

# Synthesis and Performance of Nanostructure Templated Silica Membranes Surface-modified by Two Different Procedures

F. Assa,<sup>a</sup> A. A. Babaluo,<sup>a,\*</sup> K. Ghasemzadeh,<sup>a</sup> M. A. Abdi,<sup>a</sup>  
D. Kahforoushan,<sup>b</sup> A. Jabbari,<sup>a</sup> and M. J. Vaezi<sup>a</sup>

<sup>a</sup>Nanostructure Material Research Center (NMRC),  
Chemical Engineering Faculty, Sahand University of Technology,  
Sahand New Town, Tabriz, Iran

<sup>b</sup>Environmental Engineering Research Center (EERC),  
Chemical Engineering Faculty, Sahand University of Technology,  
Sahand New Town, Tabriz, Iran

doi: 10.15255/CABEQ.2014.2071

Original scientific paper

Received: July 2, 2014

Accepted: September 3, 2015

In this study, the microporous silica membrane was prepared by the template assisted sol-gel method. The surface of the templated silica membranes was modified via two procedures; selective layer, and layer by layer surface modification. The obtained results confirmed that the surface modification procedure is very crucial to the final performance of the membrane. Thus, for the templated silica membrane modified by the first procedure, CO<sub>2</sub>/N<sub>2</sub> permselectivity was achieved at 3.0 and CO<sub>2</sub> permeance was 6.3×10<sup>-9</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>, while for the templated silica membrane modified by the second procedure, the CO<sub>2</sub>/N<sub>2</sub> permselectivity was achieved at 11.3 and CO<sub>2</sub> permeance was 4.0×10<sup>-8</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>, at room temperature.

## Key words:

gas separation, carbon dioxide, templated silica membrane, sol-gel method, surface modification

## Introduction

Uncontrolled population growth and increased consumption of fossil fuels have led to the emission of pollutants and greenhouse gases. This is mostly a concern for reducing emissions of greenhouse gases, such as carbon dioxide because of its impact on global climate change<sup>1,2</sup>. The presence of carbon dioxide in the natural gas mixture can lead to lower heating value of gas, corrosion of processing facilities and pipelines<sup>3-5</sup>. Thus, the separation of carbon dioxide from gas streams by a proper and highly efficient process is essential.

Membrane processes, owing to their various advantages, are the interest of researchers in the field of gas separation. Meanwhile, the use of inorganic membranes has increased because of their chemical resistance in high temperatures and corrosive environments, appropriate selectivity, abrasion resistance and stable pore structure in carbon dioxide separation from flue gas<sup>6-8</sup>.

The microporous silica membranes are the most important examples of non-crystalline or amorphous membranes<sup>9</sup>. These kinds of membranes

have a thin separator layer (about 50–200 nm) with the molecular sieve property, resulting in high permeate flux and selectivity. Therefore, in comparison with other inorganic membranes, they are utilized for separation of acid gases<sup>10</sup>.

The most common method to fabricate microporous silica membranes is the sol-gel method. The sol-gel method was firstly used by Leenaars *et al.*<sup>11</sup> Controlling the pore size of the membrane, especially the smaller pores, the porosity control, simplicity and homogeneity of the layer are the main advantages of the sol-gel method<sup>11,12</sup>. The silica membranes modified by metal oxides or hydrophobic silanes with respect to pure silica membranes, show high stability in the presence of hot steam<sup>13-15</sup>. Thus, displacement of hydroxyl groups (–OH) with hydrophobic groups (–CH<sub>3</sub>) with a hydrophobic methyl template is an easy strategy to reduce water absorption and maintain the microporous structure of silica membranes<sup>16</sup>. In this case, the micropores were produced by using the thermal degradation of organic ligands (templates), which are covalently bonded to the silica network. The silica membranes with methyl template had high separation rates, and change in the carbon dioxide permeance with time was less observed<sup>17</sup>. It is notable that micropores created in this way, have controlled size (depending

\*Corresponding author: e-mail: a.babaluo@sut.ac.ir (Ali Akbar Babaluo); tel. & Fax: +98-41-33458084; P.O.Box: 51335-1996

on the size and shape of the organic ligands), controlled volume (depending on the amount of added organic template) and narrow size distribution<sup>18–21</sup>.

Numerous studies have been conducted in the construction of high quality silica membranes with methyl templates such as methyltriethoxysilane (MTES)<sup>22–28</sup>. Raman and Brinker<sup>22</sup> synthesized silica membranes using MTES template, and also studied calcination time and temperature on the performance of membranes. De Vos *et al.*<sup>23</sup> compared the performance of non-templated and MTES-templated silica membranes. Silica membranes templated by MTES were synthesized by Lee *et al.*<sup>26</sup> and used for separating carbon dioxide from nitrogen. Moon *et al.*<sup>27,28</sup> fabricated silica membranes by MTES as a template and analyzed their performance in gas reforming processes.

Modification of the membrane surface can improve the membrane performance by changing the average pore sizes, and better interactions with the membrane surface and passing molecules<sup>29</sup>. In studies carried out by researchers, two most common types of surface modifications are discussed. Of the two procedures, the dipping method, due to the low cost and simplicity of operation, was chosen as an appropriate procedure to achieve optimal efficiency of the membranes. The membrane surface modification by the chemical vapor infiltration (CVI) method at low temperatures has been used by Koutsonikolas *et al.*<sup>30</sup> The surface modification of silica membranes by dipping in tetraethyl orthosilicate (TEOS): ethanol (EtOH) solution was presented in the work of Raman and Brinker<sup>22</sup>, Kusakabe *et al.*<sup>25</sup>, Lee *et al.*<sup>26</sup>, and Moon *et al.*<sup>27</sup> In all of these studies, the surface modification process resulted in improved membrane selectivity. In general, the surface modification procedures are vaguely explained in literature. In addition, no research has been conducted to compare the effect of different surface modification procedures on the final membrane performance.

Therefore, in this study, two templated silica membranes were synthesized while their surface modification procedures were carried out by two different methods: selective layer surface modification (M1 membrane), and layer by layer surface modification (M2 membrane). As a first approach, the main aim of this work was to compare two different surface modification procedures. Finally, the influence of the surface modification method on the synthesized membrane performance for carbon dioxide separation was investigated.

## Experimental

### Materials

The chemicals used in this research were obtained from the following sources: aluminium tri-sec-butylate 97 % ( $\text{Al}[\text{OCH}(\text{CH}_3)\text{C}_2\text{H}_5]_3$ , Merck) as an alkoxide agent, polyethylene glycol (PEG) 6000 ( $\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{H}$ , Merck) as a stabilizer, TEOS 99 % ( $\text{C}_2\text{H}_5\text{O})_4\text{Si}$ , Merck) as a silicon source, MTES 99 % ( $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ , Aldrich) as an organic template, EtOH 99.9 % ( $\text{C}_2\text{H}_6\text{O}$ , Merck) as a solvent, hydrochloric acid 32 % (HCl, Merck) and nitric acid with a purity of 65 % ( $\text{HNO}_3$ , Merck) were used for synthesizing the intermediate and selective top layers. Carbon dioxide (purity 99 %), nitrogen (purity 99.9 %) and hydrogen (purity 99.99 %) were used in the gas permeance measurement experiments. Furthermore, argon (purity 99.99 %) was used as a sweep gas flow.

### Synthesis of the supports and intermediate layers

The porous  $\alpha$ -alumina tubular membrane supports (diameter, length and thickness were 12, 70 and 3.2 mm, respectively) were prepared by the gel casting method<sup>31–33</sup>. Before synthesis of the silica membrane layers, surface modification was necessary to reduce the support's pore size to 5–10 nm due to the silica layer formation<sup>34</sup>. For the boehmite sol preparation, aluminum tri-sec-butylate was added to deionized water dropwise at 80 °C, while the stirring was carried out at high speeds. In this procedure, per each mole of alkoxide, 2 liters of deionized water were used. The solution was stirred vigorously at 90 °C for 30–60 minutes after the addition of alkoxide (for peptizing the boehmite sol particles). The nitric acid (0.07 mol/1 mol alkoxide) was added to the prepared mixture. The resulting colloidal sol was kept in stirring and boiling situation at 80 °C to evaporate the large amounts of butanol. To prepare the PEG solution, an amount of 1 wt% of PEG6000 was dissolved in deionized water and added to the stirring sol. Thereupon, the resulting sol was under reflux for 16 h (to compensate evaporated water). The pH of the final sol was in the range of 3–4. The prepared sol was kept at 80 °C and reflux conditions for 16 h<sup>11</sup>.

