



Evaluating the gas permeation properties and hydrothermal stability of organosilica membranes under different hydrosilylation conditions



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ABSTRACT

Organosilica membranes were fabricated under controlled sol-preparation conditions such as the ratio of triethoxysilane (TRIES) and vinyltrimethoxysilane (VTMS) and the hydrosilylation temperature. The single-gas permeation properties and hydrothermal stability of organosilica membranes were evaluated to clarify the relationship between hydrothermal stability and organosilica structure. Pt-catalyzed and thermally cured hydrosilylation was applied to evaluate the effect that hydrosilylation temperature exerts on the properties of membranes. Organosilica membranes (Pt-catalyzed hydrosilylation at 40 °C) showed H₂ permeance of approximately 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ with H₂ selectivity (H₂/CH₄:15, H₂/CF₄:950) at 500 °C, and were stable under an oxidative atmosphere at 500 °C. The organosilica network size derived by thermal curing at 500 °C was smaller than that by Pt-catalyzed hydrosilylation, even though the units (Si–C–C–Si, Si–O–Si) were the same. Hydrosilylation reactivity derived by thermal curing (500 °C, N₂) strongly depended on the TRIES/VTMS (=H/V) ratio in the SQ sol, and an H/V ratio of 1.25 showed a higher level of hydrosilylation reactivity. Its hydrothermal stability was better than that of amorphous silica membranes, due to the incorporation of Si–(CH₂)₂–Si units in the networks via hydrosilylation, based on the decreased ratio of He and H₂ permeance, the He/H₂ permeance ratio, and the activation energy before/after steam treatment.

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1. Introduction

Membrane-based separation is expected to be an alternative to conventional distillation, cryogenic separation, and pressure-swing adsorption applications in the purification of natural gas, CO₂ separation, H₂ separation, olefin/paraffin separation, and the dehydration of alcohol/acid (H₂O/ethanol, H₂O/isopropyl alcohol (IPA), H₂O/acetic acid) [1]. Membranes are categorized as either inorganic or polymer based on the membrane materials. The utilization of polymeric membranes is generally restricted to temperatures sufficiently low to not promote polymer transition and/or decomposition of polymer networks, due to a lack of thermal stability [2]. By contrast, inorganic membranes show promise for practical utilization at high temperatures, because the thermal and chemical stability are significantly higher than that of organic polymer membranes. Of all inorganic materials, silicon carbide (SiC) and silicon oxycarbide (SiOC) show the best hydrophobic properties and are resistant to high temperatures and corrosive chemicals [3–5]. Thus, microporous membranes with Si–C units

are expected to overcome the fatal issues of inorganic membranes, which include an instability of the silica structure against steam at high temperatures, high cost, the CO poisoning of Pd and Pd-alloys, and the poor oxidative stability of carbon molecular-sieves [6].

The formation of the SiC structure was generally carried out by pyrolyzing poly (silastyrene) [7], poly (carbosilane) (PCS) [8–12], and polydimethylsilane (PMS) [13] containing both Si and C elements in the polymer chain. Next came the oxidation curing [8,9,13] and electron beam (EB) irradiation [10,12] method that was used to create SiOC structures. The published studies suggested that the optimization of pyrolysis conditions would tailor the SiOC networks so that He and H₂ could permeate. Improvements in hydrogen permeation performance (H₂ permeance: ~3.0 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ and H₂/N₂ selectivity: ~800) for SiOC membranes were achieved via oxidation of the SiC structure, as well as thermal cross-linking of uncross-linked and cross-linked PCS at a low temperature [9]. However, further efforts are required to improve the gas permeation properties (permeance, selectivity) through pyrolyzed SiOC membranes by controlling the network size.

The sol–gel method is much more flexible in controlling the network size compared with pyrolysis of a polymer precursor

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containing both Si and C elements in the polymer chain. Control of the organosilica network size via a sol–gel method was proposed to utilize organoalkoxysilane, both a bridged-type [14–18] with a Si–R–Si unit (R: organic groups) and a pendant-type [19–21] with organic groups, that is directly connected to a Si atom. The presence of organic groups in an organosilica structure can enlarge the network size to greater than that of tetraethoxysilane (TEOS) membranes [15,17]. Castricum et al. [14] evaluated the pervaporation properties (dehydration of n-butanol (5 wt% water) at 150 °C) of conventional silica and organosilica membranes by measuring the long-term time course of separation properties (water flux, separation factor). Organosilica membrane derived by bis (triethoxysilyl) ethane (BTESE, Si–C–C–Si unit) showed only a slight decrease (4% per month) in water flux keeping the water concentration of 98 wt% in the permeate side during almost 2 years. On the other hand, SiO₂ membrane lost the separation property within days even at 95 °C. Thus, they concluded that the organosilica membranes showed improved hydrothermal stability compared with SiO₂ membranes, due to the incorporation of carbon units in the silica structure. However, the pyrolysis of organic groups at temperatures higher than 400 °C under air is expected to degrade hydrothermal stability and decompose the network structure [15,17].

