Nanostructured Palladium-Doped Silica Membrane Layer Synthesis for Hydrogen Separation: Effect of Activated Sublayers

Masoud Majidi Beiragh, Ahmad Gholizade Atani, Nesa Rafia, Ali Akbar Babaluo*, Mohammad Javad Vaezi

Nanostructure Material Research Center, Sahand University of Technology, P.O.Box 51335-1996, Tabriz, Iran

Abstract

Palladium doped silica membranes were synthesized by the sol-gel method using two different procedures. The first palladium-doped silica membrane (M1) was synthesized with a coating of four layers of silica-palladium sol. The second membrane (M2) was synthesized with a coating of two silica layers followed by a coating of two silica-palladium layers. Scanning electron microscopy (SEM) proved the formation of uniform γ-alumina interlayers on the supports. SEM results for M1 showed that synthesis of a membrane with this procedure leads to the formation of crack on the membrane selective layer. Single gas permeation measurements of H_2 and N_2 were carried out at room temperature, 100 °C and 550 °C. Gas permeation results revealed that Knudsen diffusion was dominant in permeation of these gases through membrane M1 while the dominant mechanism in permeation of gases through membrane M2 was activated transport which has exhibited different behavior in comparison with M1. This result is due to the activated sublayers of membrane M2. In this case, H_2 permeance increases and N_2 permeance decreases with increasing temperature, leading to better separation perforamce of membrane M2 over M1 in separation of H_2. Therefore, using the activated silica sublayer in the synthesis of M2 can be used as a high potential method to synthesize a selective palladium-doped silica membrane.

1. Introduction

Today, hydrogen is introduced as a clean energy carrier and a key solution for different energy issues such as global climate change and local air pollution. Hence, demand for hydrogen production has significantly increased in recent years. The conventional processes to produce hydrogen are coal gasification, steam

methane reforming and water-gas shift reaction. In these processes, hydrogen separation and purification is a crucial step for hydrogen production. Several processes such as pressure swing adsorption (PSA), cryogenic distillation, and membrane separation can be used for separation and purification of hydrogen. Among these, the membrane separation process can provide many benefits over conventional separation processes (PSA and cryogenic distillation) due to its inherent advantages such as low cost, high energy efficiency, simplicity and flexibilty [1-3]. Among the utilizied membranes, microporous silica membranes shows good potential for hydrogen separation due to their molecular sieving properties at a wide range of temperatures. The permeation of gases through the silica membranes follows temperature dependency flux or activated transport. This property causes better separation of small molecules, such as H_2 and He, from molecules with larger kinetic diameter, such as N_2, CO_2, and CH_4, at high temperatures [4-6]. Microporous silica membranes are mainly fabricated by dip-coating the synthesis sol on tubular porous ceramic substrates. In this kind of membranes, high quality and performance of selective layer are highly associated with interaction of selective layer and the membrane support. So, modification of the main support has an important role in preparing membranes with high performance. To address this issue, most silica-derived membranes reported in the literature are deposited on an alumina-based support modified by γ-alumina interlayers with an average pore size in the range of 2-4 nm [7, 8]. The support modification is crucial to prevent infiltration of silica sol into pores of the alumina support and to generate a uniform defect-free silica layer [19].

A major drawback with silica membranes is their low hydrothermal stability. So, the morphology of silica alters when exposed to water and water vapor especially at high temperatures. This is mainly attributed to densification of the microporous silica network by the breakage of siloxane bonding, the formation of silanol groups, and their subsequent rearrangement into the siloxane network. [2, 9]. One of the effective mechanisms to overcome this problem is doping transition metals into the amorphous silica network. Doped metals may exist as metal ions, covalently bound compounds, or tiny crystals dispersed in amorphous silica networks and increase stability under hydrothermal conditions [9-15]. Kanezashi and Asaeda prepared Ni-doped silica membranes with different Ni contents (Si/Ni = 4/1-1/1) by the sol–gel technique for hydrogen separation at high temperatures. These membranes showed suitable stability and separation performance after exposure to steam [12].