### Synthesis of the selective templated silica layers

To synthesize the templated silica sol, 1.72 mL MTES, 17.36 mL TEOS, 19.2 mL EtOH, 1.72 mL deionized water, and 0.002 mL HCl (1 mol L<sup>-1</sup>) were stirred for 90 minutes at 60 °C as precursors. After 90 minutes, deionized water and 1 mol L<sup>-1</sup> HCl were added to the sol at room temperature. The final molar ratio of MTES, TEOS, EtOH, deionized water and HCl in the dip coating sol was 0.1: 0.9:

3.8: 5.1: 0.056, respectively. After adding deionized water and 1 mol L<sup>-1</sup> HCl, the sol was aged for  $t/t_{\text{gel}} = 0.24$  at 50 °C, and subsequently diluted with EtOH before coating (volume ratio of sol to EtOH was equal to 1:2)<sup>22</sup>. The coating, dipping and calcination steps were repeated to achieve a uniform silica layer with desired performance.

### Strategy for surface modification of silica layer

In order to control the pore size of the silica membrane and its modification, the solution of TEOS: EtOH with a volume ratio of 1:12 was used<sup>22</sup>. In this study, for synthesizing the silica membranes, two different procedures of surface modification were applied for the silica layer. In the first membrane (M1), the final selective silica layer was modified, while in the second membrane (M2), after each template silica coating step, the surface modification process was performed.

Table 1 describes in detail the intermediate, top layers and surface modification formation conditions.

A systematic labeling has also been presented for the first and second membranes (M1 and M2) with more details in Table 2, where M1a and M1b describe M1 membrane after and before modification, respectively.

### Membrane characterization and gas permeation/separation measurement

In order to characterize structural defects, such as cracks and holes, as well as perform a characteristic analysis of the modified silica membranes, the scanning electron microscope (SEM, CamScan MV2300, England) was used.

The performance of the fabricated templated silica membrane was investigated by applying the carbon dioxide, nitrogen and hydrogen pure gases permeance test at the temperature range of 25–200 °C and pressure range of 0.5–4 bar. The flux passing through the membrane (permeate flow) at atmospheric pressure was measured by a bubble flowmeter.

To evaluate the synthesized membrane performance, the mixture of carbon dioxide and nitrogen with ratio of 50/50 (vol%) was also used. The real selectivity of mixed gases was monitored by the gas chromatograph device (GC Chrom. Teif Gostar Faraz, Iran). Figure 1 schematically shows the gas permeation measurement set up.

## Results and discussion

### Silica membrane microstructures

The SEM images of the porous  $\alpha$ -alumina support, the  $\gamma$ -alumina intermediate layer and the finally templated silica membrane modified with two procedures are presented in Figure 2.

The SEM image of the microstructure porous ceramic support is presented in Figure 2a. Characteristics of tubular porous ceramic supports were analyzed by the Archimedes test<sup>35</sup>. The results showed 48 % open porosity, 10 % closed porosity and 42 % relative density, which indicated that the porosity of the fabricated parts is appropriate.

As may be identified in Figure 2a, no cracks in the structure of the pieces were observed because of the appropriate heat treatment of the raw supports formed by the gel casting method. In addition, the supports are a completely porous structure with fine texture and uniform microstructure.

Table 1 – Conditions of the various layers in membrane synthesis

	Calcination time	Calcination temperature	Calcination rate	Drying operation	Coating rate	Coating time
3 h	700 °C	0.5 °C min <sup>-1</sup>	24 h at room temperature	6 cm min <sup>-1</sup>	10–30 s	Intermediate layer
4 h	550 °C	1 °C min <sup>-1</sup>	5–10 min in nitrogen atmosphere	6 cm min <sup>-1</sup>	5 min	Silica layer
4 h	400 °C	1 °C min <sup>-1</sup>	5–10 min in nitrogen atmosphere	6 cm min <sup>-1</sup>	10 min	Surface modification

Table 2 – Systematic labeling of fabricated membranes

Membrane	Label	1 <sup>st</sup> Silica layer	1 <sup>st</sup> Surface modification	2 <sup>nd</sup> Silica layer	2 <sup>nd</sup> Surface modification	3 <sup>rd</sup> Silica layer	3 <sup>rd</sup> Surface modification	4 <sup>th</sup> Silica layer	4 <sup>th</sup> Surface modification
M1	a*	*	–	*	–	*	*	–	–
	b**	*	–	*	–	*	–	–	–
M2	–	*	*	*	*	*	*	*	*

