



Templated nanostructure silica membrane versus template-free one: Synthesis, characterization, and performance for hydrogen separation

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Abstract. An experimental study was carried out to investigate synthesis and performance of the MTES (methyltriethoxysilane) templated and template-free nanostructure silica membranes for hydrogen separation. The permeance of hydrogen, carbon dioxide, and nitrogen pure gases and permselectivity and separation factor of gas mixtures were investigated at 25°C, 100°C, and 200°C. Activated molecular sieve with positive and negative signs and Knudsen diffusion were respectively the dominant transport mechanisms in hydrogen, carbon dioxide, and nitrogen gas molecules permeances. Although the hydrophobic property of templated membrane is a good option for gas separation in hydrothermal conditions, the dense structure of the membrane results in lower permeance and permselectivity in comparison with template-free one. Hydrogen permeance at 200°C and 3 bar, which was measured as $30.5 \times 10^{-8} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$ for template-free silica membrane, decreased to $2.37 \times 10^{-8} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$ for MTES templated silica membrane. Permselectivity and separation factor of H_2/N_2 in the same conditions, which were respectively measured as 31.2 and 21 for template-free membrane, reached 21.5 and 8 for templated membrane. In addition, H_2/CO_2 permselectivity in the same conditions was measured as 23.4 and 13.9 for template-free and templated membranes, respectively.

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1. Introduction

Hydrogen plays a very important role in manufacturing a wide range of products in large-scale processes of the chemical, petrochemical, pharmaceutical, metallurgical, and textile industries [1]. The application of hydrogen as an energy source could address issues relating to global climate change, energy security, and

local air pollution [2]. The hydrogen has also attracted increasing interest as clean energy for fuel cell power generation. These potential uses have resulted in an enormous increase in hydrogen demand. Hydrogen can be economically produced by steam reforming in which the process runs at rather high temperatures to obtain maximum efficiency out of the equilibrium-limited reaction [3]. There are many byproducts associated with hydrogen production. For example, in the water-gas shift reaction, high-purity hydrogen is obtained by separating it from its mixture with carbon dioxide.

There are major advantages for gas separation at higher temperatures to avoid energy penalties as-

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sociated with cooling down gases. Therefore, high-temperature gas separation can be attained by employing inorganic membranes derived from ceramics and metal alloys. The dense metal membranes based on Pd-alloys are expensive and cannot be fabricated on a large scale; they are susceptible to poisoning by sulfur, which is usually present in feedstocks derived from natural gas or coal. In addition, in the presence of hydrogen, at temperatures below 300°C, two distinct hydride phases are formed in the palladium structure, and the associated volume change deteriorates the mechanical properties of these membranes [4]. In contrast, the porous silica membranes with tunable pore sizes can be processed by a simple dip-coating procedure and used potentially in a large variety of gas separations [5]. In the silica membranes, the transport mechanism is regimented by molecular sieve properties [6,7], in which hydrogen exhibits temperature-activated transport, while carbon dioxide shows the opposite trend [8,9]. This behavior forms part of an important engineering property, as the hydrogen permeation and H_2/CO_2 selectivity increase with temperature [10]. This advantage features the use of silica membranes for hydrogen purification in thermochemical processes such as steam reforming [11,12].

However, microporous silica membranes suffer from water sorption due to the interaction between water molecule and hydroxyl surface groups of silica membranes that causes changes in pore structure. Then, the silica membranes developed by several researchers showed the loss of permeability and selectivity upon exposure to moisture [13]. This behavior has been attributed to the removal of Si-OH groups, leading to the formation of Si-O-Si bonds that close pore channels [14]. This phenomenon, called densification, is catalyzed by moisture at high temperatures. To solve this problem, researchers have attempted to modify the silica network [15–18] or its functional groups [19–22] to minimize the interaction of water molecules with the membrane structure. An attractive strategy for achieving stable silica membranes in hydrothermal conditions is incorporation of the hydrophobic terminal methyl groups ($\equiv Si-CH_3$) via various precursors used during the sol-gel synthesis. In our previous work, the synthesis method of MTES templated silica membrane, strategy for surface modification of silica layer, and the influence of surface modification method on the membrane performance were investigated [23]. As presented in the literatures [24–28], compared to template-free silica membranes, templating the silica membranes results in low H_2/CO_2 selectivity and/or low permeability at high temperatures. Despite high hydrothermal stability of templated silica membranes and preference for a suitable silica membrane (templated and/or template free) for hydrogen separation at high temperatures, both of the membranes and

their performance in the same conditions deserve much research.

Therefore, this study aims to compare the identical performance of the synthesized MTES templated and template-free silica membranes. For this purpose, synthesis of both template-free and templated silica membranes with MTES is carried out. The characterization and performance of both synthesized membranes in hydrogen permeation and its separation from carbon dioxide and nitrogen are evaluated to distinguish the capability of the templated silica membrane in comparison to that of template-free one.

