 1,2-bis(triethoxysilyl)ethane (BTESE) $(CH_3CH_2O)_3SiCH_2CH_2Si(OCH_2CH_3)_3$ [14,15,18–20] and bis(triethoxysilyl)methane (BTESM) $(CH_3CH_2O)_3SiCH_2Si(OCH_2CH_3)_3$ [22]. Castricum and coworkers [18–20] first reported on the BTESE-derived silica membrane, and applied it to pervaporation dehydration of solvents of 95 wt.% n-butanol-5 wt.% water in an attempt to increase hydrothermal stability. The membrane was stable after 1.5 years, even though the test temperature was as high as 150 °C, while TEOS-derived silica membrane completely lost its separation ability within weeks at a much lower temperature of 95 °C. The excellent hydrothermal stability endowed by the organic–inorganic structures appears to be very promising for practical application. In 2009, our research group proposed a "spacer" technique to control silica networks, using BTESE for the development of highly permeable hydrogen separation membranes with hydrothermal stability [14,15]. The pore diameter of BTESE-derived silica membrane was successfully shifted to a larger size than that of the traditional silica membrane prepared with TEOS, resulting in unprecedented H_2 permeance. It was clearly understood that the formation of a looser structure and improved hydrothermal stability was due to the presence of a Si–C–C–Si minimum unit in the silica networks.

* Corresponding author. Tel.: +81 82 424 7741; fax: +81 82 424 5494.
E-mail address: tsuru@hiroshima-u.ac.jp (T. Tsuru).

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Another pore size tuning strategy is the "template" technique, which utilizes another typical kind of organoalkoxysilane, a mono-silicon alkoxide with a pendant group, such as methyltriethoxysilane (MTES) [13,16], (trifluoropropyl)triethoxysilane (TFPTES) [21], ethylenetriethoxysilane (ETES) [23] or 3-methacryloxypropyltrimethoxysilane (MPS) [25]. The template effect of pendant groups of mono-silicon alkoxides has been studied by several research groups [24–28]. It was proposed that additional pores could be formed after burning out the incorporated pendant groups in the membranes, and the pore sizes and shapes in the membranes could be controlled by the pendant groups. Without burning out organic pendant groups, hybrid hydrophobic silica membranes could be obtained via the sol–gel process, which was first reported by de Vos et al. using TEOS and MTES as co-precursors [13]. The hybrid membranes prepared via this route also showed good hydrothermal stability, and have been used for both gas separation [13,21,23] and pervaporation [16]. Considerable research on silica membranes prepared by mono-silicon alkoxides with pendant groups has led to a great deal of progress in understanding both the sol–gel process and the membrane characteristics. However, it is still not clear how the pore structure changes after pendant groups are embedded into silica networks. Moreover, previous studies used mixed Si source systems, such as TEOS mixed with MTES [13,16,24,26,27]. Since different Si precursors may lead to different pore sizes and pore size distributions, it is extremely important to investigate a single system in order to gain insight into the influence of Si precursors on the pore structures of silica membranes.

In the present study, we focused on hybrid silica membranes derived from a single Si precursor system, using a mono-silicon alkoxide with a pendant group. Two mono-silicon alkoxides, MTES and phenyltriethoxysilane (PhTES), were chosen as starting precursors to study the effect of pendant groups on the gas permeation properties and pore structures of hybrid silica membranes. Normalized Knudsen-based permeance (NKP) was applied to quantitatively evaluate the pore size of hybrid silica membranes.

2. Experimental

2.1. Preparation of hybrid silica sols, gels and membranes

Hybrid silica sols were obtained by acetic acid-catalyzed hydrolysis and condensation of MTES (>99.8%, Tokyo Chemical Industry Co., Ltd.) and PhTES (Gelest, Inc.), respectively. First, the organoalkoxysilanes were homogeneously dissolved in ethanol with a molar ratio of Si/ethanol = 1/40–50. A mixture of water, acetic acid, and ethanol was then added dropwise to the solution under vigorous stirring, resulting in final solutions with molar ratios of MTES/H_2O/ethanol/acid = 1/30/62/0.12 and PhTES/H_2O/ethanol/acid = 1/30/87/0.16. After this addition, both solutions were kept in closed systems under continuous stirring at 60 °C for 24 h to develop silica sols. TEOS-derived silica sols were prepared for comparison, and details of the preparation procedure can be found in the literature [5]. Silica gels were prepared by drying the corresponding silica sols at around 40 °C, followed by grinding into powder.

