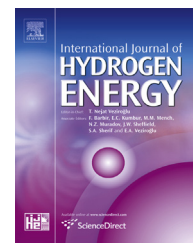


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Surface modification of α -alumina support in synthesis of silica membrane for hydrogen purification

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ABSTRACT

Keywords:

Hydrogen purification
Amorphous silica membrane
Aluminum hydroxide
 γ -Alumina layer
Activated molecular sieving

In this work, an experimental study was carried out on the synthesis of silica membrane for hydrogen purification, in which synthesis of γ -alumina intermediate layer using cheaper and safer source was investigated. For this purpose, aluminum hydroxide was selected and the bohmite sols were prepared by acid or base catalyzed hydrolysis of the different salts for comparing with alkoxide source. The SEM micrographs showed no distinct γ -alumina layer on the substrate coated by base catalyzed sol of salt (sample 1), while a homogeneous γ -alumina layer was formed by acid catalyzed sol of salt (sample 2). After γ -alumina layer formation, the gas permeance mechanism was approximately changed. These results were similar to SEM results and N_2 permeance experiments of sample 3 in which substrate was coated with alkoxide sol. However, the γ -alumina layer of sample 2 had no good adhesion to the substrate. Nevertheless, use of aluminum hydroxide can be promised to synthesis of γ -alumina layer; the membrane was synthesized on the modified support with aluminum tri-sec-butylate sol. In particular, in the synthesized silica membrane as the temperature increases, permselectivity of H_2/CO_2 and H_2/N_2 increases from 4.7 and 7.3 at room temperature to 9.4 and 11.6 at 100 °C and to 23.4 and 31.3 at 200 °C, respectively.

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Introduction

Hydrogen as a clean energy carrier, allowing for its reaction with oxygen and generating water as an environmentally friendly exhaust emission, has attracted a great deal of

attention around the world in recent years. This is mainly due to the utilization in fuel cell systems and environmental pressures including climate change issues. At the moment, conventional fossil fuel sources are the best economically viable option towards a hydrogen economy [1]. In general, for

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<http://dx.doi.org/10.1016/j.ijhydene.2014.05.056>

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hydrogen production from fossil fuels using thermochemical processes, the separation and purification stages are critical technologies. Although Hydrogen can be economically produced by steam reforming processes at rather high temperatures to achieve maximum efficiency [2], to obtain high purity hydrogen during mentioned processes, separation of H_2 from other gas streams such as CO_2 and CO is necessary.

Hydrogen can be purified through several techniques, namely pressure swing adsorption (PSA), cryogenic distillation or membrane separation. PSA and cryogenic distillation processes are commercially available separation techniques, however they are energy intensive [3]. Membrane-related processes are economical [4], environmental and not too much bulky. Furthermore, membrane separation processes consume low energy with the possibility of continuous operation [5]. Membrane based processes are considered to be one of the most promising technologies for the production of high purity hydrogen [6]. It can provide an attractive alternative to PSA and cryogenic distillation, depending on the purity and scale of production [7].

The ceramic membranes owing to their good separation performance, their intrinsic thermal stability and high pressure stability have potential for applications in chemical, petrochemical and energy industry, where gas separation can usually increase the process efficiency under harsh conditions [8]. According to the literature, the microporous ceramic membranes have been considered as one of the candidates for separation problems involving small gas molecules. The main classes of microporous membranes include amorphous silica and zeolite membranes that among them the amorphous silica membranes have been extensively investigated for H_2/CO_2 separation [9]. The silica membranes are usually composite ones consisting of several layers of one or more different ceramic materials [10]. They generally have a macroporous support, one or two mesoporous intermediate layers and a microporous (or a dense) top-layer [10]. The surface modification of inorganic supports, in the fabrication of asymmetric microporous ceramic membrane such as silica membranes, plays a critical role in the synthesis of the homogeneous membrane selective layer. This is due to the defects eliminating and preventing of silica sol particles diffusion in pores of support. The γ -alumina sub-layer is extensively used as an intermediate membrane layer for surface modification in the synthesis of microporous membranes. But this method is well-known as expensive procedure due to the high cost of the γ -alumina precursor and higher humid sensitivity that cause problems with reservation. Moreover, the γ -alumina layer can be prepared by hydrolysis and condensation of aluminum alkoxide precursors such as aluminum-tri-sec butoxide (ASTB), aluminum isopropoxide (AIP) and aluminum-tri-sec-butylate (ASB). Therefore, finding a proper precursor for replacing the alkoxides, can affect the extent of the silica and also other ceramic membranes.

