



Nano-templates to fabricate highly porous organosilica membranes by atmospheric-pressure plasma surface modification

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Abstract

Organosilica membranes have excellent chemical and mechanical stability and are expected to be applied to a variety of processes ranging from gas to liquid-phase separations [1]. Organosilica membranes exhibit high permselectivity with the H₂ permeance of 2-8×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ and the H₂/SF₆ permeance ratio of 1000-25000 by forming a thin separation layer of less than a hundred nanometer [2]. On the other hand, zeolite membranes, one of the most representative inorganic membranes, have a thickness from several sub-micrometer to micrometer order but still exhibit molecular sieving properties and high permeance with the H₂ permeance of 0.2-2×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ [3]. In general, low porosity would be one of the factors contributing to the small permeability of amorphous silica membranes, and control of the porous structure is required to achieve higher permselectivity of organosilica membranes. Atmospheric-pressure plasma would have great potential to engineer the membrane structure because of its high activity at room temperature and ambient pressure, which enables to modify large membrane areas continuously. In order to improve the permeation properties, we employed the atmospheric-pressure plasma surface modification techniques to control the porous structure of the organosilica membranes. Specifically, as shown in Fig. 1, we used organosilica precursors with side chain groups as nano-templates and aimed to control the porous structure by the decomposition of the nano-templates by plasma irradiation.

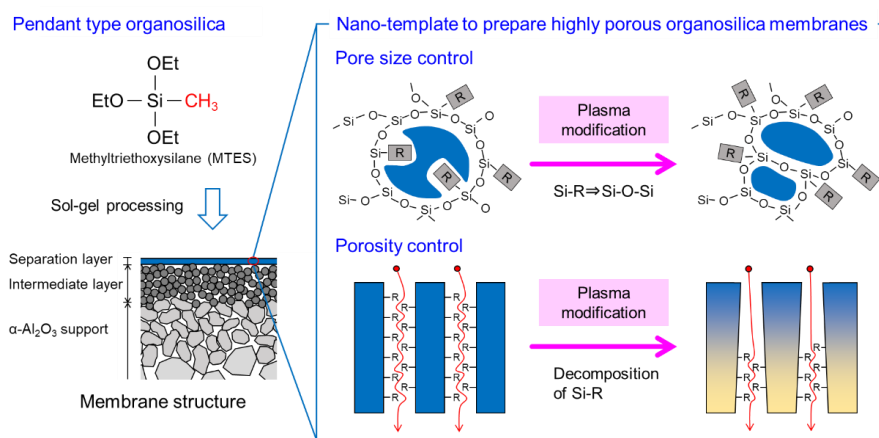


Fig. 1. Conceptual illustration of this study to develop highly porous organosilica membranes by a nano-template method.

Organosilica sol was obtained by mixing the MTES monomer with EtOH, H₂O, and HCl (MTES: H₂O: HCl = 1: 30: 0.01, monomer concentration: 5 wt%) to proceed a hydrolytic condensation polymerization reaction at 50°C for 1 h. The SiO₂-ZrO₂ layer was formed on the $\alpha\text{-Al}_2\text{O}_3$ support as an intermediate layer, and the organosilica membrane was obtained by coating the organosilica sol onto the SiO₂-ZrO₂ intermediate layer and firing at 300°C under N₂ atmosphere. The surface of the organosilica membrane was then modified by irradiating the surface with atmospheric-pressure plasma for a predetermined time [4,5].

Fig. 2.(a) shows the molecular size dependence of gas permeance of the MTES-derived membranes before and after plasma modification [4]. The permeance of small molecules such as H₂ and He was only slightly reduced by the plasma modification, while the permeance of medium-sized molecules such as N₂ and CH₄ was significantly reduced. Fig. 2 (b) shows the depth profile of the O/Si atomic ratio measured by XPS [4]. That of the pristine sample was at the stoichiometric ratio assumed from the MTES precursor, whereas that of the plasma-modified sample increased near the surface. This indicates that the membrane surface was oxidized. The above results suggest that the oxidation of the membrane surface and the change to a silica-like structure improved the molecular sieving property.