\* After modification

\*\* Before modification

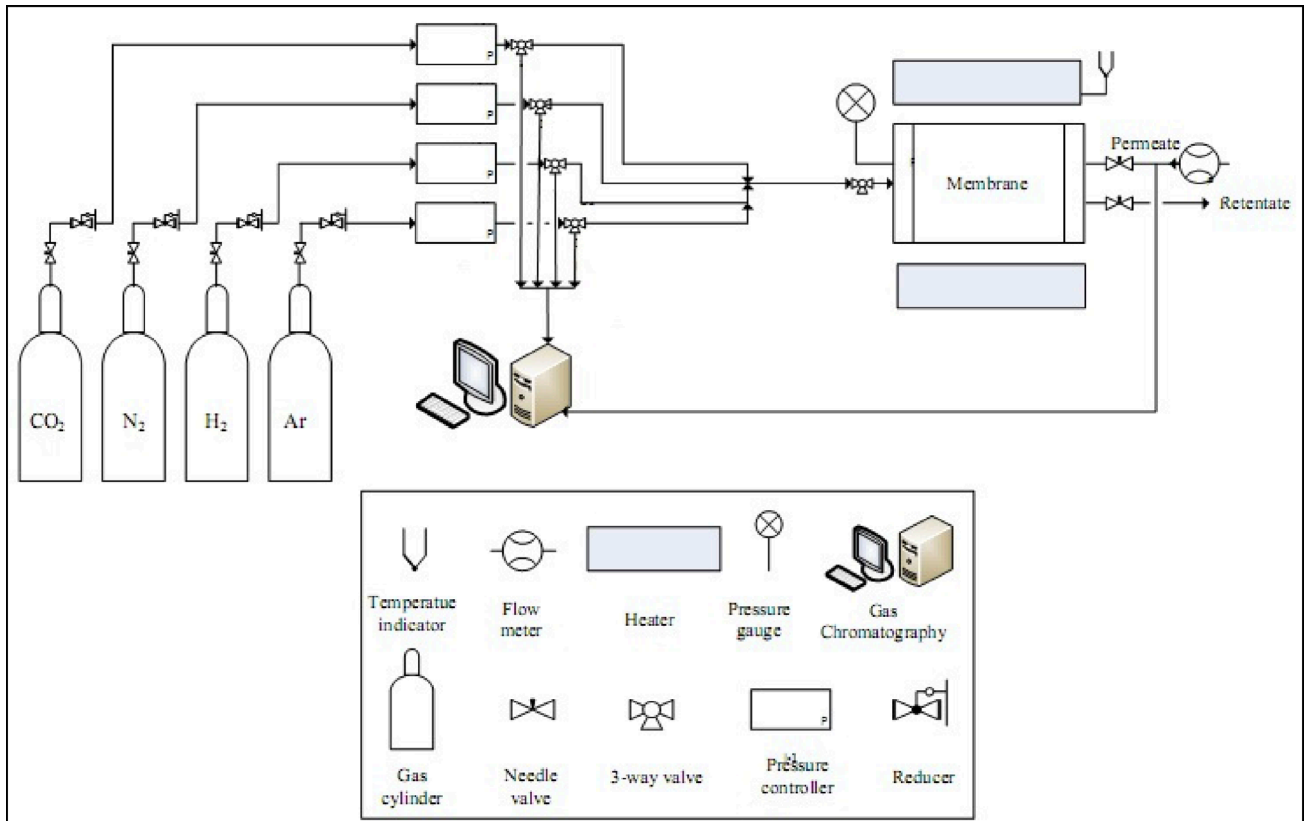


Fig. 1 – Schematic of the gas permeation measurement set up

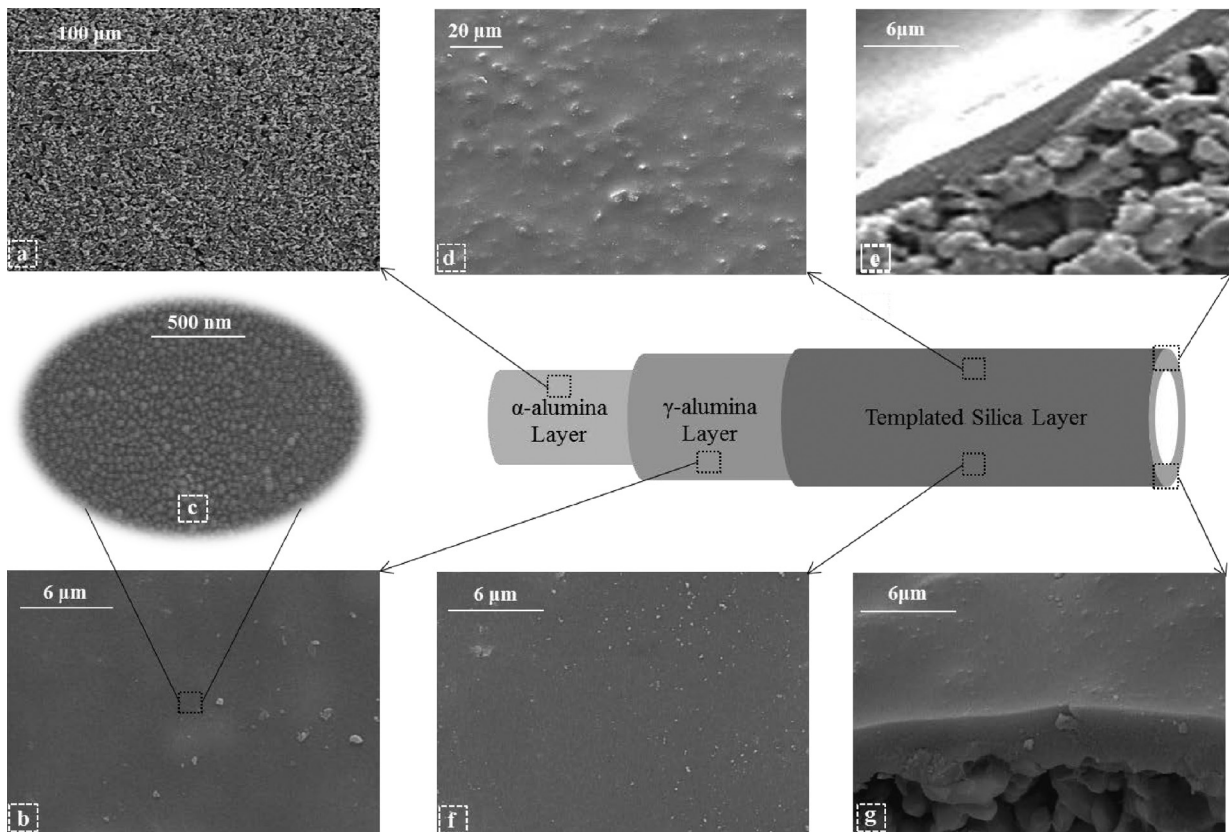


Fig. 2 – SEM images; a) surface of porous  $\alpha$ -alumina support (1kx), b) surface (5kx) and c) surface (60kx) of  $\gamma$ -alumina layer; d) surface (1kx) and e) cross-section of the templated silica membrane M1a (5kx), f) surface (5kx) and g) cross-section of the templated silica membrane M2 (5kx)



The main effective properties, such as pore size distribution, tortuosity on the surface, and the connections of layers have the most important influence on the performance of microporous membranes. The ceramic supports have a rough surface with large pores preventing the formation of a uniform silica layer on the membrane surface thus affecting efficiency. Therefore, the modification of supports seems necessary. For this purpose, the  $\gamma$ -alumina surface modification on the support was applied to improve the surface and decrease the pore size distribution. The  $\gamma$ -alumina layer thickness increases with increasing of sol viscosity, immersion time and coating rate. As presented in literature<sup>36</sup>, to control the thickness of the  $\gamma$ -alumina layer, the immersion time and coating rate should be in the range of 5–20 s and 5–20 cm min<sup>-1</sup>, respectively. According to the properties of the  $\gamma$ -alumina layer reported in literature, the  $\gamma$ -alumina layer thickness is expected to be between 0.5–25  $\mu\text{m}$ <sup>37,38</sup>. Figure 2b and c illustrates the SEM images of the  $\gamma$ -alumina layer.

As seen in Figure 2b, the repetition of the coating process resulted in a smooth and crack-free surface on the  $\alpha$ -alumina sublayer. The uniform intermediate layer may be due to the lack of microbubbles formation (the main source of cracking), the appropriate distribution of boehmite in sol, proper stirring during addition of PEG and increased coherence (viscosity) of sol. Therefore, the primary requirements for achieving the microporous selective layer (i.e. smooth surface, uniform pore size, micron thickness and stability of the intermediate layer) have been obtained. Also, SEM images with high magnification (Figure 2c) from the surface of the samples verified that the nanostructure  $\gamma$ -alumina intermediate layer had formed on the  $\alpha$ -alumina porous support.

Figures 2d and e illustrate the SEM images of the silica membrane with the first procedure of surface modification by the relatively uniform templated silica layer. According to the surface image, the silica layer that formed on the intermediate layer of  $\gamma$ -alumina was uniform and regarding the cross-section image, a thin silica layer had formed on the  $\gamma$ -alumina coated support. The penetration of the silica sol into the pores of the macroporous  $\alpha$ -alumina support was inhibited by the  $\gamma$ -alumina intermediate layer, which could have led to the formation of selective microporous silica layer<sup>36,39</sup>.

In Figures 2f and g, the formation of a uniform and thin layer of modified silica membranes by the second procedure is verified. Comparison of the SEM images of the membranes surface suggests that the uniformity of the modified silica membrane in the second procedure is higher. Therefore, the layer-by-layer surface modification of silica mem-

branes can result in high quality microporous selective layers, which is investigated in more detail in the following section.

## Membranes performance

### Pure gases permeance

Permeance and selectivity data for different layers of the membranes were compared and analyzed. For this purpose, nitrogen permeance data of the  $\alpha$ -alumina support and the intermediate  $\gamma$ -alumina layer were investigated previously to confirm the governing mechanism. Thereupon, the permeance data of different gases ( $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{N}_2$ ) in the modified silica membrane, modified by the first procedure, were analyzed. The effect of the surface modification on the performance of silica membranes was analyzed by comparing the permeance data before and after surface modification. Moreover, apparent activation energy of the mentioned gases was calculated for the modified templated silica membranes. Finally, surface modification procedures were compared and the final permeance and selectivity data of silica membranes fabricated by the second procedure were proposed for single and mixed gases.

The performed tests include permeance of pure gases versus pressure (mean pressure range 1.25–3.0 bar) and temperature (range 25–200 °C). It should be noted that the obtained data of each experiment was repeated several times, and all permeance charts are provided with mean data and error bar.