In this study, we tried to find a new precursor for synthesizing γ -alumina layers in silica membranes fabrication. For this purpose, synthesis of silica membrane for hydrogen purification at high temperatures was carried out, in which synthesis of γ -alumina layers was investigated via cheaper and much safer precursors. To surface modification of homemade α -alumina

support, after primarily experimental analyses, among different possible sources the aluminum tri-sec-butylate and aluminum hydroxide were selected for a comprehensive investigation. Aluminum hydroxide precursor is much cheaper, has no problems in reservation and also synthesis of γ -alumina layer with this precursor is much easier. However, achieving the stable γ -alumina layers is one of the technical targets for surface modification. After selecting the most proper precursor for γ -alumina layers, the silica layer is coated on the synthesized γ -alumina layers. Finally, the performance of silica membrane for hydrogen separation is studied.

Experimental procedure

Materials

In this experimental study, the material sources used as follows: tetraethyl orthosilicate (TEOS, 98%, Acros) as silicon source, nitric acid (HNO_3 , 65%, Merck) and sodium hydroxide (NaOH, 99%, Merck) as catalyst for silica sol preparation, ethanol (EtOH, 99.9%, Merck) as solvent, and polyethylene glycol (PEG, Merck, Molecular weight: 35,000) as stabilizer. Also, aluminum-tri-sec-butylate (97%, Merck) and aluminum hydroxide ($Al(OH)_3$, Merck) as source of γ -alumina.

Membrane supports

The homemade supports used for membrane synthesis were α -alumina tubes with thickness of 4 mm, diameter of 12 mm, length of 70 mm, average pore size of $\approx 0.57 \mu m$ and average porosity of 47.2%. Before the γ -alumina synthesis, the supports were cleaned in distilled water by an ultrasonic regenerator for 10 min and then dried at $40^\circ C$ for 12 h.

γ -Alumina sub-layer preparation

After primary investigation on γ -alumina sources, γ -alumina intermediate layer was prepared using two different sources of aluminum-tri-sec-butylate and aluminum hydroxide. The prepared samples were summarized in Table 1, which are presented with more details in the following sections.

γ -Alumina sub-layer preparation with aluminum hydroxide precursor

For γ -alumina intermediate layer synthesis, two different methods were performed in which aluminum hydroxide was catalyzed by acidic or basic catalyst.

γ -Alumina sub-layer preparation with aluminum hydroxide precursor catalyzed by base. The γ -alumina intermediate layer

Table 1 – The details of samples prepared as intermediate layers.

Code	Source	Catalyst
Sample 1	Aluminum hydroxide	Base (NaOH) catalyzed
Sample 2	Aluminum hydroxide	Acid (HNO_3) catalyzed
Sample 3	Aluminum-tri-sec-butylate	–

was prepared by dip-coating of the sintered α -alumina supports in a bohmite (γ -AlOOH) sol followed by drying and calcining operation. The bohmite sol was prepared by adding aluminum hydroxide drop-wise to distilled water at 80 °C under vigorous stirring. Then sodium hydroxide was added and the pH of the sol was kept in the range of 9–10. After 1 h stirring under mentioned conditions, PEG (5 wt% of bohmite) was added and the bohmite sol (5wt% sodium hydroxide) was prepared after 16 h reflux. The dip-coating process was carried out at room temperature for dipping time of 10 s and speed of 1 mm s⁻¹. After dipping, the coated support was dried for 24 h at 60 °C and then it was sintered at 700 °C for 3 h inside of the atmospheric furnace with a heating and cooling rate of 0.5 °C/min. The whole processes of dipping, drying and calcining were repeated 4 times, in order to obtain defect-free intermediate γ -alumina layer. The support coated with this method was nominated as sample 1.