Smart et al. synthesized high quality cobalt oxide silica membranes on alumina supports using a sol-gel and dip coating method. These membranes were tested for single gas permeation of He, H_2, N_2 and CO_2 at temperatures up to 600 °C and feed pressures up to 600 kPa and exhibited proper separation performances [13]. Lee et al. synthesized Pd particle-deposited microporous silica membranes using a vacuum-impregnation method. These membranes exhibited H_2 permeance of 2.3×10^{-8} mol. m^{-2}. s^{-1}. Pa^{-1} and a H_2/N_2 permselectivity of 120 at 350 °C [14]. Kanezashi et al. synthesized palladium-doped silica membranes using the sol-gel method. They dispersed Pd particles 2–30 nm in size in a SiO_2 layer, and the separation layer thickness was approximately 300 nm. Single gas permeation through the Pd–SiO_2 membranes was investigated in a temperature range of 300–500 °C. According to their results, H2/He selectivity increased by increasing the Pd content in SiO_2 and was higher than SiO_2 membranes [15]. Also, binary metals, such as PdCo [20], FeCo [21] and LaCo [22], were incorporated during sol preparation which resulted in a wide range of beneficial effects. Because of the high affinity of Hydrogen to Pd, which in the solution-diffusion mechanism allows only H_2 molecules to permeate, Pd particles in silica networks are expected to be a H_2 permeation path resulting in an increase in the H_2 separation performance. Also, the incorporation of Pd particles to amorphous silica networks can prevent densification in hydrothermal conditions similar to Ni and Co-doped silica membranes [14,15]. To the best of our knowledge, the number of studies done in this area is limited.

In the present study, palladium was selected as a doping metal into a silica network in order to improve the H_2 permeability of the amorphous silica membranes. These kind of membranes were synthesized by two different procedures on α-alumina supports modified by γ-alumina interlayers. Four layers of silica-palladium were coated in the synthesis of membrane M1, , and two layers of silica were coated followed by coating two layers of silica-palladium in M2. The morphology of the γ-alumina interlayers and silica layers were investigated by SEM images. The structural properties of the palladium-doped silica membranes were studied using XRD patterns. Comparison between these two distinct procedures is done by gas permeation tests at different temperatures in order to investigate the effects of activated silica sublayers on the separation performance of these membranes. H_2 and N_2 pure gas permeation measurements were carried out at room temperature, 100 °C, and 550 °C to characterize the quality of the synthesized Pd-doped silica membranes.

2. Experimental

2.1. Materials

In this experimental study, the material sources were used as follows: tetraethyl orthosilicate (TEOS, 98%, Sigma) as the silicon source, nitric acid (HNO_3, 65%, Merck) as catalyst for the silica sol preparation, ethanol (EtOH, 99.9%, Merck) as the solvent, polyethylene glycol (PEG, Merck, Molecular weight: 35,000) as the stabilizer, aluminum-tri-sec-butylate (97%, Merck) as the source of γ-alumina, and palladium(II) chloride ($PdCl_2$, 59% Pd, Merck) and hydrogen chloride (HCl, 37%, Merck) as the catalyst for silica-palladium sol preparation.

2.2. Membrane supports

The tubular α-alumina supports purchased from Danesh Pazhouhane Sanate Nano Co. (DPSN, Tabriz,

Iran) with a thickness of 4 mm, diameter of 12 mm, length of 70 mm, average pore size of 0.57 mm and average porosity of 47.2% were used for membrane synthesis.