Recently, amorphous organosilica structures were designed using Si–O–Si units via the hydrolysis and condensation of silsesquioxane (SQ) and by using Si–C–C–Si units via the *in-situ* hydrosilylation of Si–CH=CH₂ and Si–H groups in a Si precursor, as schematically shown in Fig. 1 [22]. The gas permeation properties and thermal stability of organosilica membranes (VTT-type prepared by vinyltrimethoxysilane (VTMS), triethoxysilane (TRIES), and tetramethyldisiloxane (TMDSO); and VT-type prepared by VTMS and TRIES) were evaluated to discuss the effect of Si precursor on network structures. Both (VTT- and VT-type) membranes showed H₂ permeance on the order of 10^{−7} mol m^{−2} s^{−1} Pa^{−1} with moderate H₂/N₂ and high H₂/CF₄ permeance ratios at temperatures ranging from 200–500 °C. Regarding the thermal stability of the organosilica structure, slight changes in permeance were confirmed for each of the organosilica (VT-type) membranes after heat treatment at 550 °C under air for 10 h. However, the heat-treated membrane (VTT-type) recorded a drastic decrease (from 485 to 90) in the H₂/CF₄ permeance ratio as H₂ permeance was increased. Thus, the organosilica structure (VT-type) was the preferred form for gas separation under hydrothermal conditions of high temperatures, due to the presence of the Si–C–C–Si unit via hydrosilylation.

In the design of networks via hydrosilylation, the ratio of TRIES and VTMS directly affects the properties of the organosilica structure. In addition hydrosilylation temperature, which can be generally controlled by utilizing chloroplatinic acid hexahydrate (H₂PtCl₆ 6H₂O) as a catalyst, Pt-catalysis and thermal curing are important in order to optimize the organosilica structure. In the

present study, therefore, organosilica membranes (VT-type) were fabricated by controlling the SQ sol preparation conditions such as the ratios of VTMS and TRIES and the hydrosilylation temperature. The single-gas permeation properties and hydrothermal stability of organosilica membranes were evaluated in order to clarify the relationship between hydrothermal stability and the organosilica structure. Organosilica structures synthesized under different synthesis conditions were characterized by ²⁹Si and ¹³C NMR, respectively.

2. Experimental

2.1. Membrane fabrication via hydrosilylation

Silsesquioxane (SQ) sols (VT-type) were synthesized via the hydrolysis and polymerization of vinyltrimethoxysilane (VTMS) and triethoxysilane (TRIES) [22]. A specified amount of TRIES and VTMS was mixed with isopropyl alcohol (IPA), then H₂O and HCl was added as a catalyst at 25 °C for 1 h. The molar ratios of the solution were TRIES (Si–H)/VTMS (Si–CH=CH₂) (=H/V)=0.5~5, H₂O/(TRIES+VTMS)=240, and HCl/(TRIES+VTMS)=1/10, and the Si precursor was maintained at 1 wt%. A catalyst, chloroplatinic acid hexahydrate (H₂PtCl₆ 6H₂O), was added into the SQ sol with vigorous stirring to control the kinetics of hydrosilylation: H₂PtCl₆ 6H₂O (Pt/Si=1.6 × 10^{−3}). In the present study, Pt-catalyzed and thermally cured hydrosilylations were conducted at 40 and 500 °C, respectively, under N₂ to create an organosilica structure and to evaluate the effect of hydrosilylation temperature on organosilica structures.

Organosilica membranes with 50% porosity and an average pore size of 1 μm were coated onto porous α-alumina tubes [22]. Before coating the SQ sol onto alumina substrates, a SiO₂–ZrO₂ intermediate layer with an average pore size of 1–2 nm, as measured by nanoporometry, was calcined at 550 °C under air to prevent the penetration of the SQ sol into the substrate. Then, SQ sols with/without a Pt catalyst were diluted to 0.5 wt% and coated onto the intermediate layer to form the organosilica layer, which was then dried and calcined at 500 °C under N₂.

2.2. Characterization of organosilica gels

Powdered samples of the gels were prepared by drying at 40 °C under air, followed by calcination at 500 °C for 1 h under an atmosphere of air and/or N₂. Organosilica structures were characterized by ²⁹Si and ¹³C NMR, respectively. The details of the measurement conditions were described in a previous paper [22].

2.3. Gas permeation measurement and thermal, hydrothermal

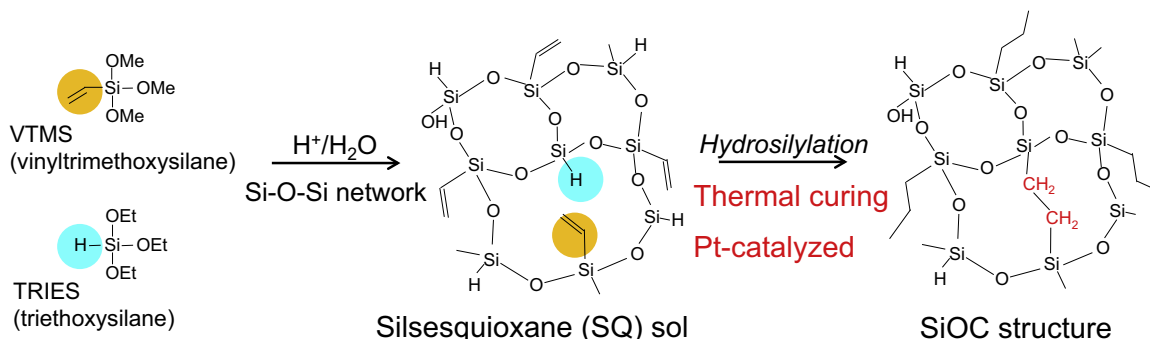


Fig. 1. Schematic image of the organosilica structure (VT-type) by hydrosilylation.

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