The obtained results of permeance data for the  $\alpha$ -alumina support in comparison with the  $\gamma$ -alumina intermediate layer are discussed as shown in Figure 3. In addition, the mechanism of nitrogen in  $\alpha$ -alumina and  $\gamma$ -alumina layers, and the relations between them were examined. Since the average pore size of the support (570 nm<sup>40</sup>) compared to the mean free pass (MFP) of nitrogen gas (equal to 94.7 nm<sup>41</sup>) was much larger, it was predicted that the viscous flow model for  $\alpha$ -alumina support was satisfied<sup>42,43</sup>. According to equation 1<sup>44</sup> in the viscous flow model, permeance increased linearly with enhancement of average pressure at constant temperature, and decreased with increasing temperature at a constant pressure difference.

$$Q_{vis} = \frac{-J_v}{\Delta P} = \frac{\varepsilon}{8\eta\tau} \frac{r_p^2 P_m}{RTL} \quad (1)$$

Where  $Q_{vis}$ ,  $J_v$ ,  $\Delta P$ ,  $\varepsilon$ ,  $\eta$ ,  $\tau$ ,  $r_p$ ,  $P_m$ ,  $R$ ,  $T$  and  $L$  are permeance of viscous flow, molar flux of viscous flow, the pressure gradient, porosity, viscosity, tortuosity, pore radius, mean pressure, gas constant, absolute temperature, and membrane thickness, respectively. According to the mechanism of viscous

flow, it should be noted that the rate of penetration of gases (which is controlled by the gas viscosity and flow) was not affected by molecular size. The aim of the deposition of  $\gamma$ -alumina layer was to achieve uniform mesoporous structure with minimum permeance loss, and reach the Knudsen diffusion mechanism where the permeance parameter is independent of mean pressure, as follows<sup>44</sup>:

$$Q_{kn} = \frac{-J_{kn}}{\Delta P} = \frac{2\varepsilon r_p}{3\tau L} \left(\frac{8}{\pi RTM}\right)^{1/2} \quad (2)$$

Where  $Q_{kn}$ ,  $J_{kn}$ ,  $\pi$  and  $M$  are permeance of Knudsen diffusion, molar flux of Knudsen diffusion, pi number, and molecular weight of permeating gas, respectively.

Figure 3 indicates the nitrogen permeance for  $\alpha$ -alumina support and  $\gamma$ -alumina-coated support. A significant increase in nitrogen permeance in the  $\alpha$ -alumina support with enhancement of the mean pressure was observed. Therefore, regarding the obvious influence of the pressure parameter on nitrogen permeance, the governing mechanism for penetration of gases in the  $\alpha$ -alumina support was the viscous flow model. In addition, the application of uniform  $\gamma$ -alumina layer led to the elimination of larger pores, so that the effect of pressure on the nitrogen permeance significantly reduced in the  $\gamma$ -alumina-coated support. Therefore, it can be concluded that the dominant mechanism of nitrogen permeance in the intermediate layer of  $\gamma$ -alumina layer was Knudsen diffusion, confirming the formation of a mesoporous microstructure on the macroporous support.

The governing mechanisms on the  $\alpha$ -silica membrane fabricated by the first procedure for different gases were investigated. Figure 4 illustrates the gases permeance versus mean pressure in the templated silica membrane. Due to the molecular

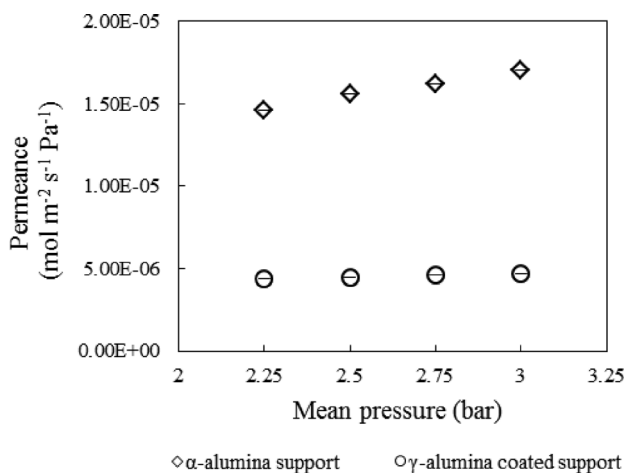


Fig. 3 – Pure nitrogen permeance versus mean pressure for the  $\alpha$ -alumina support and the  $\gamma$ -alumina-coated support

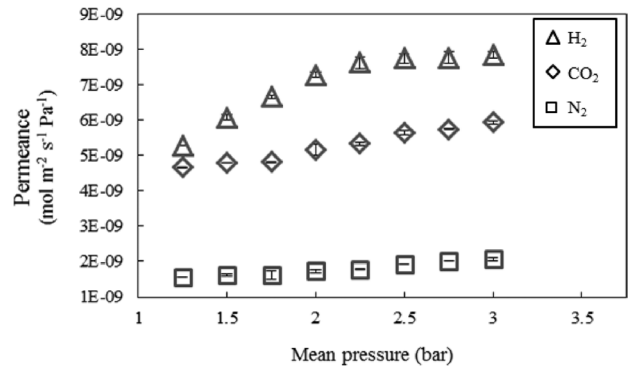


Fig. 4 – Pure gases permeance versus mean pressure for the M1a silica membrane at room temperature

sieve properties of the fabricated templated silica membranes, the permeance of small molecule gases is higher compared to the gases with large molecule size (such as nitrogen).

Figure 5 presents the variations of gases permeance versus temperature at constant pressure in the templated silica membranes.

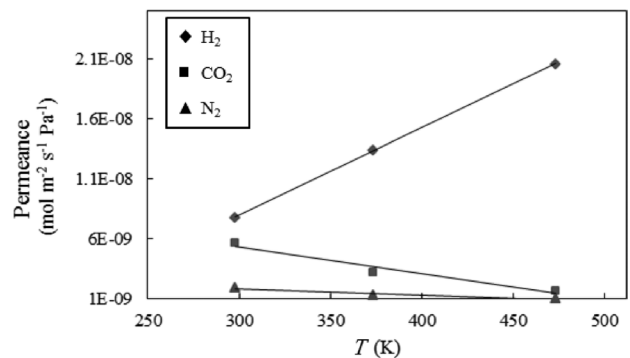


Fig. 5 – Pure gases permeance versus temperature for the M1a silica membrane at pressure 2.5 bar

The permeance of carbon dioxide and nitrogen decreased with increased temperature. Therefore, the surface diffusion or Knudsen diffusion was the explainable mechanism, but with increased temperature the hydrogen permeance increased. Knudsen and surface diffusion models could not interpret the hydrogen permeance, because the gas flux decreased with increased temperature in these mechanisms. To explain the behavior of hydrogen permeance in the templated silica membrane, the activated transport models can be considered. The hydrogen permeance severely increased by enhancement of temperature, this behavior is described by the following equations<sup>21,45</sup>:

$$P = P_0 \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

Where  $P$ ,  $E_a$ ,  $R$  and  $T$  are components permeance, apparent activation energy, gas constant and abso-

lute temperature, respectively.  $P_0$  is also calculated by equation 4.

$$P_0 = \frac{k_0}{\sqrt{MRT}} \quad (4)$$

Where  $k_0$  and  $M$  are the characteristic constant of the porous membrane, and the molecular weight of the gas, respectively.

For heavier gases such as carbon dioxide, the surface diffusion mechanism was established. The surface penetration rate was discussed as an interaction of adsorbed gases and pore surfaces. Thus, the molecules penetrated along the pore walls, because the strength of this interaction and separation of carbon dioxide had been achieved by the difference in the degree of this interaction. Therefore, because the dominant mechanism for carbon dioxide and hydrogen was the surface diffusion and the activated transport, respectively, the apparent increase in permeance with enhancement of pressure for these gases was observed. Whereas, due to the Knudsen diffusion mechanism for nitrogen, a significant change in the permeance of nitrogen with pressure parameter was not found.

As can be seen in Figure 6, pure gases permeance at different temperatures is plotted versus the kinetic diameter. A sharp decrease in gas permeance with the increase in kinetic diameter established the molecular sieve mechanism at the templated silica membranes.