2. Experimental procedure

2.1. Materials

The chemicals used were obtained from the following sources: tetraethylorthosilicate (TEOS, 98%, Acros) was used as a silicon source. Methyltriethoxysilane (MTES, 99%, Aldrich) was used as template. Nitric acid (HNO_3 , 65%, Merck), ethanol (EtOH, 99.9% Merck), hydrochloric acid (HCl, Merck), and polyethylene glycol (PEG, Merck, Molecular weight: 6000) were used in sols preparation. Aluminum-tri-sec-butylate (97%, Merck) was used in intermediate layer synthesis. All chemicals were used as received without further purification.

2.2. Membrane supports

The home-made supports used for membrane synthesis were porous α -alumina tubes with thickness of 4 mm, diameter of 13 mm, length of 70 mm, average pore size of 0.57 μm , and average porosity of 47.2%. The synthesis method of the supports was gel casting and explained elsewhere [29–31]. The supports were first cleaned in distilled water by ultrasonic bath for 10 min and, then, dried at 40°C for 12 h.

2.3. γ -alumina sublayer preparation

γ - Al_2O_3 intermediate layer was prepared by dip-coating the α -alumina supports in a boehmite (γ - Al_2O_3) sol followed by drying and calcination steps. Boehmite sol was prepared by adding drop-wise aluminum-tri-sec-butylate to distilled water at 80°C, while the stirring was carried out at high speeds. A white solution was obtained, which was peptized with HNO_3 . Additional information about sol preparation has been presented in our previous work [32]. PEG solution was made by dissolving PEG (1 wt.% of sol) in distilled water under vigorous stirring and, then, was added to sol. Nitric acid was added to adjust pH and, then, sol was refluxed for 16 h to form a stable boehmite sol. The dip-coating process was performed at room temperature. The substrate speed and the dip time were 1 $mm s^{-1}$ and 10 s, respectively. After dipping, the membranes were dried in a climate chamber at 40°C for at least 24 h to avoid any crack

formation in the boehmite layer. The γ - Al_2O_3 layer was formed by subsequent calcination at 700°C for 3 h in air with a heating and cooling rate of $0.5^\circ\text{C}/\text{min}$. The whole process of dipping, drying, and calcination was repeated 4 times in order to obtain defect-free intermediate γ - Al_2O_3 layer.

2.4. Template-free silica sol and membrane layer formation

The microporous silica membrane top-layer was prepared by dipping the γ - Al_2O_3 mesoporous substrates in a polymeric silica dip solution, followed by calcining (Figure 1). Polymeric silica sols were prepared by acid catalyzed hydrolysis and condensation of tetraethylorthosilicate in ethanol. A mixture of acid and water was carefully added to a mixture of TEOS and ethanol under vigorous stirring, while, during the addition of the acid/water mixture, the TEOS/ethanol mixture was placed in an ice-bath to avoid partial hydrolysis [8]. After completing the addition, the reaction

mixture was refluxed for 3 h at 60°C in a silicon oil bath under constant stirring. The reaction mixture had final TEOS/ethanol/water/acid molar ratios of 1/3.8/6.4/0.085 [6,8]. The reacted mixture was cooled and diluted 19 times with ethanol to obtain the final dip solution [8]. The γ - Al_2O_3 substrate was coated with the final solution. The coating speed and the dip time were 1 mm s^{-1} and 10 s, respectively. After dipping, the membrane was calcined at 600°C for 3 h in air with a heating and cooling rate of $1^\circ\text{C}/\text{min}$. The whole process of dipping and calcining was repeated 5 times to repair any defects in a silica membrane layer.

2.5. Templated silica sol and membrane layer formation

The microporous templated silica membrane top-layer was prepared by dipping the γ - Al_2O_3 mesoporous substrates in a templated silica dip solution, followed by calcining and modifying (Figure 2). Sols were prepared by co-polymerization of MTES and TEOS

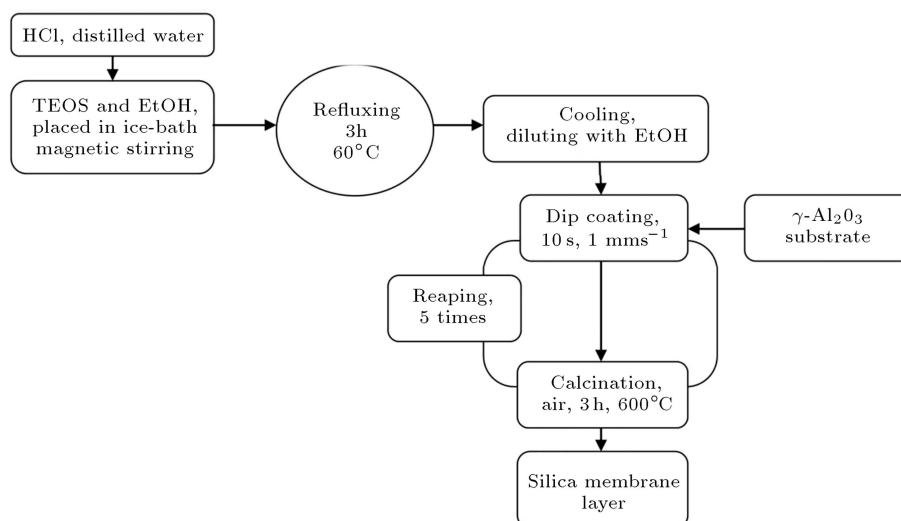


Figure 1. Schematic diagram of the synthesis procedure of template-free silica membrane layer.