γ -Alumina sub-layer preparation with aluminum hydroxide precursor catalyzed by acid. The main difference of this procedure with respect to the first method is related to kind of acid or base agents for sol preparation. The bohmite sol was prepared by adding aluminum hydroxide drop-wise to distilled water at 80 °C under vigorous stirring. Then nitric acid (1.6 M) was added and the pH of the sol was kept in the range of 3–4. After 1 h stirring under mentioned condition PEG (5wt% of bohmite) was added and the bohmite sol (0.5 M sodium hydroxide) was refluxed for 16 h at 80 °C. Then dipping, drying and calcining steps were performed similar to method 1 with 4 times replicates. The support coated with this method was indicated as sample 2.

γ -Alumina sub-layer preparation with aluminum-tri-sec-butylate precursor

In this case, the bohmite sol was prepared by adding aluminum-tri-sec-butylate drop-wise to distilled water, in which about 1.5 L of water was added per mole alkoxide at 80 °C and under vigorous stirring [11]. A white solution was obtained, which was peptized with nitric acid (0.07 mol HNO₃ per mole alkoxide was added). The resulting colloidal suspension was kept boiling until the most of the butanol be evaporated. The PEG solution was made by dissolving PEG (1 wt% of sol) in distilled water under vigorous stirring, then added to sol. The nitric acid was added to decrease the range of pH till 3–4 and after this step sol was refluxed for 16 h to form a stable bohmite sol. The dip-coating process was performed at room temperature. The substrate speed and dip-time were 1 mm s⁻¹ and 10 s, respectively. After the dipping step, the membranes were dried in a climate chamber at 40 °C at least for 24 h. Subsequently, the γ -alumina layer was formed by calcining at 700 °C for 3 h in atmospheric condition with a heating and cooling rate of 0.5 °C/min. The whole processes of dipping, drying and calcining were repeated 4 times. The support coated with this method was named as sample 3.

Synthesis of silica membrane

The microporous silica membrane top-layer was prepared by dipping the γ -alumina mesoporous substrates in the silica standard solution, followed by calcining. A mixture of acid

and water is 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 is placed in an ice-bath to avoid partial hydrolysis [12]. After the addition was completed, the reaction mixture was refluxed for 3 h at 60 °C in oil bath under uniform stirring. The reaction mixture had a final molar TEOS/ethanol/water/acid ratio of 1/3.8/6.4/0.085 [12,13]. The reacted mixture was cooled and diluted 19 times with ethanol to obtain the final dip solution [12]. The γ -alumina substrate was coated by final solution. The withdrawal speed was 1 mm s⁻¹ and the dip-time was 10 s. After dipping, the membrane was calcined at 600 °C for 3 h at atmospheric condition with a heating and cooling rate of 1 °C/min. The whole processes of dipping and calcining were repeated 5 times to modify the defects in the silica membrane layer structure.

Gas permeation measurements

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 allows measuring at temperatures up to 200 °C. Pure gas (H₂, N₂ and CO₂) was fed to the outside (upstream) of the tubular membrane at the range of 0.5–4 bar over ambient. The downstream pressure was kept constant at the atmospheric pressure and the permeation rate was measured by a bubble flow meter. The silica membrane performance was investigated at different temperatures of room temperature, 100 °C and 200 °C at a mean pressure of 2 bar. Therefore, the permselectivity (F_{α}) was obtained by the ratio of single gases permeances.

Results and discussion

γ -Alumina intermediate layers

In the preparation of microporous ceramic membranes, the quality of the support is very effective on the membrane layer integrity. The surface roughness and homogeneity of the support determines not only the integrity of the membrane layer, but also the minimal thickness of the membrane layer for complete surface coverage [14]. The use of thin intermediate layers is an attractive alternative which can be used to generate a smooth surface, to improve the chemical adhesion of the silica layer to the support, to limit the effect of differential thermal expansion coefficients, and finally, to limit the diffusion of the silica sol in the support pores.