2.3.γ-alumina interlayer synthesis

The synthesis of a γ-alumina interlayer on the surface of the α-alumina supports was carried out by dip coating the supports into a boehmite sol. The boehmite sol was prepared by adding aluminum-tri-sec-butylate into distilled water. The obtained solution was peptized with nitric acid. The resulting colloidal suspension was kept boiling until most of the butanol was evaporated. Then, a PEG solution in distilled water was added to the solution. The final solution was refluxed for 16 h to form stable boehmite sol. The boehmite sol preparation procedure was described in details in our previous works [16,18]. The dip-coating process was performed at room temperature. The withdrawal speed and immersion time of dip-coating were 60 mm. min⁻¹ and 10 s, respectively. Then, the boehmite-coated support was dried at 40 °C for 24 h followed by calcination at 700 °C for 3 h with a heating/cooling rate of 0.5 °C. min⁻¹.

2.4. Synthesis of silica and palladium-doped silica membranes

Silica membrane layers were synthesized by dip-coating multilayer γ-alumina supports in silica sol. The silica sol was prepared as described in our previous works [16, 18].

Palladium-doped silica membrane layers were synthesized by dip-coating multilayer γ-alumina supports in silica-palladium sol prepared as follows: 0.75 g of TEOS was added into 99.25 g of water followed by 1.49 g of $PdCl_2$ and 1 g of HCl. This solution was refluxed for 12 h at 60 °C in order to progress hydrolysis and condensation reactions.
After preparation of silica-palladium sol, the surface modified supports were immersed into the mentioned sol for 10 s with a withdrawal speed of 60 mm. min⁻¹.

After each coating step, the membrane layers were calcined at 550 °C for 3 h with a heating/cooling rate of 0.5 °C. min^{-1}. It should be noted that calcination of palladium-doped silica membranes were performed in hydrogen atmosphere.

According to the procedures mentioned above, two types of membranes were prepared and coded as M1 and M2. The membrane M1 was synthesized by coating four layers of palladium-doped silica, and membrane M2 was synthesized by coating two layers of silica followed by two layers of palladium-doped silica.

2.5. Gas permeation measurements

The gas permeation measurements were carried out at room temperature, 100, and 550 °C using a custom-made gas permeation unit as shown in Fig. 1. The membrane ends were sealed in the module using graphite o-rings which enables measuring at high temperatures. Pure H_2 and N_2 gases were fed to the upstream of the membrane. The permeance was measured by a bubble flowmeter. Finally, the permselectivity was calculated by the ratio of single gas permeances.

3.Result and Discussion

3.1 Membrane layers characterizations

Fig. 2 shows the surface and cross section SEM images of α-alumina supports modified by a γ-alumina layer. As can be seen, a crack-free and uniform γ-alumina layer with 2 µm thickness was formed on the supports. Given that, the synthesis of a thin and selective microporous silica membrane is highly assoiciated with a uniform sublayer with small pore size. Therefore, the γ-alumina layer on the α-alumina support as an intermediate layer is ideal for coating silica layers to achieve ultra-microporous silica-derived membranes.

Fig. 3 shows the cross section and surface SEM images of M1 membrane after four coatings of palladium-doped silica on the modified supports. As can be seen, although a proper palladium-doped silica layer has formed on the γ-alumina interlayer, this layer is not crack-free. This might be due to the accumulation of Pd particles on some parts of the γ-alumina interlayer surface causing a reduction in the thickness of the interlayer. So that, the agglomerated particles were detached after repeating the coating