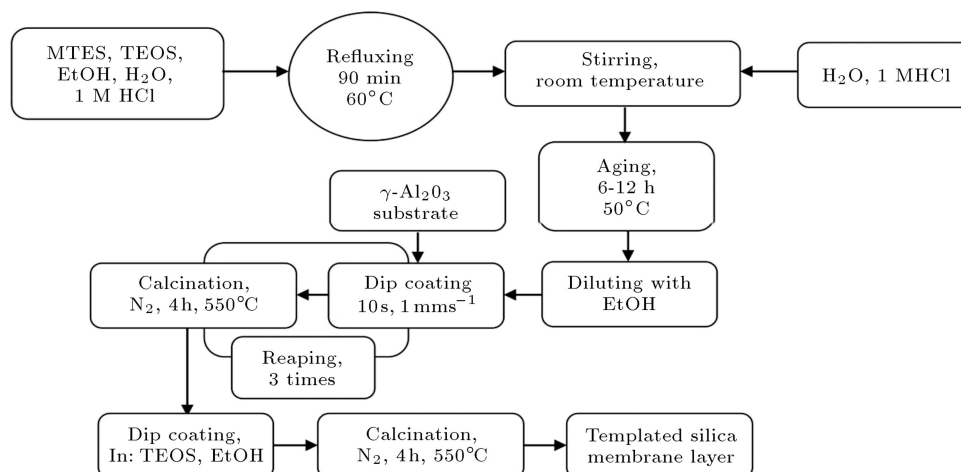


Figure 2. Schematic diagram of the synthesis procedure of templated silica membrane layer.

in a two-step acid-catalyzed process using a recipe of silica sol preparation, as defined in [33,34]. In the first step, MTES, TEOS, EtOH, H₂O, and 1 M HCl with a molar ratio of 0.1: 0.9: 3.8: 1.1: 7.0×10^{-4} were refluxed at 60°C for 90 min under vigorous stirring. In the second step, additional water and 1 M HCl were added at room temperature, resulting in the final molar ratio of 0.1: 0.9: 3.8: 5.1: 0.056. The sol was aged at 50°C for 6–18 h and diluted 1:2 (volume sol:volume EtOH) with ethanol to obtain a sol suitable for coating. The γ -Al₂O₃ substrate was dip coated with the final solution. After dipping, the membrane was calcined at 550°C for 4 h in nitrogen atmosphere with a heating and cooling rate of 1°C/min. The whole process of dipping and calcination was repeated three times. In order to control the pore sizes of templated silica membrane and its modification, the solution of TEOS: EtOH with a volume ratio of 1:12 was used. The dip-coating procedure and the calcination treatment were very similar to that used for the membrane layer. The strategy for surface modification of silica layer was detailed elsewhere [23].

2.6. Gas permeation measurements

The gas permeation properties of the support, γ -alumina intermediate layer, and templated and template-free silica membranes were determined with the experimental setup, as shown in Figure 3. The permeation tests were carried out using a custom-made stainless steel module, designed for 70 mm tubular membranes. The membrane ends were sealed in the module using viton O-rings, which allow measuring at temperatures up to 200°C. Pure gases (hydrogen, nitrogen, and carbon dioxide) and binary gas mixture (H₂/N₂) were fed to the outside (upstream) of the tubular membrane in the range of 0.5 to 4 bar over ambient pressure. The downstream pressure was kept constant at the atmospheric pressure, and the permeation rate was measured by a soap bubble flow meter.

The temperature of the permeance measurement cell was kept constant at specified temperatures of 25°C, 100°C, and 200°C.

The separation factor (α) for a binary gas mixture (A, B) was calculated from the gas concentrations on retentate (x) and permeate (y) sides according to:

$$\alpha_{A/B} = \frac{y_A}{y_B} \cdot \frac{x_B}{x_A} \quad (1)$$

The mole fractions of permeate and retentate sides were measured using Teif Gostar Co. gas chromatograph (Cat. No. TR-110222, Serial No.: p2085307, TRB-1, Tecknokroma, l:25 m, ID:0.25). In addition, the permselectivity (F_α) was obtained by the ratio of gases permeances.

