



Micropore structure stabilization in organosilica membranes by gaseous catalyst post-treatment



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ABSTRACT

A post-treatment involving repeated exposure to gaseous HCl alternated with heating is demonstrated to strongly accelerate the recently reported structural evolution in organically bridged silica networks. Films, powders and membranes derived from 1,2-bis(triethoxysilyl)ethane were exposed to in-situ synthesized HCl gas, alternated with heat treatments at 150–300 °C in air or N₂. The film thickness, network condensation, chemical integrity and micropore structure were monitored with X-ray reflectivity, ²⁹Si direct-excitation magic-angle spinning nuclear magnetic resonance, Fourier-transform infrared spectroscopy and gas permeation. Treatment with HCl was found to predominantly catalyze hydrolysis, enabling network optimization via iterative bond breakage and reformation. Network shrinkage, widening or opening of the smallest pores and densification of the overall pore structure were accelerated while the ethylene bridges remained intact. The achieved acceleration of material evolution makes iterative hydrolysis and condensation a promising approach for increasing the long-term micropore stability of molecular sieving membranes.

1. Introduction

Hybrid organosilica networks, in which part of the Si-O-Si linkages are replaced by Si-R-Si, provide a valuable combination of inorganic and organic material properties. For membrane applications, the introduction of organic bridging segments to microporous silica yields networks with tunable pore sizes and affinities and a highly superior hydrothermal stability [1–8]. Hybrid organosilica membranes have replaced inorganic silica membranes in various molecular sieving applications under hydrothermal conditions. However, this new generation of membranes displays a slow ongoing flux decline during operation at 95–150 °C for more than a year [1,2,9], causing practical difficulties in industrial processes. To date, this problem has not been solved.

Recently, we reported a detailed study on long-term consolidation in powders, films and membranes derived from 1,2-bis(triethoxysilyl)ethane (BTESE) [10]. Subtle but persistent chemical and structural changes were demonstrated to continue for days to weeks at temperatures up to 300 °C without approaching an end state. Ongoing chemical condensation was accompanied by network shrinkage and decreasing density. This led to a decreasing gas permeance through relatively large pores > 0.4 nm but an increasing gas permeance through small pores

~0.3 nm. The structural changes were speeded up by exposure to HCl vapor, which was previously reported as a method to increase condensation and reduce micropore sizes in BTESE-derived membranes by Wang et al. [11,12]. The process observed in our recent study was proposed to be the origin of the problem of slow flux decline in industrially employed organically bridged silica membranes over periods of months to years. As for solutions to this instability issue, we proposed a post-synthesis treatment to catalyze both condensation and hydrolysis in a combined or alternating fashion. This facilitates evolution of the network into a more favorable configuration via iterative reconnections. This iterative approach differs from the single-step catalyst post-treatments generally reported in literature for (organo)silica materials. Liquid-phase hydrothermal treatment with NH₄OH and HCl has been reported to increase the structural stability and condensation degree and tune textural properties of mesoporous inorganic silica [13–15]. Vapor-phase HCl treatment has been used to tune the micropore size and increase the condensation degree of microporous ethylene-bridged membranes [11,12,16].

The present study introduces a post-treatment involving iterative hydrolysis and condensation to achieve extensive reorganization and stabilization of organosilica networks in a controlled fashion. The chemical reaction scheme shown in Fig. 1a. BTESE-derived films,

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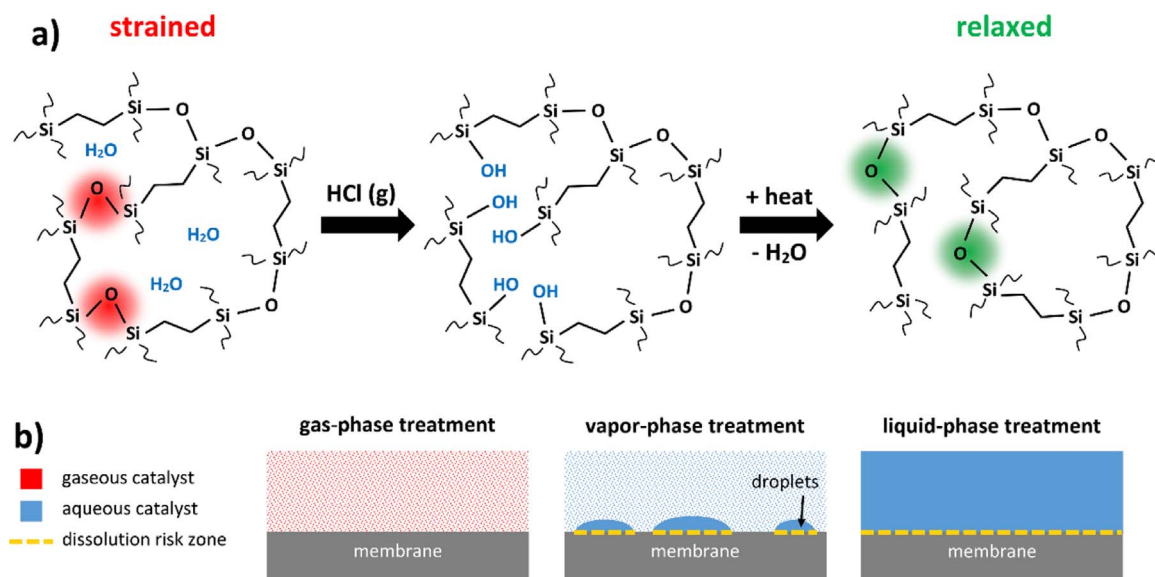