The γ -alumina layer is however almost exclusively used as an intermediate membrane layer for the development of gas separation membranes. These layers are not susceptible to crack-formation and peeling-off effects during the firing process [9].

To modify the homemade α -alumina tubular supports, two precursors were tested. First, the supports were dip-coated in acid or base catalyzed sol of aluminum hydroxide, followed by drying and calcining. Fig. 1 shows SEM images of sample 1 (a, b) and sample 2 (c, d). As seen, there is no distinct γ -alumina

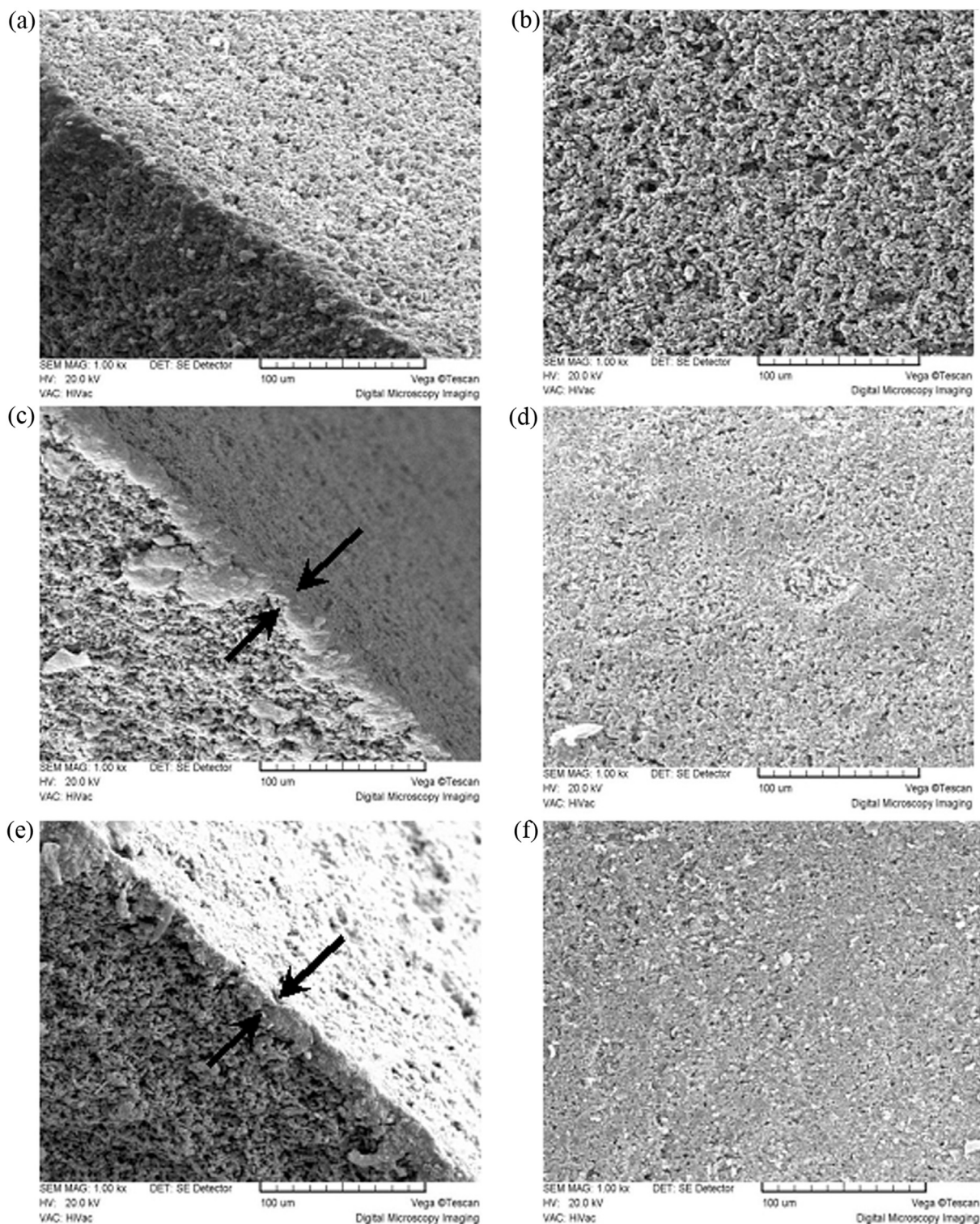


Fig. 1 – SEM images of (a) cross section and (b) surface of sample 1; (c) cross section and (d) surface of sample 2; (e) cross section and (f) surface of sample 3; (locations of γ -alumina layer are indicated by arrows).

layer on the substrate coated by base catalyzed sol of aluminum hydroxide (sample 1), while a homogeneous γ -alumina layer was formed by acid catalyzed sol of the salt (sample 2). This is due to the stability of the acid catalyzed sol which is probably related to the zeta potential in this medium.

Afterward, α -alumina support was dip-coated in aluminum-tri-sec-butylate sol, followed by drying and calcining. SEM images of the sample 3 are shown in Fig. 1(e) and (f). As shown the structure of the sample 2 is similar to the sample 3 with lower homogeneity. Therefore, sample 2 and

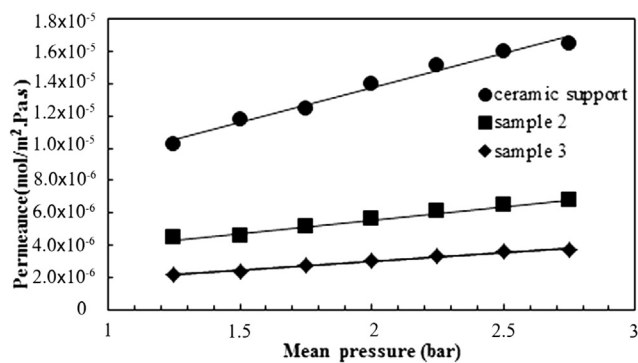


Fig. 2 – N₂ gas permeance of support, sample 2 and sample 3.