Fig. 1. Schematically presentation of custom permeation outfit
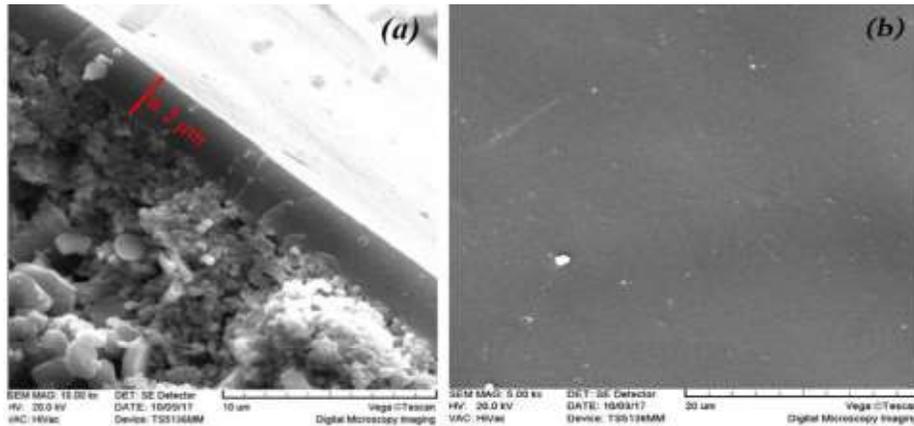
Fig. 2. The a) cross section and b) surface SEM images of α-alumina supports modified by a γ-alumina interlayer
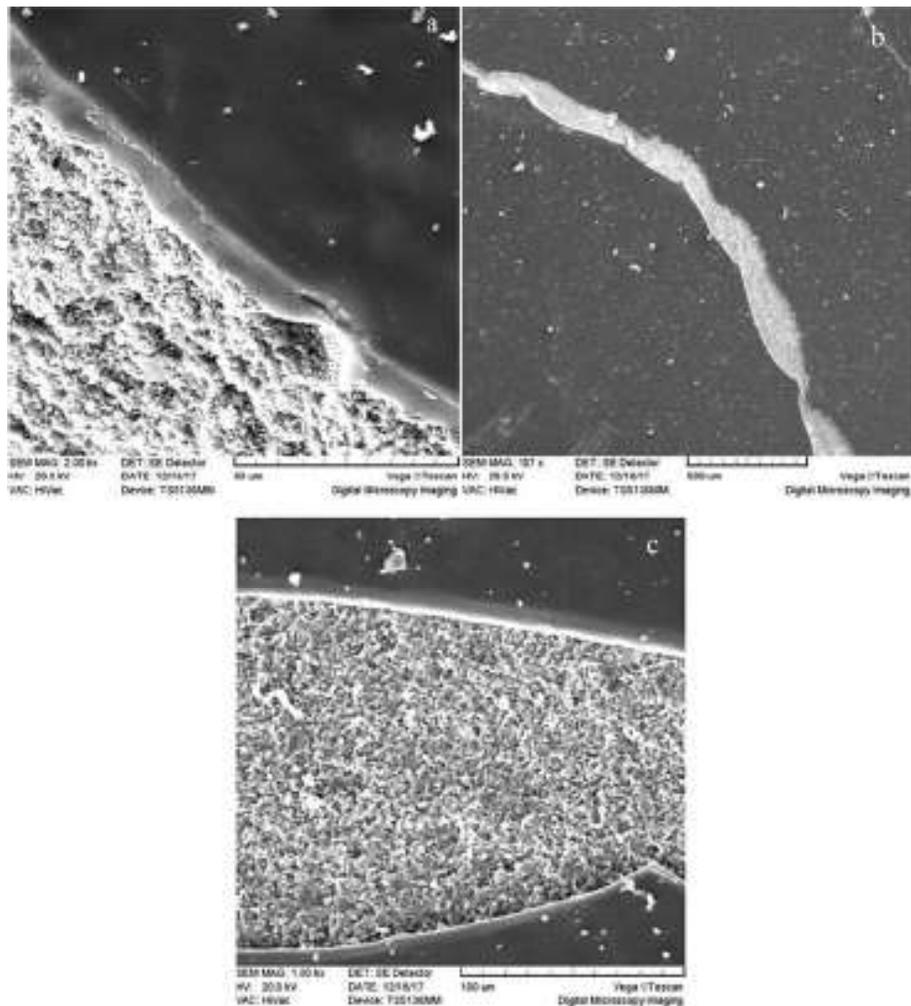
Fig. 3. The cross section and surface SEM images of M1 after four coatings of palladium-doped silica on the modified support

step four times which leads to the formation of some cracks as shown in Fig. 3. The existence of these micrometric cracks on the surface of the membrane M1 can obviously affect its separation performance in a negative way.