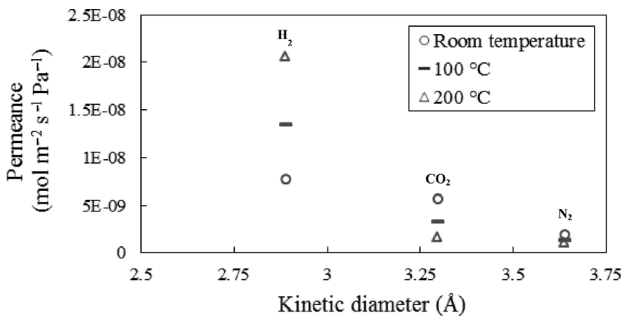


Fig. 6 – Pure gases permeance versus kinetic diameter at different temperatures for the M1a silica membrane

The molecular sieve membranes contained channels and cages in their structures, so their separation property depends on the size of these channels and the kinetic diameter of the gases. Considering that the driving force of the gas separation process by the molecular sieves mechanism is the pressure gradient between two sides of the membrane, the presence of macropores or cracks in the membrane could result in poor performance. Therefore, one of the essential proceedings in the synthesis of silica membranes is the reduction of membrane defects and the decrease in pore size of the

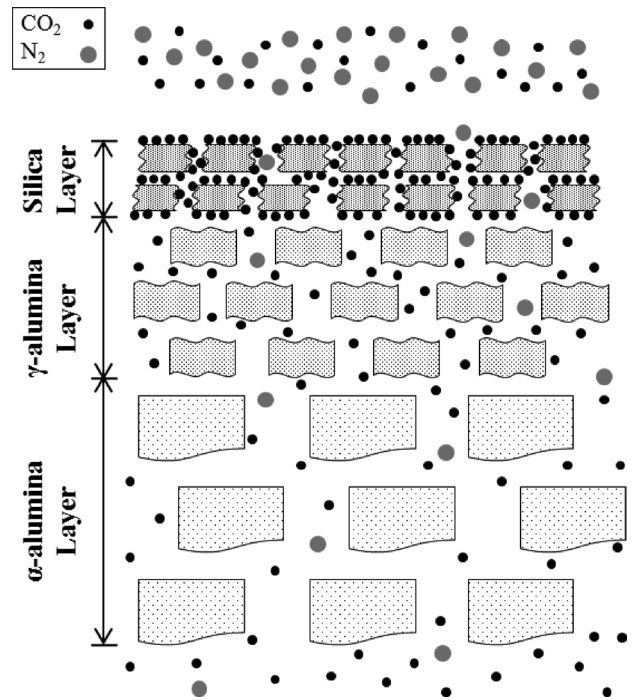


Fig. 7 – Schematic of the governing mechanism in the synthesized silica membrane

selective layer with keeping the permeance rate. The scheme of the governing mechanisms for CO<sub>2</sub> and N<sub>2</sub> gases in the synthesized silica membrane is illustrated in Figure 7.

Therefore, the surface modification effect on the membrane performance was discussed. Figure 8 illustrates the permeance and permselectivity variation of the gases in the membrane with and without surface modification of the silica selective layer.

As shown in Figure 8, it was observed that, when the surface modification was performed once, the CO<sub>2</sub>/N<sub>2</sub> permselectivity value increased (from 1.5 to 3) due to the decrease in pore size and in-

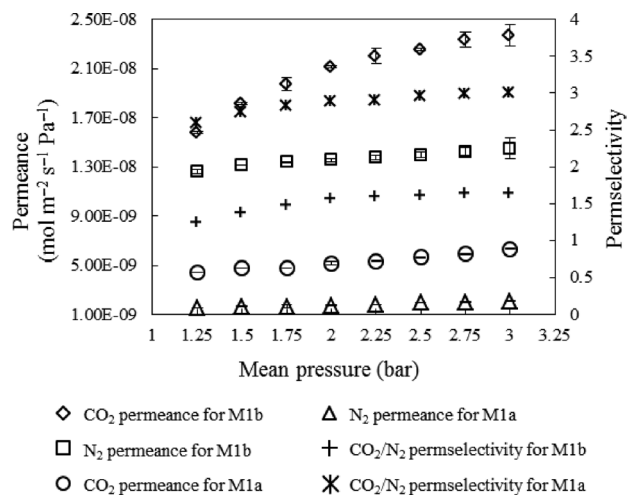


Fig. 8 – Permeance and permselectivity versus mean pressure of M1a and M1b silica membranes

crease in adsorption of carbon dioxide on the surface of the silica. This is in good agreement with the research of Lee *et al.*<sup>26</sup>, in which the separation factor of CO<sub>2</sub>/N<sub>2</sub> was doubled for nanoporous silica composite membranes with MTES template, and 5 surface modifications with a solution of TEOS: EtOH. As a result, surface modification has an important role on the performance of the synthesized membranes.

The achieved apparent activation energy of the silica membrane was  $-4.99 \text{ kJ mol}^{-1}$  before surface modification, while it decreased to  $-7.67 \text{ kJ mol}^{-1}$  after the first surface modification. The negative sign of apparent activation energy can be related to exothermic adsorption of carbon dioxide. Moreover, when the species separation is based on size differences of molecules and pores, the apparent activation energy value is positive, but if the Knudsen diffusion mechanism or adsorption process are dominant, the apparent activation energy will be a negative value<sup>10,24,25,46,47</sup>.

On the other hand, the obtained results confirmed that surface modification of silica membrane leads to more negative apparent activation energy, and thus increases the carbon dioxide adsorption on the silica pores.

Regarding the appropriate effect of surface modification on the silica membrane, another membrane with layer-by-layer surface modification was fabricated, the results of which are shown in Figure 9, compared to those of the membrane modified by the first procedure. In the first membrane, the surface modification process was carried out only on the final layer of silica, whereas the surface modification process of the second membrane was carried out after coating each layer of silica.

In the silica membrane with layer-by-layer surface modification, CO<sub>2</sub>/N<sub>2</sub> permselectivity improved

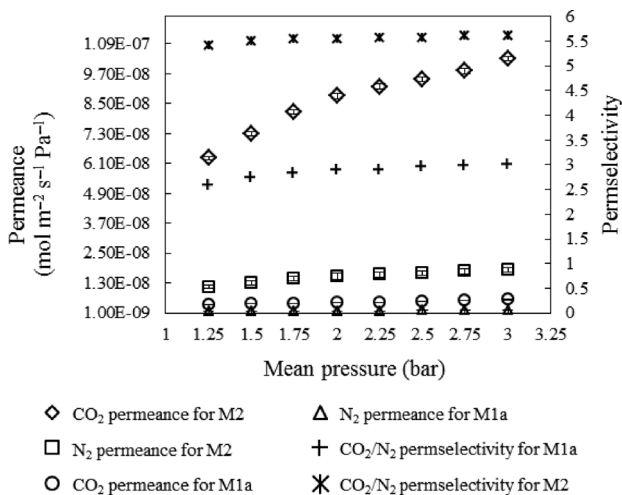


Fig. 9 – Comparison of permeance and permselectivity versus mean pressure of M1a and M2 silica membranes

up to 5.8, due to the high molecular sieve performance of these membranes, and enhancement of the carbon dioxide adsorption. For more selectivity, membrane coating and surface modification were repeated one more time, and the results are given in Figure 10.

Permselectivity of silica membrane reached 11.3 after coating once with acid-catalyzed silica sol, and one surface modification, indicating an increase in carbon dioxide permeance (due to increase in carbon dioxide adsorption on silica surface), and a reduction in nitrogen permeance (due to reduction in pore size, increase in thickness, omitting the existing defects, and improving the molecular sieve silica membrane performance).

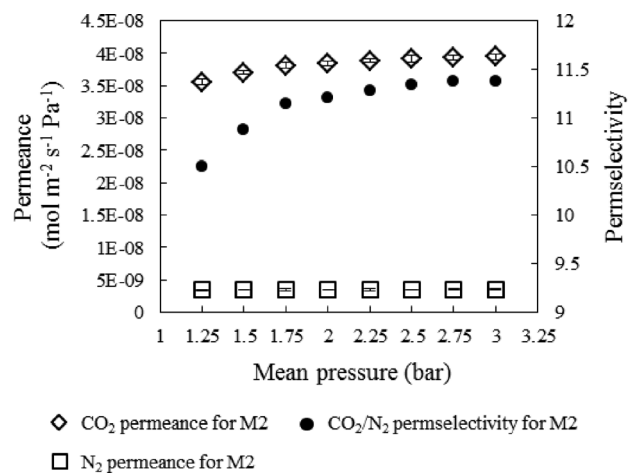


Fig. 10 – Permeance and permselectivity of gases (CO<sub>2</sub>/N<sub>2</sub>) for the M2 silica membrane

During the surface modification procedures, TEOS molecules were hydrolyzed to the  $-\text{Si}(\text{OH})_x$  and penetrated the larger pores, and decreased the nitrogen permeance<sup>25</sup>. Thus the silica membrane with layer-by-layer surface modification shows high performance compared to the membrane modified by the first procedure.