Porous α-Al_2O_3 tubes (porosity: ~46%; average pore size: 150 nm; length: 70 mm; outer diameter: 3.0 mm; inner diameter: ~2.2 mm, NOK, Japan) were used as supports for membrane preparation. First, 10 mm of each end of the supports was glazed for sealing, resulting in an active length of 50 mm. Then, silica–zirconia (SiO_2/ZrO_2 = 1/1) sols were coated on the supports, and subsequently fired at 550 °C in air. This procedure was repeated 5 times to form the intermediate layers that finally gave a pore size of approximately 2 nm [5], and showed Knudsen-selectivity for the gas pairs. After that, the hybrid silica sols were deposited onto the intermediate layers using a hot coating method, followed by firing at 400–550 °C in a N_2 atmosphere for 15 min. The coating and firing process was repeated twice in order to obtain separation layers. Silica membranes derived from different alkoxides were denoted as Si-alkoxides.

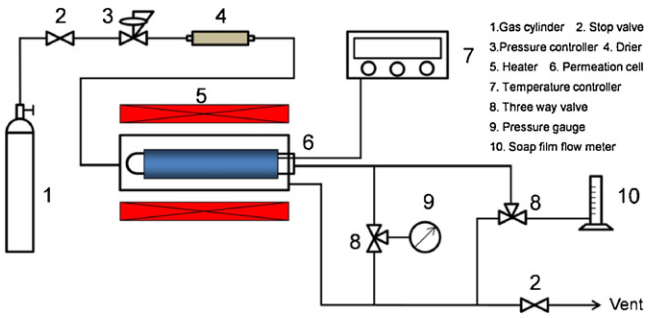

Fig. 1. Schematic diagram of the apparatus for single gas permeation tests.

2.2. Characterization of hybrid silica sols, gels and membranes

The non-volatile residue of the hybrid silica sols was measured using thermogravimetric analysis (TGA) (TGA-50, Shimadzu) at 140 °C for 30 min at a heating rate of 5 °C min^{-1} under a N_2 flow of 50 ml min^{-1} as a measure of the hydrolysis state. The weight percent of the non-volatile residue was calculated by the weight ratio of the non-volatile residue to the corresponding silica sol [29]. Fourier transform infrared (FT-IR) spectroscopy (FTIR-8300, Shimadzu) was carried out to confirm the presence of pendant groups in the silica networks. The sample for measurement was prepared by coating the silica sols on a KBr plate, followed by firing at 400–600 °C in a N_2 atmosphere. Thermogravimetric analysis-mass spectrometry (TGA-MS) (ThermoMass/DH, Rigaku) was performed to investigate the decomposition behavior of organic groups in the silica matrix, in a temperature that ranged from 150 to 950 °C at a heating rate of 10 °C min^{-1} in a He flow of 300 ml min^{-1}. The silica gel powder was preheated at 150 °C to remove the absorbed water in the silica pores before the measurement. A N_2 adsorption isotherm (Belsorp 28SA, BEL Japan, Inc.) was carried out at 77 K to study the micropore structures of the silica gels. Prior to the measurement, all the silica gel samples were evacuated at 150–300 °C for 12 h. Silica films were prepared by coating the silica sols on glass slides, followed by firing in a N_2 atmosphere. The contact angle of a water droplet on the surface of the silica films was used to characterize the hydrophobicity of the hybrid silica. A scanning electron microscope (SEM) (JCM-5700, JEOL) was used to examine the membrane morphology and thickness, using an acceleration voltage of 20 kV.

2.3. Single gas permeation tests

Gas permeation tests were performed at 200 °C using a single component of He, H_2, CO_2, N_2, CH_4, C_3H_8 and SF_6. The permeation side was maintained at atmospheric pressure, and the pressure drop through the membranes was maintained at 1 bar. Prior to the measurement, all membranes were outgassed in a He flow of 50 ml min^{-1} at 200 °C for 8–12 h to remove the water absorbed in the membranes. A schematic diagram of the apparatus for the single gas permeation tests is shown in Fig. 1.

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