3. Results and discussion

3.1. Characterization

Porous α -alumina tubes were used as supports for the silica membranes. Cross-section and surface images of the support are shown in Figure 4(a) and (b), respectively. As can be seen, a macroporous structure with a very rough surface was observed. First, the support with γ -alumina layer was modified in order to reduce pore size and surface roughness of the support. Figure 4(c) and (d) show FE-SEM images of the support modified by γ -alumina. As is clear, surface roughness of the support was significantly reduced on a nanometric scale. In addition, the nitrogen permeance of the support and modified support is shown in Figure 5. The nitrogen permeance of the support increased significantly with the mean pressure difference, confirming that there is a viscous flow contribution to the total flow through the support; then, the support is too porous to obtain a suitable silica top-layer. Following the modification of support with γ -alumina layer, nitrogen permeance was nearly constant with increasing mean pressure. It means that the contribution of Knudsen

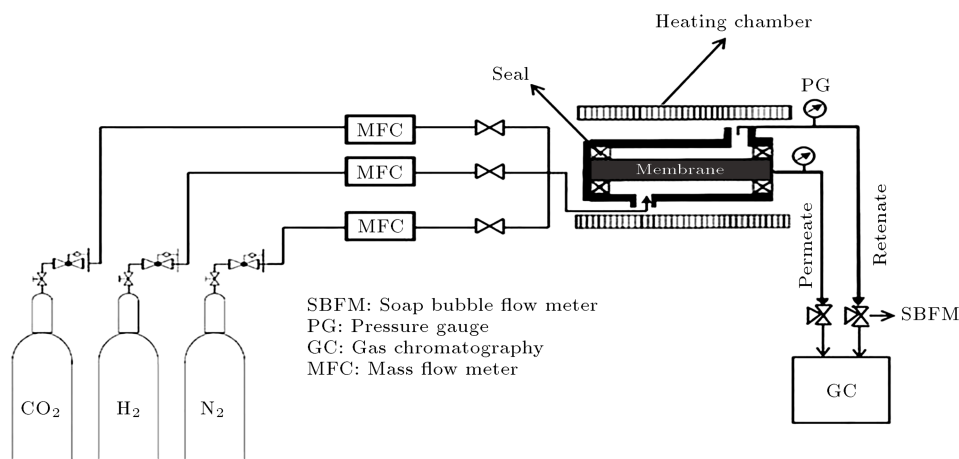


Figure 3. Schematic diagram of experimental setup for gas permeation measurement.

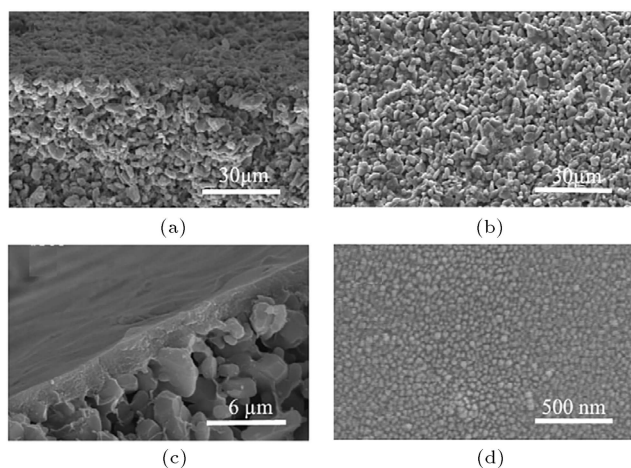


Figure 4. FE-SEM images of (a) cross-section and (b) surface of support, (c) cross-section, and (d) surface of γ -alumina layer.

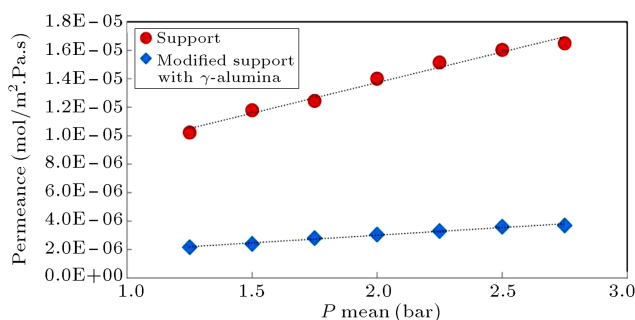


Figure 5. N₂ permeance of support and γ -alumina layer.

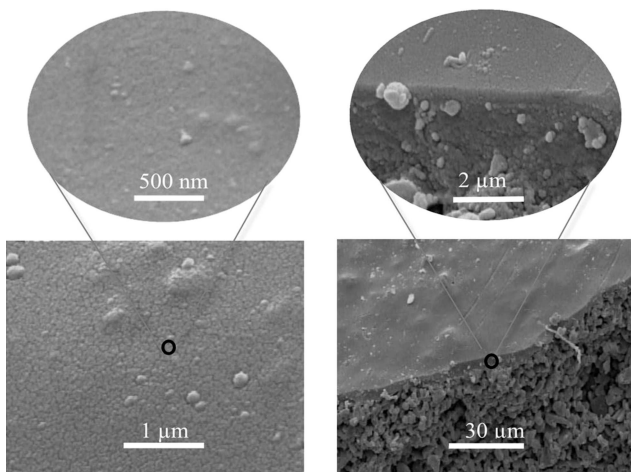


Figure 6. FE-SEM images of template-free silica top-layer on the modified support with γ -alumina layer.

diffusion increased by modifying the support with γ -alumina layer, which is suitable for preparing stable silica top-layers. Similar results of reducing pore size and shifting N₂ gas permeance regime toward Knudsen diffusion were reported earlier in support modification of silica membrane for hydrogen purification [35].