According to permeance values of the synthesized silica membranes, it was found that carbon dioxide and nitrogen follow the surface diffusion and Knudsen mechanisms, respectively. As the temperature increased, permeance of carbon dioxide and nitrogen reduced. According to the gas permeance experiment, the permselectivity of carbon dioxide over nitrogen changed from 11.3 at ambient temperature to 9.6 at 200 °C, due to the reduction in carbon dioxide adsorption by increasing the temperature.

As shown in Figure 11, the performance of the synthesized silica membranes was compared with similar research results<sup>24,26,48,49</sup>. These membranes had the closest structure with M1a and M2 mem-



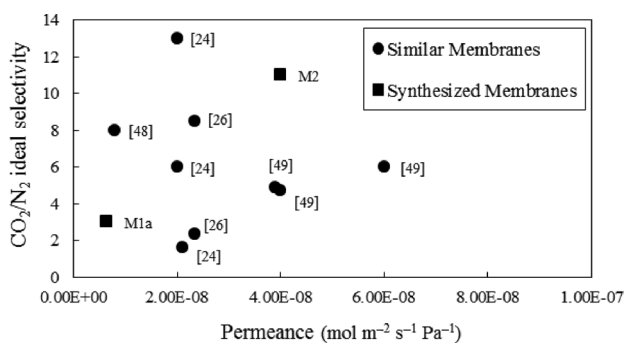


Fig. 11 – Relationship between the  $\text{CO}_2/\text{N}_2$  permselectivity and  $\text{CO}_2$  permeance for silica membranes

branes and some of them were surface modified by the TEOS:EtOH solution. According to the good position of the synthesized membrane in trade-off chart, it can be found that the templated silica membrane modified by the second procedure had appropriate performance based on the permeance and selectivity aspects.

#### Gas mixture test

The performance of silica membranes in the gas mixture of carbon dioxide and nitrogen, with a 50/50 ratio (vol%) at room temperature was investigated, and the results are presented in Figure 12.

According to Figure 12, the modified membrane modified with the second procedure had appropriate performance. In particular, the real selectivity achieved was 5.27 for the membrane modified by the second procedure, and 2.03 for the membrane modified by the first procedure. Moreover, the results show that the real selectivity in both cases had increased by increasing the mean pressure. According to the increase in the component adsorp-

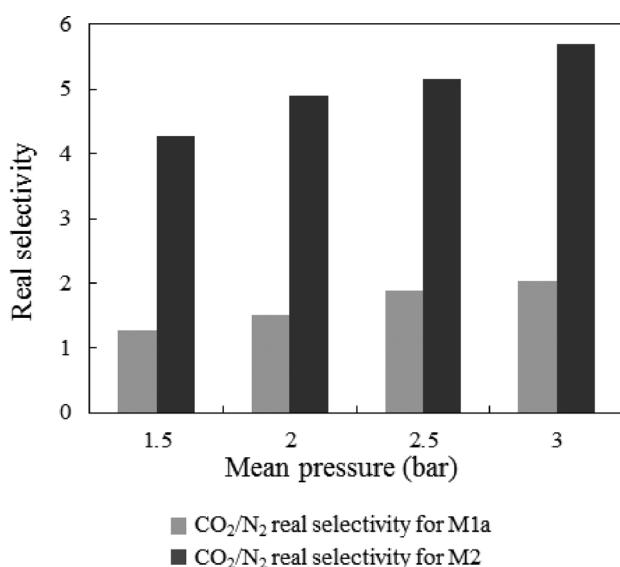


Fig. 12 – Real selectivity versus mean pressure for M1a and M2 silica membranes

tion by increasing the pressure, enhancement of real selectivity at higher pressure was more sensible. This means that at lower pressure, the back diffusion phenomenon could have a negative effect on the real selectivity (Figure 12).

The back diffusion created by collisions of gas molecules in a gas mixture is decreased by enhancement of gradient pressure. According to the literature<sup>26</sup>, this is probably related to the concentration polarization phenomenon. This phenomenon causes an increase in nitrogen concentration in the feed and carbon dioxide concentration on the other side of the membrane.

## Conclusions

Nanostructure microporous silica membranes were synthesized by the templated sol-gel method using TEOS as precursor and MTES as template on  $\gamma$ -alumina-coated tubular  $\alpha$ -alumina supports. Nitrogen permeance data of the  $\gamma$ -alumina layer also revealed the gas flow through the Knudsen mechanism. In the templated silica membrane, hydrogen, carbon dioxide, and nitrogen follow activated transport, surface diffusion, and Knudsen mechanisms, respectively. Carbon dioxide permeance decreased with increased temperature due to the reduction in membrane adsorption of silica at high temperatures. The apparent activation energy of the silica membrane, before surface modification was  $-4.99 \text{ kJ mol}^{-1}$ , and after one surface modification it equaled  $-7.67 \text{ kJ mol}^{-1}$ . Two surface modification procedures (selective layer surface modification and layer-by-layer surface modification) were performed on the silica membranes to confirm the best surface modification procedure. The permeance and selectivity data confirm that the silica membrane modified with the layer-by-layer procedure had higher performance. Finally, the surface modified templated silica membrane permeance for carbon dioxide was approximately  $4.0 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ , and ideal selectivity for  $\text{CO}_2/\text{N}_2$  was 11.3 at room temperature. Due to low preferential adsorption of carbon dioxide at high temperatures, the separation of carbon dioxide from gas mixtures is suggested to perform at room temperature.

## ACKNOWLEDGEMENTS

The authors are grateful to Nanostructure Material Research Center for the financial support useful for the contents of this manuscript. The authors are also grateful to the support of the Iran Nanotechnology Initiative Council.

## Nomenclature and units

- M1a – The first templated silica membrane after surface modification
- M1b – The first templated silica membrane before surface modification
- M2 – The second templated silica membrane with layer-by-layer surface modification
- $t_{\text{gel}}$  – Gelation time, s
- MFP – Mean free pass
- $Q_{\text{vis}}$  – Permeance of viscose flow,  $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$
- $Q_{\text{kn}}$  – Permeance of Knudsen diffusion,  $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$
- $J_{\text{v}}$  – Molar flux of viscose flow,  $\text{mol m}^{-2} \text{s}^{-1}$
- $J_{\text{kn}}$  – Molar flux of Knudsen diffusion,  $\text{mol m}^{-2} \text{s}^{-1}$
- $\Delta P$  – Pressure gradient, Pa
- $\varepsilon$  – Porosity
- $\eta$  – Viscosity,  $\text{kg m}^{-1} \text{s}^{-1}$
- $\tau$  – Tortuosity
- $r_p$  – Pore radius, m
- $P_m$  – Mean pressure, Pa
- $R$  – Gas constant,  $\text{J mol}^{-1} \text{K}^{-1}$
- $T$  – Temperature, K
- $L$  – Membrane thickness, m
- $\pi$  – Pi
- $M$  – Molecular weight of permeating gas,  $\text{g mol}^{-1}$
- $P$  – Components permeance,  $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$
- $P_0$  – Constant
- $E_a$  – Apparent activation energy,  $\text{kJ mol}^{-1}$
- $k_0$  – Characteristic constant of the porous membrane