sample 3 were selected for N₂ gas permeation tests and sample 1 was deposited.

N₂ gas permeance of supports before and after modifying with aluminum hydroxide and aluminum-tri-sec-butylate was carried out (Fig. 2). The slope of N₂ permeance decreased after modifying the support with γ -alumina layer in both samples, and then pressure dependency of gas

permeance decreased. Concluding that after modification of support the Knudsen diffusion can be dominant mechanism. It should be noted, for synthesis of defect-free membrane layer it is necessary to fine the pores with surface modification which is illustrative in gas permeance results.

However, the magnitude of permeance in sample 3 is lower. This is due to the more homogeneous and denser structure which is visible in SEM images. It is noticeable that γ -alumina layer of sample 2 is loose and has no good adhesion to the substrate, so the surface of this sample after tests was changed and partially missed (see Fig. 3). Probably, it can be related to the metastable sol of aluminum hydroxide or heat treatment problems of coated samples. Nevertheless, use of aluminum hydroxide can be promised to synthesis of γ -alumina layer in preparation of microporous membrane.

Silica membrane layer

According to lower stability of γ -alumina for sample 2, the silica membrane was synthesized on the modified support with aluminum tri-sec-butylate sol (sample 3) via sol–gel method. SEM images of silica membrane surface and cross section are shown in Fig. 4. As depicted, α -alumina support, γ -

