Journal of Membrane Science 511 (2016) 219–227

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Network engineering of a BTESE membrane for improved gas performance via a novel pH-swing method

Xin Yu, Lie Meng, Takuya Niimi, Hiroki Nagasawa, Masakoto Kanezashi, Tomohisa Yoshioka, Toshinori Tsuru *

Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagami-yama, Higashi-Hiroshima 739-8527, Japan

ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form
29 March 2016
Accepted 31 March 2016
Available online 2 April 2016

Keywords:
Organosilica
pH-swing
Sol size
Gas permeation
Thermostability

ABSTRACT

Organosilica microporous membranes were fabricated from 1, 2-bis (triethoxysilyl) ethane (BTESE)-derived sols prepared in acidic pH via the pH-swing method. This method includes two steps whereby a specific amount of NH_3 was added into the acid sols and switched to acid after a reaction of several minutes. We found that the size of the BTESE-derived sols by pH-swing could be controlled via the H_2O/BTESE molar ratio and the reaction time in alkali. Under the same H_2O/BTESE ratio of 60, the BTESE-derived sols prepared in the pH-swing method showed an increase sol size in contrast with the acid method, and the sol size was easily controlled by the dominating reaction in alkali pH – the condensation reaction. Gas permeation results showed that some gases (He, H_2, N_2, C_3H_8, SF_6) permeated the membrane that was prepared using the pH-swing sols (pH-swing membrane) at approximately twice the rate shown by the membrane prepared using acid sols (acid membrane); H_2 permeance levels of the pH-swing membrane and the acid membrane were 3.4×10^{-6} and 1.6×10^{-6} mol m^{-2} s^{-1} Pa^{-1} at 200 °C, respectively. The pH-swing membrane also maintained similar H_2/C_3H_8 permeance ratios of ranging from 2600~5800, confirming that pH-swing processing is an innovative method for improvement in the gas permeance of BTESE-derived organosilica membranes. One possible reason for these results could be that the membranes prepared using the pH-swing sols increased the size of the sols, which reduced the sol penetration into the intermediate layer. Moreover, the high cross-linking that was caused by pH-swing increased the thermostability of the BTESE-derived organosilica networks. The CO_2/CH_4 and CO_2/N_2 permeance ratios for the pH-swing membrane were as high as 90 and 28, respectively, at 50 °C.

1. Introduction

Hydrogen is considered a source of clean energy and is expected to play a significant role in the reduction of the emissions of greenhouse gases for the environment [1]. To reduce fossil fuel consumption, highly efficient separation processes should be developed to obtain high-grade H_2 production on a large scale, but many fundamental scientific and technological challenges are yet to be overcome.

A feasible approach to efficient hydrogen purification is to use inorganic membranes, particularly the silica-based versions [2–4]. These membranes have attracted considerable attention for excellent molecular sieving effect and the thermostability, which enables their applicability to gas separation under conditions where polymeric membranes cannot be used [5, 6]. The purification of hydrogen from organic compounds (such as CH_4, C_3H_8) could be one of the most important applications. Tetraethoxysilane (TEOS) is the most commonly used silicon precursor for the preparation of sol-gel derived silica membranes due to its excellent selectivity [7]. However, the low stability of the silica structure to water severely limits its application in many industrial processes that include hydrothermal conditions [8]. In addition, molecular simulation has revealed that most of the membrane pores are smaller than H_2 molecules and only a small number of pores are available for H_2 permeation, which results in poor gas permeance [9].

A possible approach to improving the hydrothermal stability and gas permselectivity of silica membranes is to incorporate organic functional groups in the silica networks. The shape, flexibility and length of the organic units in a hybrid silica network are known to influence the membrane pore size, structure and affinity [10]. Recently, a new class of organoalkoxysilanes with double silicon and linking organic groups, such as 1, 2-bis (triethoxysilyl) ethane (BTESE), was used as a precursor to prepare organic-inorganic hybrid membranes for the pervaporation dehydration of aqueous solutions. The pore sizes of the BTESE-derived networks

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* Corresponding author.
E-mail address: tsuru@hiroshima-u.ac.jp (T. Tsuru).

http://dx.doi.org/10.1016/j.memsci.2016.03.060
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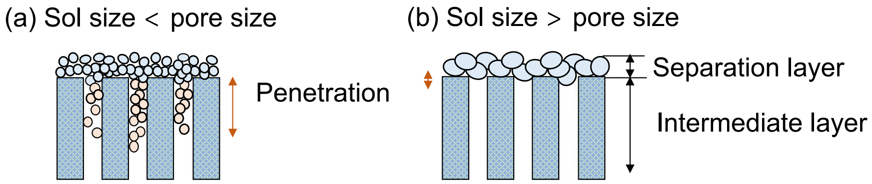

Fig. 1. Schematic structure of small and large size sols-derived membranes.

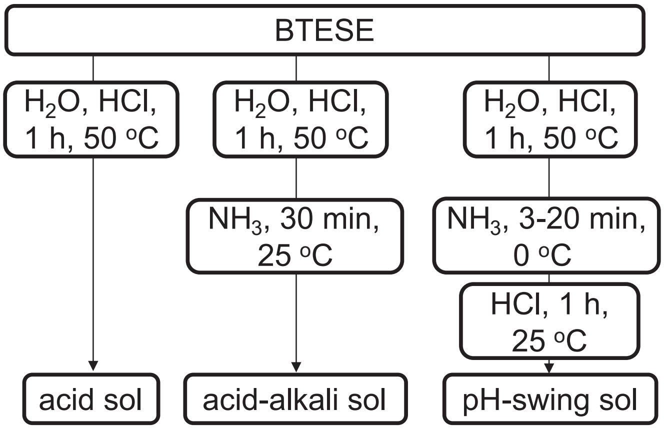

Fig. 2. A schematic procedure of acid, acid-alkali and pH-swing sols preparation.