## References

- Song, C., Global challenges and strategies for control, conversion and utilization of CO<sub>2</sub> for sustainable development involving energy, catalysis, adsorption and chemical processing, *Catal. Today* **115** (2006) 2.  
doi: <http://dx.doi.org/10.1016/j.cattod.2006.02.029>
- Ebner, A. D., Ritter, J. A., State-of-the-art Adsorption and Membrane Separation Processes for Carbon Dioxide Production from Carbon Dioxide Emitting Industries, *Sep. Sci. Technol.* **44** (2009) 1273.  
doi: <http://dx.doi.org/10.1080/01496390902733314>
- Ahmad, F., Lau, K. K., Shariff, A. M., Removal of CO<sub>2</sub> from natural gas using membrane separation system: modeling and process design, *J. App. Sci.* **10** (2010) 1134.  
doi: <http://dx.doi.org/10.3923/jas.2010.1134.1139>
- Tabe-Mohammadi, A., A Review of the Applications of Membrane Separation Technology in Natural Gas Treatment, *Sep. Sci. Technol.* **34** (1999) 2095.  
doi: <http://dx.doi.org/10.1081/SS-100100758>
- Mohammadi, T., Asarehpour, S., Samei, M., Effects of Synthesis Temperature and Support Material on CO<sub>2</sub> and CH<sub>4</sub> Permeation through SAPO-34 Membranes, *Sep. Sci. Technol.* **47** (2012) 2320.  
doi: <http://dx.doi.org/10.1080/01496395.2012.677924>
- Ismail, A. F., David, L. I. B., A review on the latest development of carbon membranes for gas separation, *J. Membr. Sci.* **193** (2001) 1.  
doi: [http://dx.doi.org/10.1016/S0376-7388\(01\)00510-5](http://dx.doi.org/10.1016/S0376-7388(01)00510-5)
- Gallucci, F., Basile, A., Hai, F. I., Introduction – A Review of Membrane Reactors, Basile, A. and Gallucci, F., (Eds.), *Membranes for Membrane Reactors: Preparation, Optimization and Selection*, John Wiley & Sons, Ltd, New York, 2011, pp 1–61.  
doi: <http://dx.doi.org/10.1002/9780470977569>
- Aaron, D., Tsouris, C., Separation of CO<sub>2</sub> from Flue Gas: A Review, *Sep. Sci. Technol.* **40** (2005) 321.  
doi: <http://dx.doi.org/10.1081/SS-200042244>
- Li, K., Transport and Separation of Gases in Porous Ceramic Membranes, *Ceramic Membranes for Separation and Reaction*, John Wiley & Sons, Ltd, England, 2007, pp 97–134.  
doi: <http://dx.doi.org/10.1002/9780470319475.ch4>
- Tsai, C. -Y., Tam, S. -Y., Lu, Y., Brinker, C. J., Dual-layer asymmetric microporous silica membranes, *J. Membr. Sci.* **169** (2000) 255.  
doi: [http://dx.doi.org/10.1016/S0376-7388\(99\)00343-9](http://dx.doi.org/10.1016/S0376-7388(99)00343-9)
- Leenaars, A. F. M., Keizer, K., Burggraaf, A. J., The preparation and characterization of alumina membranes with ultra-fine pores, *J. Mater. Sci.* **19** (1984) 1077.  
doi: <http://dx.doi.org/10.1007/BF01120016>
- Li, K., Preparation of Ceramic Membranes, *Ceramic Membranes for Separation and Reaction*, John Wiley & Sons, Ltd, England, 2007, pp 21–57.  
doi: <http://dx.doi.org/10.1002/9780470319475.ch2>
- Qi, H., Han, J., Xu, N., Effect of calcination temperature on carbon dioxide separation properties of a novel microporous hybrid silica membrane, *J. Membr. Sci.* **382** (2011) 231.  
doi: <http://dx.doi.org/10.1016/j.memsci.2011.08.013>
- Boffa, V., ten Elshof, J. E., Petukhov, A. V., Blank, D. H. A., Microporous niobia-silica membrane with very low CO<sub>2</sub> permeability, *ChemSusChem* **1** (2008) 437.  
doi: <http://dx.doi.org/10.1002/cssc.200700165>
- Wei, Q., Wang, F., Nie, Z. R., Song, C. L., Wang, Y. L., Li, Q. Y., Highly hydrothermally stable microporous silica membranes for hydrogen separation, *J. Phys. Chem. B* **112** (2008) 9354.  
doi: <http://dx.doi.org/10.1021/jp711573f>
- Wei, Q., Wang, Y. -L., Nie, Z. -R., Yu, C. -X., Li, Q. -Y., Zou, J. -X., Li, C. -J., Facile synthesis of hydrophobic microporous silica membranes and their resistance to humid atmosphere, *Microp. and Mesop. Mater.* **111** (2008) 97.  
doi: <http://dx.doi.org/10.1016/j.micromeso.2007.07.016>
- West, G. D., Diamond, G. G., Holland, D., Smith, M. E., Lewis, M. H., Gas transport mechanisms through sol-gel derived templated membranes, *J. Membr. Sci.* **203** (2002) 53.  
doi: [http://dx.doi.org/10.1016/S0376-7388\(01\)00746-3](http://dx.doi.org/10.1016/S0376-7388(01)00746-3)
- Brinker, C. J., Sehgal, R., Hietala, S. L., Deshpande, R., Smith, D. M., Loy, D., Ashley, C. S., Sol-gel strategies for controlled porosity inorganic materials, *J. Membr. Sci.* **94** (1994) 85.  
doi: [http://dx.doi.org/10.1016/0376-7388\(93\)E0129-8](http://dx.doi.org/10.1016/0376-7388(93)E0129-8)
- Lu, Y., Cao, G. Z., Kale, R. P., Delattre, L., Brinker, C. J., Lopez, G. P., Controlling The Porosity of Microporous Silica By Sol-Gel Processing Using An Organic Template Approach, *Mater. Res. Soc.* **435** (1996) 271.  
doi: <http://dx.doi.org/10.1557/PROC-435-271>
- Zhu, W., Han, Y., An, L., Synthesis of ordered mesostructured silica nanotubular arrays, *Microp. Mesop. Mater.* **84** (2005) 69.  
doi: <http://dx.doi.org/10.1016/j.micromeso.2005.04.020>
- Kanezashi, M., Yada, K., Yoshioka, T., Tsuru, T., Organic-inorganic hybrid silica membranes with controlled silica network size: Preparation and gas permeation characteristics, *J. Membr. Sci.* **348** (2010) 310.  
doi: <http://dx.doi.org/10.1016/j.memsci.2009.11.014>