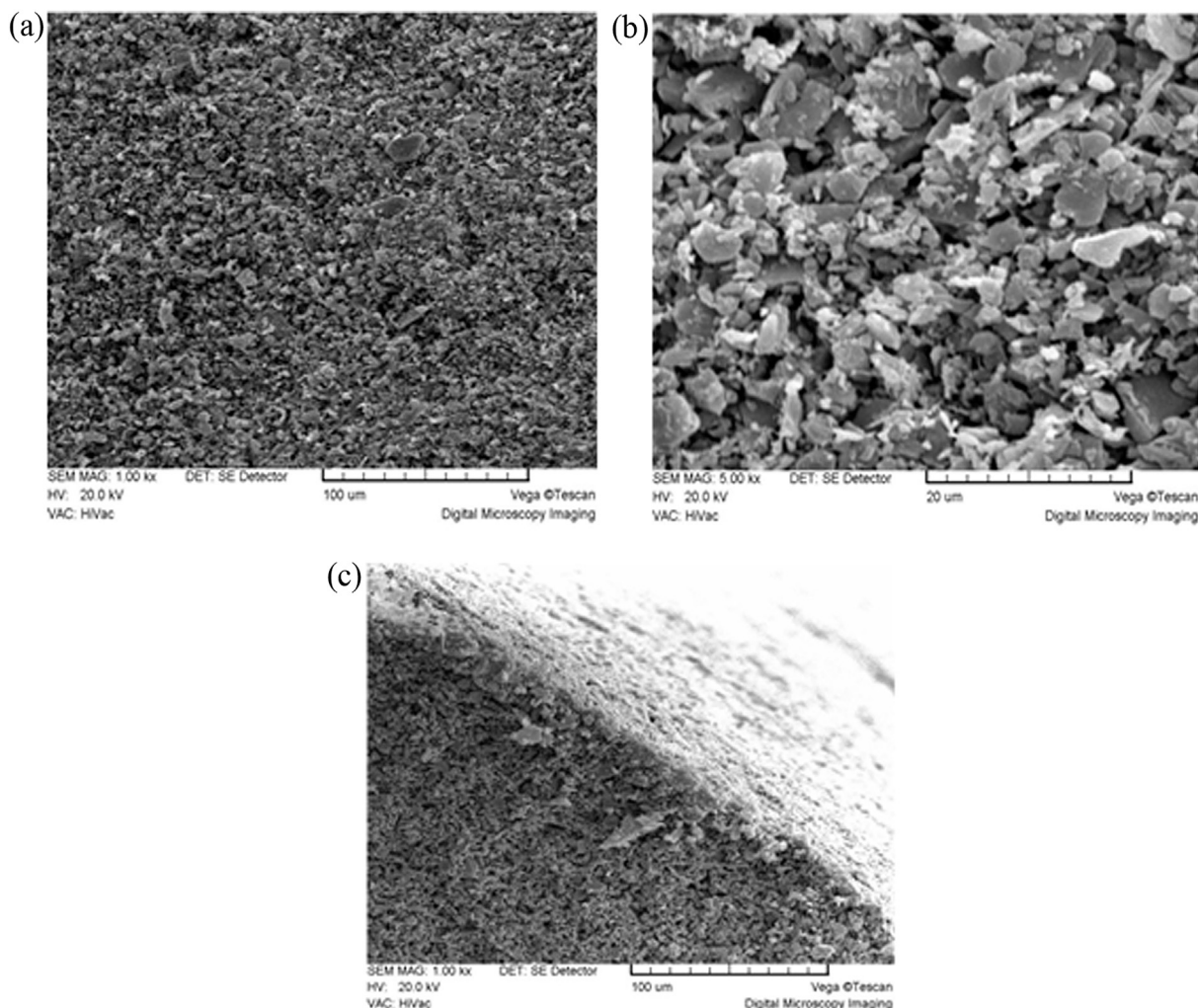


Fig. 3 – SEM images of sample 2 after gas permeance tests (a) surface; (b) surface with higher resolution and (c) cross section.