were enlarged due to the existence of the linking units compared with TEOS, which was proposed as a spacer technique for tuning subnanopores [11]. BTESE-derived membranes were reportedly applied to pervaporation [12], reverse osmosis [13] and membrane reactors[14,15]. The formation of a loose structure and improved hydrothermal stability have clearly been due to the presence of a Si-C-C-Si unit in silica networks [16]. BTESE-derived network pore sizes have been successfully controlled via the water ratio [17]. With an increase in the H_2O/BTESE ratio of from 6 to 240, the membrane permeance for H_2 was decreased from 2×10^{-6} mol m^{-2} s^{-1} Pa^{-1} to 1×10^{-6} mol m^{-2} s^{-1} Pa^{-1}, while the permeance ratio of H_2/C_3H_8 was increased from 40 to 6000. In addition, the pore sizes of BTESE networks has been controlled via the acid ratio [18]. By optimizing the acid ratio, BTESE membranes obtained a H_2/N_2 permselectivity that ranged from 50 to more than 400 [19].

In general, for the fabrication of inorganic membranes, a separation layer is coated onto an intermediate layer, as shown in Fig.1(a). When the pore size of the intermediate layer is larger than the size of BTESE-derived sols, these would penetrate the mesoporous intermediate layer and decrease the gas performance. Therefore, if it is possible to increase the sol size enough to prevent penetration, as shown in Fig. 1(b), it would be possible to increase the gas permeance of BTESE-derived membranes with a thin film coating. The hydrolysis and condensation reaction rates of alkoxysilanes are known to be dependent on pH [20]. The size and shape of sols is controlled by pH in the sol-gel method [21–23]. The rate of hydrolysis in a BTESE reaction is high in an acidic pH, while that of condensation is high under an alkali pH. Therefore, it should be possible to enlarge the size of BTESE-derived sols by increasing the condensation rate in an alkali pH. In addition, through condensation cross-linking network could affect the thermostability and gas permeability of organosilica membranes.

In the present study, we attempted to control the sols by adjusting the pH during their preparation. Three types of BTESE-derived sols were prepared: acid sols, acid-alkali sols and pH-swing sols. The pH-swing is a novel process where sol pH is manipulated from acidic to alkali, and returned to acidic. This process was investigated for its ability to tune the colloid sol sizes for BTESE-derived membranes in terms of the H_2O/BTESE molar ratio and pH values in BTESE hydrolysis and condensation. BTESE-derived sols were prepared by manipulating the pH of a sol from acid (pH=2) to alkali (pH=10) with H_2O/BTESE ratios of 60 and 240, respectively. The sols were characterized by DLS, small-angle X-ray scattering NMR, TGA and N_2 adsorption. The gas permeation properties were also examined to investigate the effect of sols on gas separation.

2. Materials and methods

2.1. Preparation of BTESE sols

1, 2-bis (triethoxysilyl) ethane (BTESE) as a precursor was purchased from Aldrich, and used without further purification. Ethanol (minimum 99.5%) was used as a solvent without further purification. The amount of water contained in ethanol was assumed to be 0.5%. HCl and NH_3 were used as catalysts. Three types of BTESE-derived sols were prepared as shown in Fig. 2: acidic, acid-alkali and pH-swing (acid-alkali-acid). To prepare "acid sols," BTESE was hydrolyzed and condensed with water and hydrochloric acid at 50 °C for 1 h with molar ratios of BTESE/HCl/H_2O =1/0.1/(6-240). To prepare "acid-alkali sols," a specific amount of NH_3 was added to the acid sols with agitation at 25 °C to adjust the NH_3/HCl molar ratios from 1.56 to 12. To prepare the 'pH-swing sol,' NH_3 was added to the acid sols and maintained for 3–20 min at 0 °C, followed by the addition of HCl (HCl/ NH_3=0.8) to return the pH to approximately 2 at 25 °C. The sizes of BTESE sols were controlled by adjusting the pH values and reaction time in alkali. The concentration of BTESE in all three types of BTESE-derived sols was kept at 5.0 wt% in the final compositions.

2.2. Characterization of BTESE-derived gels and powders

The colloid size of BTESE-derived sols was determined via Dynamic Light Scattering (DLS) using a Malvern Zetasizer Nano ZS (Malvern Instruments, Ltd.) at 25 °C. Small-angle X-ray scattering (SAXS) was evaluated using a Nano-viewer (Rigaku Co., Japan).

BTESE-derived powders (H_2O/BTESE=60, acid and pH-swing) were prepared via the quick-drying method where the BTESE-derived sols were dried quickly at 180 °C under air, similar to the membrane fabrication, followed by calcination at 200 °C under an air atmosphere for 30 min, and ground using a mortar. The thermogravimetric analysis (TG) was provided by TG-MASS (TG-DTA-410s, Rigaku Co). He/O_2 mixed gas (He: 80 mol%, O_2: 20 mol%) was used as a carrier, and the temperature was increased at a ramping rate of 10 °C min^{-1} to 1,000 °C. The adsorption isotherms of N_2 for BTESE-derived powders fired at 300, 400 and 500 °C under an air atmosphere were measured at 77 K (BELMAX, BEL Japan INC). The surface area of the samples was calculated using the BET equation. The surface of the membranes was examined by Field Emission Scanning Electron Microscopy (FE-SEM, S-4800, HITACHI). The ^{29}Si-NMR spectra were recorded at 119.17 MHz on a Varian 600 PS solid NMR spectrometer.