Figures 6 and 7 show FE-SEM images of the silica

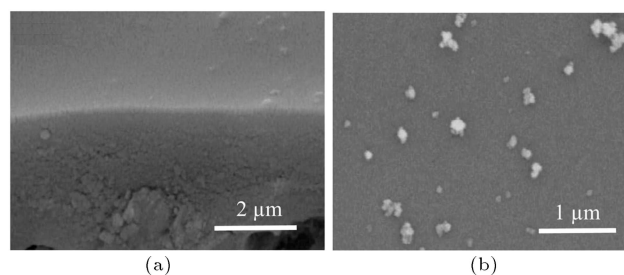


Figure 7. FE-SEM images of (a) cross-section and (b) top-layer of templated silica on the modified support with γ -alumina layer.

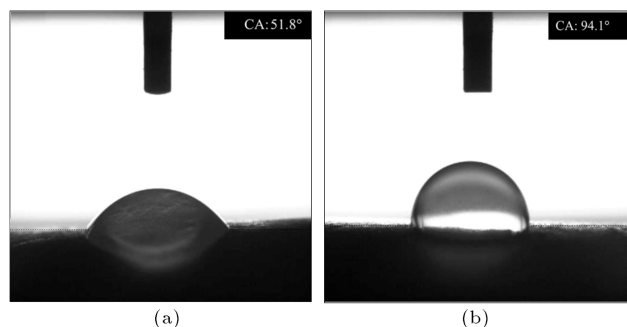


Figure 8. Water droplet images on (a) template-free and (b) templated silica membrane.

membranes prepared with template-free and templated silica sols on the modified support, respectively. The final top-layer of the silica membranes has been prepared by repeating the whole dipping-drying-calcination process to reach a uniform structure in the final membrane.

The contact angle is an important parameter for measuring surface hydrophobicity of membranes. In general, the highly hydrophobic surface shows larger contact angle with the surface, and vice versa. Figure 8 represents images of water droplets on the membrane surfaces in which the Contact Angle (CA) is measured according to the sessile drop method by the software. It is obvious from the figure that the MTES templated membrane shows more hydrophobicity than template-free one, which is favorable for separation in the hydrothermal condition.

3.2. Pure gases permeances

To understand the gas transport mechanisms in more detail, the temperature dependency of pure gas permeances on the silica membranes in the temperature range of 25–200°C was studied. As shown in Figure 9, the permeance of hydrogen through the templated and template-free membranes increased with increasing temperature, while the reverse trend was observed for carbon dioxide and nitrogen.

The transport in silica membranes occurs through the network of connected micropores due to a gradient of chemical potential of species in the gas phase [36]. The separation is mainly based on a

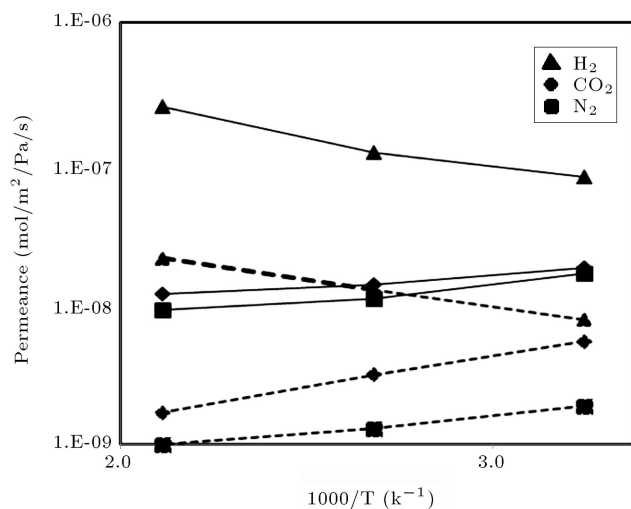


Figure 9. Pure gas permeances for the template-free (—) and templated (...) silica membranes at $P = 3$ bar.

sieving effect through ultramicropores, and a favorable combination of sorption selectivity (interactions gas molecules/membrane surface) and diffusion mobility (rate of gas passage through the membrane) produces reasonably high values for flux and selectivity [37]. Uhlhorn et al. [38] presented a qualitative model for transport of molecules through very small pores. In this model, in pores with molecular dimensions, the gas molecule and specific molecule-wall interactions can lead to distinct differences in potential energy barrier and, therefore, in the transport rate. In this way, it is possible to make a pore effectively impermeable to a molecule, even if the size of the molecule permits its entrance in the pore.