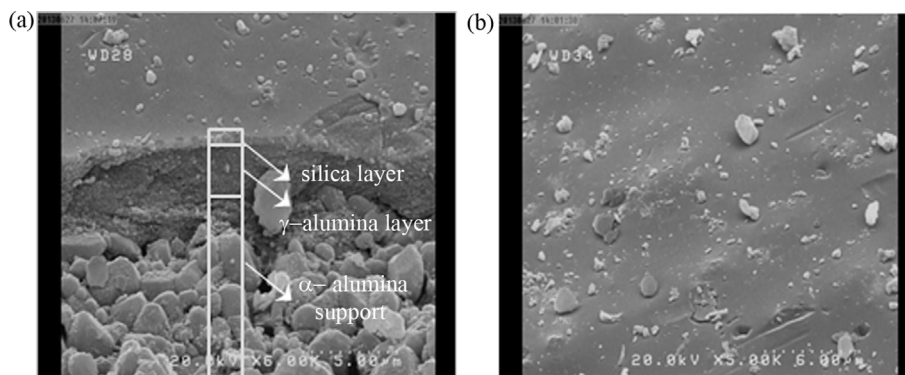


Fig. 4 – SEM images of (a) cross section and (b) surface of silica membrane (sample 3).

alumina layer and silica membrane layer separately are apparent and the homogeneous membrane layer is formed on the modified support without any crack.

Fig. 5 shows the single gas permeation results of silica membrane at the temperature range of 25–200 °C. The permeation of H_2 ($d_K = 2.9$ Å) molecules increased with temperature whilst that of CO_2 ($d_K = 3.3$ Å) and N_2 ($d_K = 3.64$ Å) decreased with temperature. These results are indicative of activated molecular sieving mechanism following an Arrhenius relation [12]:

$$J = J_0 \exp(-E_a/RT) \Delta P/L \quad (1)$$

where J is the flux ($\text{mol m}^{-2} \text{s}^{-1}$) through the membrane, J_0 is a temperature independent coefficient, R is the gas constant, T is the absolute temperature and E_a (kJ mol^{-1}) is the apparent activation energy. The activation energy for single gas permeation as shown in Fig. 5 was calculated using eq. (1) and the results listed in Table 2.

E_a is the sum of two contributions: the heat of sorption of the molecule that is a negative number, because adsorption is an exothermic process in which heat is released, and the positive activation energy of mobility of the permeating molecule inside the membrane matrix. Since these two terms have opposite signs, the apparent activation energy can be positive or negative depending on their relative magnitudes [15]. The activation energy of H_2 molecules permeation in

silica membrane is positive and the molecules have greater permeances at higher temperatures. Increased mobility of the molecules causes this, which has positive sign at the activation energy contribution. The activation energy of CO_2 molecules has negative value. This is due to the heat of sorption of CO_2 molecules on the walls of the silica micropores. Similar behavior for CO_2 transport is reported in Ref. [12].

N_2 gas molecules, with the largest kinetic diameter, permeance decreases with increasing temperature. This is due to the presence of larger pores in the silica thin film, which Knudsen diffusion of the nitrogen takes place. The increase in temperature leads to a decrease of Knudsen diffusion transport and thus a decrease of N_2 permeance. A similar transport behavior of N_2 was observed by Gavalas et al. [16]. This has

Table 2 – Activation energy for single gas permeation.

Gas	E_a (kJ/mol)
H_2	8.6
CO_2	–3.2

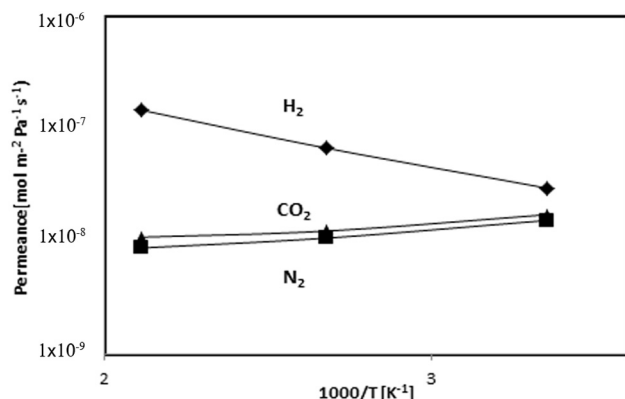


Fig. 5 – The temperature effects on the pure gases permeance for silica membrane (sample 3) at $P = 2$ bar.