22. Raman, N. K., Brinker, C. J., Organic “template” approach to molecular sieving silica membranes, *J. Membr. Sci.* **105** (1995) 273.  
doi: [http://dx.doi.org/10.1016/0376-7388\(95\)00067-M](http://dx.doi.org/10.1016/0376-7388(95)00067-M)
23. de Vos, R. M., Maier, W. F., Verweij, H., Hydrophobic silica membranes for gas separation, *J. Membr. Sci.* **158** (1999) 277.  
doi: [http://dx.doi.org/10.1016/S0376-7388\(99\)00035-6](http://dx.doi.org/10.1016/S0376-7388(99)00035-6)
24. Kim, Y. -S., Kusakabe, K., Morooka, S., Yang, S. -M., Preparation of Microporous Silica Membranes for Gas Separation, *Korean J. Chem. Eng.* **18** (2001) 106.  
doi: <http://dx.doi.org/10.1007/BF02707206>
25. Kusakabe, K., Shibao, F., Zhao, G., Sotowa, K.-I., Watanabe, K., Saito, T., Surface modification of silica membranes in a tubular-type module, *J. Membr. Sci.* **215** (2003) 321.  
doi: [http://dx.doi.org/10.1016/S0376-7388\(03\)00025-5](http://dx.doi.org/10.1016/S0376-7388(03)00025-5)
26. Lee, Y. E., Kang, B. S., Hyun, S. H., Lee, C. H., Organic-Templating Approach to Synthesis of Nanoporous Silica Composite Membranes (II): MTES- Templating and CO<sub>2</sub> Separation, *Sep. Sci. Technol.* **39** (2004) 3541.  
doi: <http://dx.doi.org/10.1081/SS-200036750>
27. Moon, J.-H., Park, Y.-J., Kim, M.-B., Hyun, S.-H., Lee, C.-H., Permeation and separation of a carbon dioxide/nitrogen mixture in a methyltriethoxysilane templating silica/ $\alpha$ -alumina composite membrane, *J. Membr. Sci.* **250** (2005) 195.  
doi: <http://dx.doi.org/10.1016/j.memsci.2004.10.027>
28. Moon, J.-H., Bae, J.-H., Bae, Y.-S., Chung, J.-T., Lee, C.-H., Hydrogen separation from reforming gas using organic templating silica/alumina composite membrane, *J. Membr. Sci.* **318** (2008) 45.  
doi: <http://dx.doi.org/10.1016/j.memsci.2008.02.001>
29. Yang, H., Xu, Z., Fan, M., Gupta, R., Slimane, R. B., Bland, A. E., Wright, I., Progress in carbon dioxide separation and capture: A review, *J. Environ. Sci.* **20** (2008) 14.  
doi: [http://dx.doi.org/10.1016/S1001-0742\(08\)60002-9](http://dx.doi.org/10.1016/S1001-0742(08)60002-9)
30. Koutsonikolas, D., Kaldis, S., Sakellaropoulos, G. P., van Loon, M. H., Dirrix, R. W. J., Terpstra, R. A., Defects in microporous silica membranes: Analysis and repair, *Sep. Purif. Technol.* **73** (2010) 20.  
doi: <http://dx.doi.org/10.1016/j.seppur.2009.07.027>
31. Babaluo, A. A., Kokabi, M., Barati, A., Chemorheology of alumina-aqueous acrylamide gelcasting systems, *J. Eur. Ceram. Soc.* **24** (2003) 635.  
doi: [http://dx.doi.org/10.1016/S0955-2219\(03\)00322-4](http://dx.doi.org/10.1016/S0955-2219(03)00322-4)
32. Barati, A., Kokabi, M., Famili, M. H. N., Drying of gelcast ceramic parts via the liquid desiccant method, *J. Eur. Ceram. Soc.* **23** (2003) 2265.  
doi: [http://dx.doi.org/10.1016/S0955-2219\(03\)00045-1](http://dx.doi.org/10.1016/S0955-2219(03)00045-1)
33. Babaluo, A. A., Kokabi, M., Manteghian, M., Sarraf-Mamoori, R., A modified model for alumina membranes formed by gel-casting followed by dip-coating, *J. Eur. Ceram. Soc.* **24** (2004) 3779.  
doi: <http://dx.doi.org/10.1016/j.jeurceramsoc.2004.01.007>
34. Jabbari, A., Ghasemzadeh, K., Khajavi, P., Assa, F., Abdi, M. A., Babaluo, A. A., Basile, A., Surface modification of  $\alpha$ -alumina support in synthesis of silica membrane for hydrogen purification, *Int. J. Hydrogen Energ.* **39** (2014) 18585.  
doi: <http://dx.doi.org/10.1016/j.ijhydene.2014.05.056>
35. Pennings, E. C. M., Grellner, W., Precise Nondestructive Determination of the Density of Porous Ceramics, *J. Amer. Ceram. Soc.* **72** (1989) 1268.  
doi: <http://dx.doi.org/10.1111/j.1151-2916.1989.tb09724.x>
36. Topuz, B., Çiftçioğlu, M., Sol-gel derived mesoporous and microporous alumina membranes, *J. Sol-Gel Sci. Technol.* **56** (2010) 287.  
doi: <http://dx.doi.org/10.1007/s10971-010-2305-7>
37. Uhlhorn, R. J. R., Keizer, K., Burggraaf, A. J., Gas and surface diffusion in modified  $\gamma$ -alumina systems, *J. Membr. Sci.* **46** (1989) 225.  
doi: [http://dx.doi.org/10.1016/S0376-7388\(00\)80337-3](http://dx.doi.org/10.1016/S0376-7388(00)80337-3)
38. Mleczko, M., Development of an Asymmetric  $\gamma$ -Alumina Nanofiltration Membrane for Carbon Dioxide Separation, Institut Européen Des Membranes, University of Waterloo, Faculty of Engineering, Nanotechnology Engineering, France, 2009, pp 1–41.
39. Qi, H., Preparation of Composite Microporous Silica Membranes Using TEOS and 1, 2-Bis(triethoxysilyl)ethane as Precursors for Gas Separation, *Chinese. Chem. Eng.* **19** (2011) 404.  
doi: [http://dx.doi.org/10.1016/S1004-9541\(09\)60228-7](http://dx.doi.org/10.1016/S1004-9541(09)60228-7)
40. Bayati, B., Bayat, Y., Charchi, N., Ejtemaei, M., Babaluo, A. A., Haghghi, M., Drioli, E., Preparation of Crack-Free Nanocomposite Ceramic Membrane Intermediate Layers on  $\alpha$ -alumina Tubular Supports, *Sep. Sci. Technol.* **48** (2013) 1930.  
doi: <http://dx.doi.org/10.1080/01496395.2013.786728>
41. Baker, R. W., Appendix, Membrane Technology and Applications, John Wiley & Sons, Ltd, England, 2004, pp. 523–534.  
doi: <http://dx.doi.org/10.1002/0470020393.app1>
42. Burggraaf, A. J., Transport and separation properties of membranes with gases and vapours, Burggraaf, A. J. and Cot. L., (Eds.), Fundamentals of inorganic membrane science and technology, Vol. 4, Elsevier, Amsterdam, 1996, pp 331–433.  
doi: [http://dx.doi.org/10.1016/s0927-5193\(96\)80001-5](http://dx.doi.org/10.1016/s0927-5193(96)80001-5)
43. Pakizeh, M., Omidkhan, M. R., Zarringhalam, A., Synthesis and characterization of new silica membranes using template-sol-gel technology, *Int. J. Hydrogen Energ.* **32** (2007) 1825.  
doi: <http://dx.doi.org/10.1016/j.ijhydene.2006.07.025>
44. Pakizeh, M., Omidkhan, M. R., Zarringhalam, A., Study of mass transfer through new templated silica membranes prepared by sol-gel method, *Int. J. Hydrogen Energ.* **32** (2007) 2032.  
doi: <http://dx.doi.org/10.1016/j.ijhydene.2006.10.004>
45. Lee, D.-W., Yu, C.-Y., Lee, K.-H., Synthesis of Pd particle-deposited microporous silica membranes via a vacuum-impregnation method and their gas permeation behavior, *J. Colloid Interf. Sci.* **325** (2008) 447.  
doi: <http://dx.doi.org/10.1016/j.jcis.2008.06.021>
46. de Vos, R. M., Verweij, H., Improved performance of silica membranes for gas separation, *J. Membr. Sci.* **143** (1998) 37.  
doi: [http://dx.doi.org/10.1016/S0376-7388\(97\)00334-7](http://dx.doi.org/10.1016/S0376-7388(97)00334-7)
47. Boffa, V., ten Elshof, J. E., Garcia, R., Blank, D. H. A., Microporous niobia-silica membranes: Influence of sol composition and structure on gas transport properties, *Microp. Mesop. Mater.* **118** (2009) 202.  
doi: <http://dx.doi.org/10.1016/j.micromeso.2008.08.038>
48. Kusakabe, K., Sakamoto, S., Saie, T., Morooka, S., Pore structure of silica membranes formed by a sol-gel technique using tetraethoxysilane and alkyltriethoxysilanes, *Sep. Purif. Technol.* **16** (1999) 139.  
doi: [http://dx.doi.org/10.1016/S1383-5866\(98\)00120-8](http://dx.doi.org/10.1016/S1383-5866(98)00120-8)
49. Iarikov, D. D., Ted Oyama, S., Review of CO<sub>2</sub>/CH<sub>4</sub> Separation Membranes, Oyama, S. T. and Susan, M. S.-W., (Eds.), Membrane Science and Technology, Vol. 14, Elsevier, Amsterdam, 2011, pp 91–115.  
doi: <http://dx.doi.org/10.1016/B978-0-444-53728-7.00005-7>