The activation energy (E_a) of molecules permeation was obtained by regressing equation (Eq. (2)) [39] to the experimental single gas permeation data.

$$P = \sqrt{\frac{K_0}{MRT}} \exp\left(\frac{-E_a}{RT}\right), \quad (2)$$

where K_0 is the characteristic constant of the microporous membrane, M is the molecular weight of permeating gas, R is the gas constant, and T is the temperature. E_a is the sum of two contributions: the heat of sorption of the molecule and the positive activation energy of mobility of the permeating molecule inside the membrane matrix [40]. Since these two terms have opposite signs, the apparent activation energy can be positive or negative depending on their relative magnitudes [40]. A negative value of E_a is generally caused by strong adsorption of the molecule on the pore surface. The corresponding apparent activation energies are listed in Table 1. The apparent activation energy is positive and negative for hydrogen and carbon dioxide permeances, respectively, for both samples. This is due to the heat of sorption of carbon

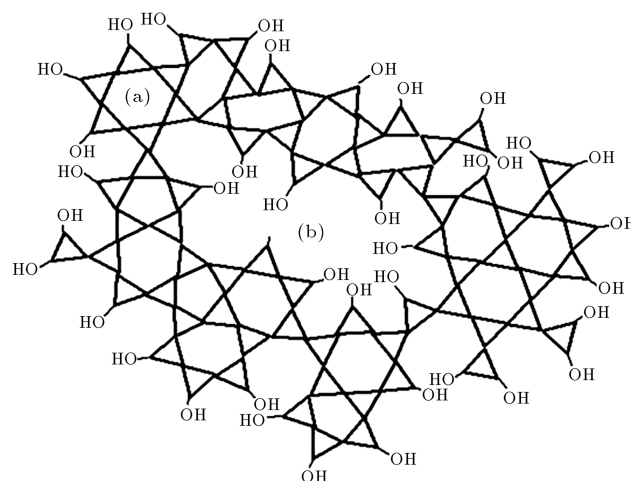


Figure 10. Schematic representation of the gas transport sites in amorphous silica membranes: $R = \text{OH}$ for template-free membrane and $= \text{CH}_3/\text{OH}$ in templated membrane.

Table 1. Apparent activation energies of hydrogen and carbon dioxide permeances in templated and template-free silica membranes, as calculated by fitting the data in Figure 9 to Eq. (2).

Gas	E_a (kJ/mol) template-free membrane	E_a (kJ/mol) templated membrane
H ₂	8.6	7.5
CO ₂	-3.2	-8.7
N ₂	-4.5	-4.7

dioxide molecules on the walls of the silica micropores. The obtained results confirmed that the application of template in the silica membrane synthesis led to more negative activation energy and, thus, higher carbon dioxide adsorption on the silica pores.

Nitrogen permeance decreases with increasing temperature and leads to negative activation energies. This is due to the presence of larger pores in the silica thin film, whose Knudsen transport of the nitrogen takes place. The temperature increase leads to a decrease in Knudsen diffusion transport and, thus, a decrease in nitrogen permeance. A bi-modal structure is proposed in [41] for silica membranes, in which small gas molecules (hydrogen and helium) are mainly transported through siloxane rings (containing at least six Si atoms shown in Figure 10(a)), while nitrogen transport should occur only through the silica cluster pores (Figure 10(b)).

Figure 11 details the results of hydrogen, carbon dioxide, and nitrogen permeation tests of templated and template-free nanostructure silica membranes. The comparison of the gas permeation results is in agreement with the molecular sieve model $P_{\text{H}_2} > P_{\text{CO}_2} > P_{\text{N}_2}$ for each of the membranes, separately.

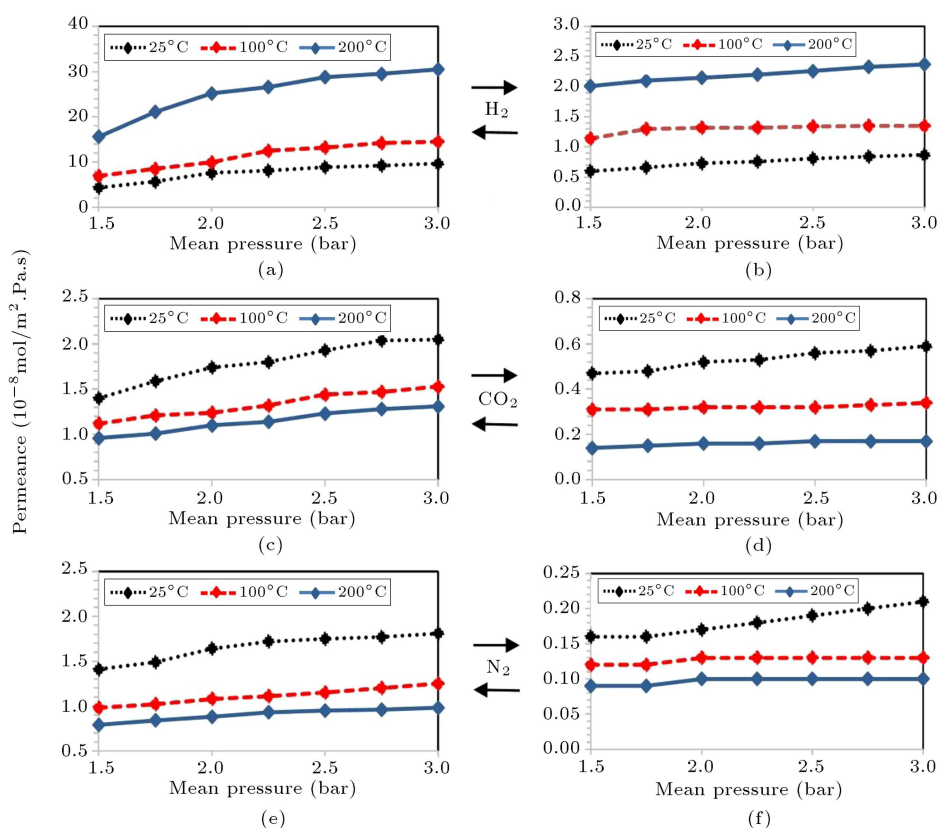


Figure 11. Gas permeances of template-free (left hand) and templated (right-hand) nanostructured silica membranes.