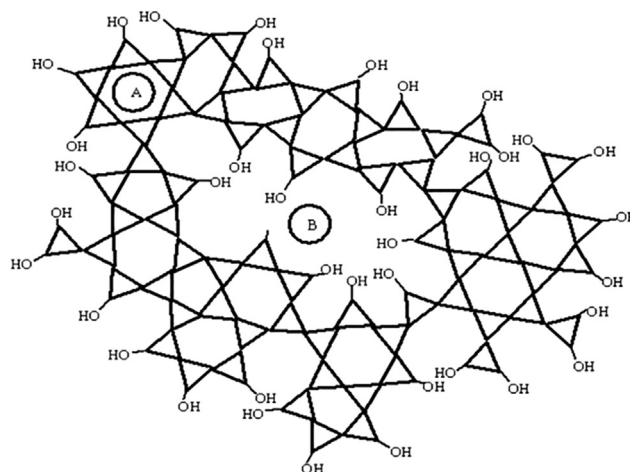


Fig. 6 – Schematic representation of the gas transport sites in amorphous silica membranes; (A) siloxane rings accessible only to small molecules and (B) pores between silica clusters accessible to bigger molecules.

Table 3 – H₂/CO₂ and H₂/N₂ permselectivity at $\Delta P = 2$ bar and a mean pressure of 2 bar.

Temperature	Room temperature	100 °C	200 °C
H ₂ /CO ₂	4.7	9.4	23.4
H ₂ /N ₂	7.3	11.6	31.3

been described in Ref. [14] with a bimodal structure for silica membranes, in which He (and also H₂) is mainly transported through siloxane rings (containing at least six Si atoms – Fig. 6A), while N₂ transport should occur only through the silica cluster pores (Fig. 6B).

Table 3 shows the permselectivity of H₂/N₂ and H₂/CO₂ at room temperature, 100 °C and 200 °C. As seen, the H₂/N₂ and H₂/CO₂ permselectivities increase with temperature. This is because H₂ molecular movements are activated by temperature and CO₂ and N₂ permeances decrease with increasing temperature.

Conclusions

The α -alumina tubular supports were modified with γ -alumina intermediate layers. For synthesis of γ -alumina, two precursors, namely aluminum-tri-sec-butylate and aluminum hydroxide salt which is much cheaper than the alkoxide were investigated. The synthesis of γ -alumina layer using the aluminum hydroxide source was investigated by two acid and base catalyzing methods. For sample catalyzed by base no effective layer was observed, while for sample catalyzed by acid an effective layer was distinguished via SEM images. The N₂ permeance of this layer showed that after modification of support the Knudsen diffusion can be dominant mechanism. These results are similar to SEM results and N₂ permeance experiments of sample 3 in which substrate is coated with aluminum tri-sec-butylate sol. However, the synthesized layer is loose and has no good adhesion to the substrate. Nevertheless, use of aluminum hydroxide can be promised to synthesis of γ -alumina layer; the membrane was synthesized on the modified support with aluminum tri-sec-butylate sol.

The silica membrane layer was synthesized by repeating the sol–gel procedure on sample 3. In the synthesized nanostructured silica membrane, the main mechanism of H₂ and CO₂ gases permeance was the activated molecular sieving. It was observed that as the temperature increases, the hydrogen permeance increases, while for carbon dioxide, it decreases significantly. So, according to Arrhenius relation the activation energy of hydrogen molecules is positive, however it is negative for CO₂ molecules. N₂ gas molecules permeance decreases with increasing temperature. This is due to the presence of larger pores in the silica thin film, which Knudsen diffusion of the nitrogen molecules takes place. Moreover, with increasing temperature, permselectivity of H₂/CO₂ and H₂/N₂ increases from 4.7 and 7.3 at room temperature to 9.4 and 11.6 at 100 °C and to 23.4 and 31.3 at 200 °C, respectively.

Nomenclature

d_k	Kinetic diameter
E_a	activation energy, kJ mol ^{−1}

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