Fig. 4 shows the cross section and surface SEM images of the M2 membrane after two coatings of silica on the modified supports. As can be seen, a crack-free nanostructured silica layer with a 2 μm thickness was uniformly formed on the γ-alumina
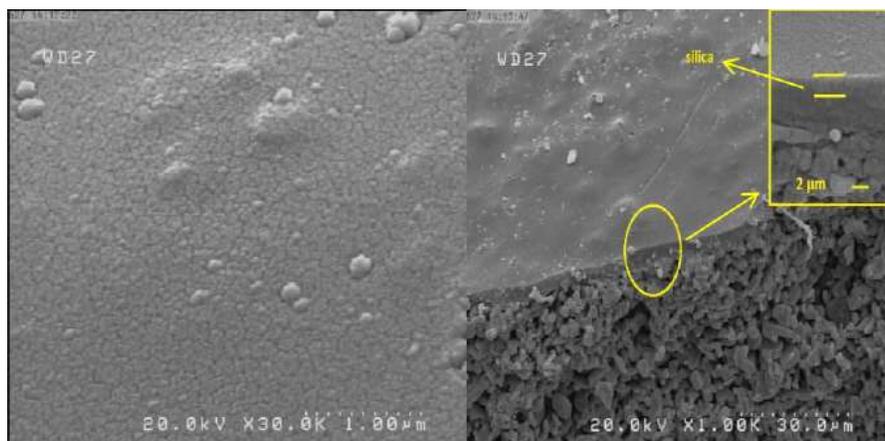
Fig. 4. The cross section and surface SEM images of M2 after two coatings of silica layer on the modified support

interlayer. This uniform sublayer with a reduced thickness can prevent the accumulation of Pd particles on different parts of the interlayer surface and ensures the synthesis of an activated silica layer on the modified support.

Fig. 5 shows the XRD pattern of a palladium doped silica membrane synthesized on a modified α-alumina support. Marked peaks at $2\theta = 40°$ and $47°$ are indicators of palladium presence within the structure [15, 23]. Other marked peaks are related to α-alumina and γ-alumina which are indicators of ceramic support and a modifying interlayer, respectively. The low intensity of the Pd peaks is due to a small amount of palladium relative to the amount of alumina in the membrane structure.
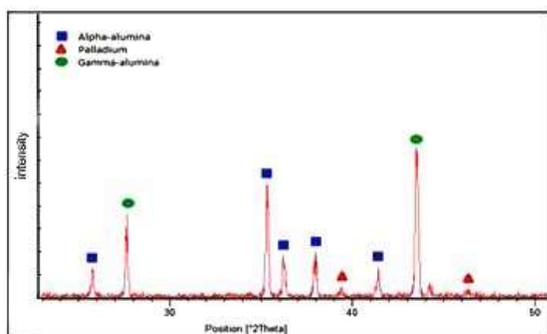
Fig. 5. XRD spectrum of palladium doped silica membrane

3.2 Membrane layers performance

Fig. 6 shows the permeance of H_2 and N_2 as a function of pressure difference through the M1 membrane at

room temperature, 100 °C, and 550 °C. As can be seen, permeance of H_2 and N_2 through the M1membrane decreases by increasing temperature. Furthermore, Fig. 7 shows that H_2/N_2 selectivity for this membrane decreases when the temperature increased from room temperature to 550 °C. Therefore, the results of gas permeation tests for membrane M1 demonstrate that after coating four layers of silica-palladium sol, no activation occurred even at 550 °C and the governing Knudsen diffusion mechanism confirms the formation of defects during the membrane synthesis.