Since the temperature dependency of gas permeation rates is detailed in the previous section, hydrogen permeance in the membranes (Figure 11(a) and (b)) increases noticeably with temperature. These results show that hydrogen passes through membranes with an activated molecular sieve mechanism. This is one of the most important advantages of silica membrane for hydrogen separation at high temperatures. Besides, the decrease of carbon dioxide and nitrogen permeances with temperature (Figure 11(c), (d), (e) and (f)) approved the use of silica membranes for the separation of hydrogen from these gas mixtures.

The comparison of each gas permeance in the membranes separately shows that the gas permeation rates of templated membrane are lower than those of template-free one. Figure 12 shows these differences at 25°C for all gases permeances. Totally, the decreases result from the dense structure of the templated membrane compared to template-free one, which is in agreement with FE-SEM images shown in Figures 6 and 7. Surface modification of the templated membrane with ethanol: TEOS solution results in a denser structure. By applying the surface modification procedures, TEOS molecules are hydrolyzed to $-\text{Si}(\text{OH})_x$ and penetrated the large pores; then, permeance of all gases decreases. Among these gases, carbon dioxide gas permeance decreases less than other gases

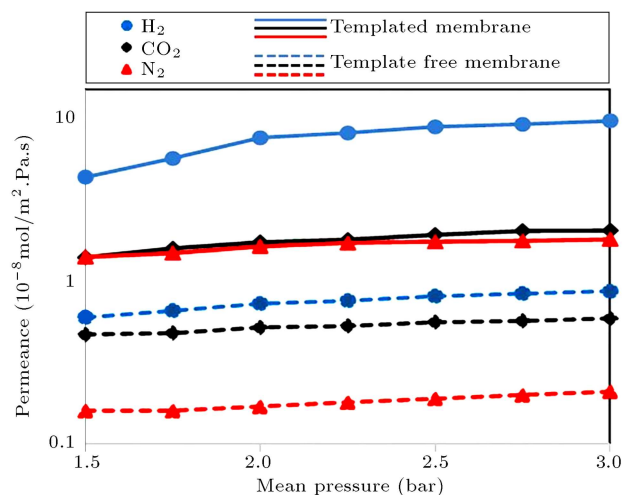


Figure 12. Gas permeances at 25°C in templated and template-free nanostructured silica membranes.

due to the sorption of carbon dioxide on the templated membrane surface, which is stronger at low temperatures and causes strong surface diffusion.

3.3. Gas mixtures separation

Permselectivities and gas separation results of template-free and templated membranes are given in Figure 13. The separation factor was measured for a feed with the same molar compositions of hydrogen

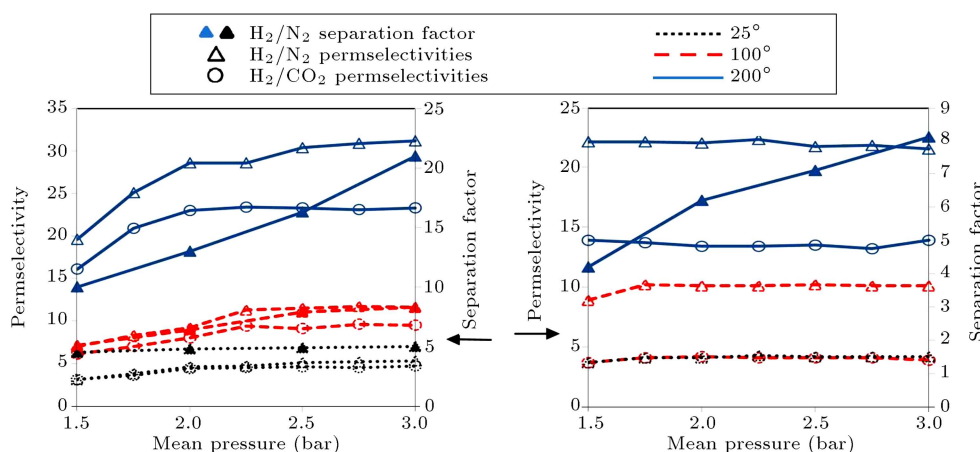


Figure 13. Gas separation results of template-free (left hand) and templated (right hand) nanostructured silica membranes.