Table 1 summarizes the H₂ and N₂ permeances, the H₂/N₂ permeance ratio, the pore size determined by the modified GT model [6], and the activation energy of H₂ determined by the modified GT model for the TEOS-derived [7,8] and the MTES-derived membranes before and after plasma modification [4]. The H₂ permeance was only slightly



reduced while the N₂ permeance was significantly reduced by the plasma modification, resulting in the improved H₂/N₂ permeance ratio of 124 which is comparable to that of the TEOS membrane. As described above, this is due to the oxidation of the membrane surface into a silica-like structure. The activation energy of H₂ for the MTES-derived membranes increased from 6.2 to 9.8 by the plasma modification, but that of the plasma-modified MTES-derived membrane was smaller compared to that of TEOS-derived membranes. The gas separation property was improved while the increase in activation energy of H₂ was moderate, indicating that the porosity was increased due to the decomposition of the side chain methyl groups that hinder the H₂ permeation although the pore size was reduced.

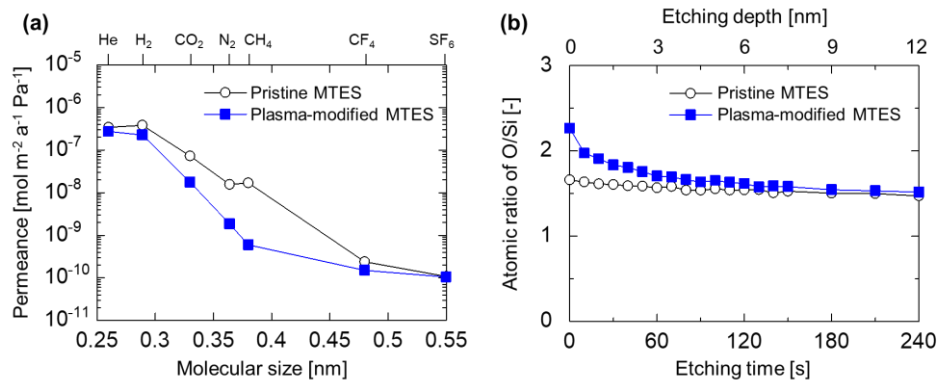


Fig. 2. (a) Molecular size dependence of single gas permeance at 200°C for the MTES-derived membranes before and after plasma modification [4]. (b) Atomic ratio determined by XPS for the MTES-derived films before and after plasma modification as a function of etching time [4].

Table 1. Comparison of membrane properties for the MTES-derived membranes and TEOS-derived membranes.

Membranes	H ₂ permeance [mol m ⁻² s ⁻¹ Pa ⁻¹]	N ₂ permeance [mol m ⁻² s ⁻¹ Pa ⁻¹]	H ₂ /N ₂ [-]	Pore size [nm]	E _p (H ₂) [kJ mol ⁻¹]	Ref.
Pristine MTES	3.8×10 ⁻⁷	1.6×10 ⁻⁸	25	0.45	6.2	[4]
Plasma-modified MTES	2.3×10 ⁻⁷	1.8×10 ⁻⁹	124	0.40	9.8	[4]
TEOS	3.1×10 ⁻⁷	7.1×10 ⁻¹⁰	432	0.38	14.1	[7]
TEOS	3.9×10 ⁻⁸	1.6×10 ⁻¹⁰	248	0.39	23.1	[7]
TEOS	1.2×10 ⁻⁸	1.2×10 ⁻¹⁰	103	0.40	14.5	[8]

We successfully fabricated highly porous organosilica membranes with high permselectivity by using side chain groups of the organosilica structure as nano-templates which were decomposed by the atmospheric-pressure plasma surface modification. This membrane fabrication method by atmospheric-pressure plasma would provide a new perspective to control the porosity of the membranes.

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