Fig. 8 shows the permeance of H_2 and N_2 as a function of pressure difference through membrane M2 at room temperature, 100 °C, and 550 °C. As can be seen, increasing temperature increases the permeance of H_2 while it decreases the permeance of N_2. In the other words, H_2 displays positive and N_2 displays negative activation energy. Consequently, H_2/N_2 selectivity for this composite membrane (M2) increases from 3.5 to 6 when the temperature increased from room temperature to 550 °C, as shown in Fig. 9. These results confirm an acceptable consistency with an activated transport mechanism, indicating the formation of a uniform silica-palladium layer [20]. Therefore, as a final result an activated silica sublayer coated before the silica-palladium layer had a significant influence on the performance of a palladium-doped silica membrane with activated transport properties.
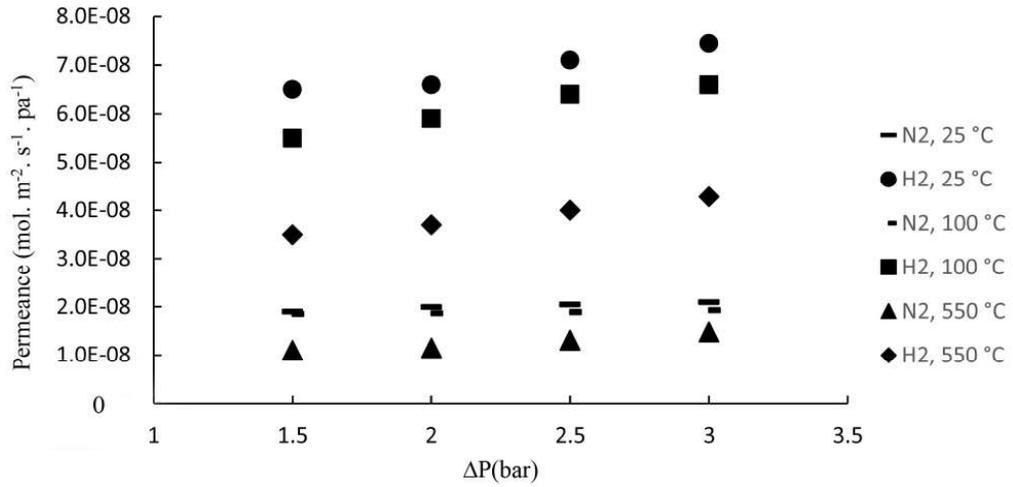
Fig. 6. H₂ and N₂ permeances as a function of pressure difference through membrane M1 at different temperatures
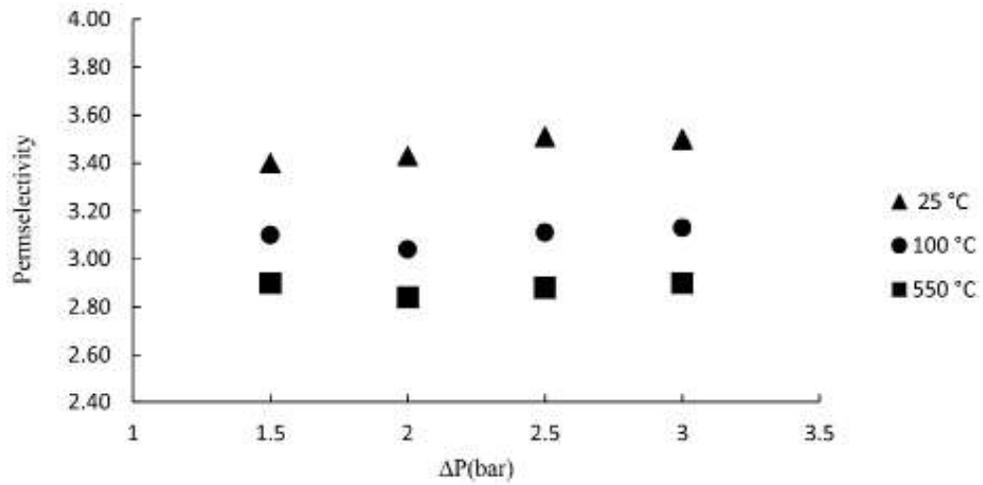
Fig. 7. H₂/N₂ permselectivity as a function of pressure difference for membrane M1 at different temperatures
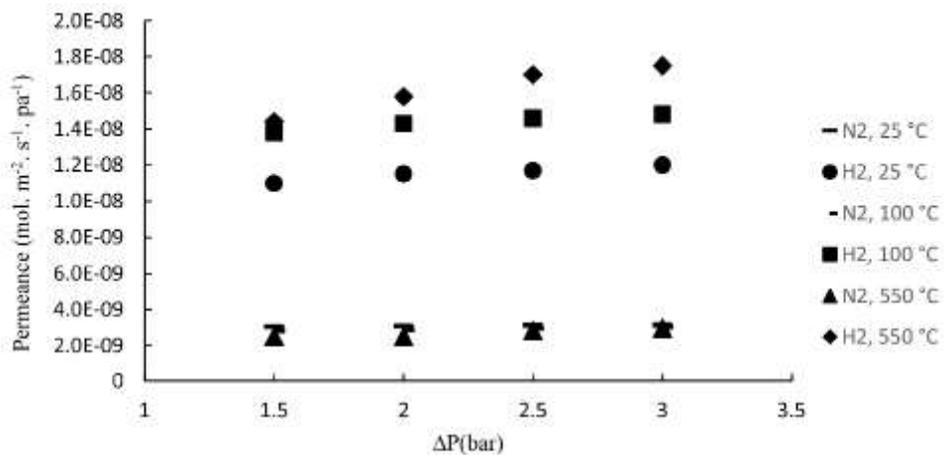