and nitrogen (or carbon dioxide). As can be seen, H_2/N_2 and H_2/CO_2 permselectivities increase with temperature. This is because H_2 molecular movements are activated with temperature, and carbon dioxide and nitrogen permeances decrease with temperature too; this supports an additional degree of an increase in permselectivity with increasing temperature. The trends of separation factors are similar to those of the permselectivities. The fact is that the gas separation factors are lower than the permselectivities of the single gas measurements for the interactions of the components. The permselectivity and separation factor also increased slightly with pressure at a fixed temperature. Accordingly, permselectivity and separation factor of H_2/N_2 at 200°C and 3 bar reached 31.2 and 21 for template-free membrane and 21.5 and 8 for templated membranes. Permselectivity in the mentioned conditions for H_2/CO_2 reached 23.4 and 13.9 for the template-free and templated membranes, respectively. An extent value for sol-gel silica membrane is reported in literatures for these separations. However, an attempt was made in this study to compare the performances of templated and template-free nanostructure silica membranes synthesized on γ -alumina layer in the same conditions. As explained in the previous section, single gas permeation rates in the templated membrane are lower than those in the template-free one. In addition, the separation factors and permselectivities are smaller than those in the templated membrane. Template makes pore size larger, compared with template-free membranes. However, the modification of the surface with ethanol:TEOS solution made the pores smaller. This trend resulted in lower permeance and, also, lower increasing permeance of hydrogen at higher temperatures and lower selectivities. However, due to the domination of the surface diffusion mechanism of carbon dioxide permeance and its strong sorption on templated silica membrane surface, CO_2/N_2 permselectivities for this membrane are higher

than those for template-free one. Then, this membrane can be useful for carbon dioxide separation from gas mixtures. Similar behavior was reported earlier [27] for carbon dioxide separations by templated membrane. It can be concluded that the performance of the template-free silica membrane is more approvable for hydrogen separation, while the templated silica membrane has hydrophobicity option. Then, for a good selection, all aspects should be considered.

As presented in Table 2, the performance of synthesized silica membranes at the mentioned temperatures was compared with those reported in similar research results. The structure of these membranes is the closest structure to those of the synthesized templated and template-free membranes. According to the results, it is found that the synthesized membranes have appropriate performance in hydrogen separation.

4. Conclusions

Templated and template-free nanostructure microporous silica membranes were synthesized by the sol-gel method using TEOS as a precursor and MTES as a template on the modified alumina supports. As reported, the application of MTES with hydrophobic terminal methyl groups ($\equiv\text{Si-CH}_3$) makes the templated membrane hydrophobic. Activated molecular sieving is the dominant mechanism for H_2 and CO_2 molecules permeance; besides, N_2 crosses the membrane with Knudsen diffusion in the synthesized membrane. Hydrogen permeance increases with temperature and has positive activation energy, while carbon dioxide and nitrogen permeances have opposite trends and negative activation energies, causing an increase in H_2/CO_2 and H_2/N_2 permselectivities with increasing temperature and justifying the use of the membranes in hydrogen separation at high temperatures. Meanwhile, it appears that the hydrophobic property of the templated membrane idealizes its utility in hydrothermal condi-

Table 2. H₂ permeances and permselectivities of silica membranes.

Membrane	H ₂ Permeance (mol/m ² s Pa)	Permselectivity	T (°C)	References
Silica (sol-gel, si(400))	17.4×10^{-7}	7.5 (H ₂ /CO ₂) 64 (H ₂ /N ₂)	200	[8]
Silica (sol-gel, si(400))	11.6×10^{-7}	4 (H ₂ /CO ₂) 61 (H ₂ /N ₂)	100	[8]
Silica (sol-gel, MTES templated)	22.3×10^{-7}	5.5 (H ₂ /CO ₂) 8.3 (H ₂ /N ₂)	200	[21]
Silica (sol-gel, MTES templated)	6.62×10^{-9}	4.4 (H ₂ /CO ₂)	200	[27]
Silica (sol-gel, MTES templated)	–	4.45 (H ₂ /CO ₂)	200	[28]
Silica (sol-gel, MTES templated)	2.43×10^{-9}	6.45	200	–
	2.85×10^{-9}	51.05	200	–
	$2.07\text{--}3.37 \times 10^{-9}$	6–24	50–200	[27]
Silica (sol-gel)	0.57×10^{-7}	17 (H ₂ /N ₂)	220	[42]
Silica (sol-gel, copolymerization of TEOS and MOTMS)	4.04×10^{-7}	22 (H ₂ /CO ₂)	200	[43]
Silica (sol-gel, ECN)	13.5×10^{-7}	10.9 (H ₂ /CO ₂)	300	[44]
Silica (sol-gel, silica(625))	3×10^{-7}	21 (H ₂ /CO ₂)	600	[45]
Template-free silica	3.05×10^{-7}	23.4 (H ₂ /CO ₂) 31.2 (H ₂ /N ₂)	200	Present work
MTES templated silica	2.37×10^{-8}	13.9 (H ₂ /CO ₂) 21.5 (H ₂ /N ₂)	200	Present work

tions. However, the dense structure of the templated membrane decreased gas permeances and permselectivities, thus affecting its performances and confining its applications in hydrogen separation. Nevertheless, the strong sorption of carbon dioxide on templated silica membrane confirms the use of this membrane in carbon dioxide separation from gas mixtures, especially at lower temperatures.

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