Fig. 1. a) Chemical reaction scheme of network stabilization. b) Schematic representation of gas-phase, vapor-phase and liquid-phase catalyst treatments.

powders and membranes were repeatedly exposed to in-situ synthesized HCl gas alternated with heat treatments. Several process parameters were varied to study the mechanism of network evolution and to commence process optimization. The film thickness, network condensation, chemical integrity and micropore structure were monitored with X-ray reflectivity (XRR), ²⁹Si direct-excitation magic-angle spinning nuclear magnetic resonance (²⁹Si DE-MAS-NMR), Fourier-transform infrared spectroscopy (FTIR) and gas permeation (GP). Though some water is required for the reactions, this gas-phase catalyst treatment involves much lower quantities of water (i.e. only atmospheric and adsorbed moisture) than previously reported liquid-phase and vapor-phase catalyst treatments. This eliminates the risk of material dissolution and pinhole formation in either the organosilica top layer or its support when applied to molecular sieving membranes, as schematically depicted in Fig. 1b.

2. Experimental

2.1. Chemicals

1,2-bis(triethoxysilyl)ethane (97% purity) was obtained from ABCR. Nitric acid (70 wt% aqueous solution), 1-butanol (99.8% purity) and Mowiol 8–88 polyvinyl alcohol were obtained from Sigma Aldrich. Ethanol (dehydrated, 99.99% purity) was obtained from VWR. Sulfuric acid (≥95% purity) was obtained from Fluka. Sodium chloride (99.7% purity) was obtained from J.T. Baker.

2.2. Powder and film preparation

BTESE-derived sols and powders were prepared as reported elsewhere [10]. 3.24 mL demi water and 0.798 mL aqueous HNO₃ (65 wt %) were added to 50 mL dry ethanol at room temperature, followed by adding 11.12 mL BTESE under stirring. The mixture was then heated to 60 °C in an oil bath for 3 h and cooled to room temperature in a water bath. Powder was obtained by drying the sol overnight in plastic petri dishes and grinding the resulting glass by ball milling. Powders of multiple synthesis batches were mixed to obtain one homogeneous stock for all experiments reported here. BTESE-derived films (50–55 nm) were prepared by mixing part of the sol for powder with 1-butanol in a 2:3 volume ratio and spin coating on silicon wafer substrates. The silicon substrates were cleaned with ethanol prior to coating. Each substrate was coated with 20 μL solution at a spinning

rate of 10,000 rpm for 10 s. The films were dried on a hot plate in air at 200 °C for 30 min. All samples were stored under ambient conditions.

2.3. Membrane preparation

Membranes with BTESE-derived top layers having effective pore sizes of either > 0.4 nm or ~0.3 nm were prepared as reported elsewhere [10]. Polished AKP30 α-alumina disks were obtained from Cobra Technologies BV and used as membrane supports. The supports were coated with a mesoporous γ-alumina layer and a BTESE-derived top layer, both applied under cleanroom 1000 conditions with a Velterop DA 3960/02 dip coater with a dipping speed of 1.4 cm s⁻¹. The preparation of the mesoporous γ-alumina coating was derived from the method described by Uhlhorn et al. [17]. 2.25 g PVA was added to 75 g 0.05 M aqueous HNO₃ solution and the mixture was heated under stirring to 80 °C for 2 h. 20 mL of the resulting PVA solution was filtered with a 0.8 μm filter and added to 30 mL 0.8 μm filtered boehmite sol prepared according to Uhlhorn et al. [17], followed by stirring and coating. The mesoporous γ-alumina layers were calcined at 650 °C in air for 3 h with heating and cooling rates of 1 °C min⁻¹. BTESE-derived top layers with > 0.4 nm pores were made with the sol recipe for powders. BTESE-derived top layers with ~0.3 nm pores were made as reported by Castricum et al. [6] with a sol of 35 mL dry ethanol, 2.91 mL demi water, 0.614 mL aqueous HNO₃ (65 wt%) and 11.0 mL BTESE prepared under otherwise identical conditions. Both sols were diluted with dry ethanol in a 1:1 volume ratio and filtered with a 0.2 μm filter before coating. The BTESE-derived top layers were cured at 300 °C in N₂ for 24 h with heating and cooling rates of 5 °C min⁻¹. All membranes were stored under ambient conditions.

2.4. X-ray reflectivity

Thickness measurements of films at 300 °C were done with X-ray reflectivity (XRR) on a PANalytical X'Pert PRO system equipped with an Empyrean tube with Cu anode, a parabolic W/Si mirror, an Anton Paar Domed Hot Stage 900 and a proportional Xe point detector. The films were kept under N₂ flow and were heated to 300 °C for varying periods of time with heating and cooling rates of 60 °C min⁻¹. Reflectivity curves were measured in-situ every 10 min. Thickness measurements of films at room temperature were done on a PANalytical X'Pert PRO system equipped with an Empyrean tube with Cu anode, a parallel beam mirror and a PIXcel^{1D} detector. Thickness values were obtained

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