Fig. 8. H₂ and N₂ permeances as a function of pressure difference through membrane M2 at different temperatures
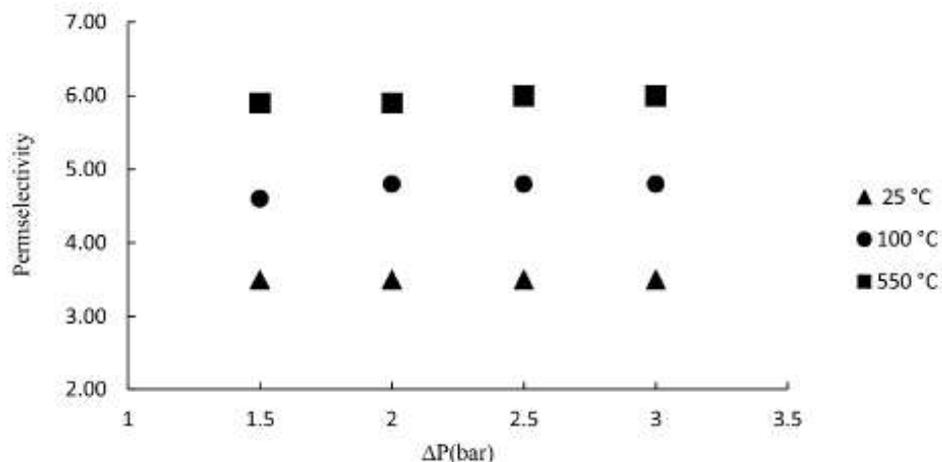
Fig. 9. H_2/N_2 permselectivity as a function of pressure difference for the M2 membrane at different temperatures

4.Conclusions

Comparison of two separate procedures for synthesizing Pd-doped silica membranes was performed. Palladium peaks in the XRD pattern revealed the presence of palladium within the structure of silica membranes. Results of gas permeation tests   for membrane M1 showed no activation occurred and the dominant gas separation mechanism was Knudsen diffusion. It can be concluded that coating four layers of as-prepared silica-palladium sol directly on the modified supports for a synthesizing palladium-doped silica membrane was unsuccessful. In contrast, membrane M2 exhibited activated transport properties, since at high temperature H_2 permeance increases and the permeance of N_2 decreases based on their activation energy. Therefore, an activated nanostructured silica layer coated as a sublayer of the silica-palladium layer significantly affected the performance of this membrane.

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