

Study of Pd Complexes Adsorption on the γ -AlOOH / γ -Al₂O₃ Layer in the Activation Step for the Preparation of Palladium Composite Membrane

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ABSTRACT: *The Pd composite membranes were fabricated by an improved electroless plating procedure. The wetness-impregnation technique was applied for ceramic substrate activation. The adsorption Pd complex on the γ -AlOOH or γ -Al₂O₃ layer was studied in this work. The obtained results showed that the Pd complexes on the γ -AlOOH layer adsorbed more than the γ -Al₂O₃ layer. Additionally, the effect of Pd precursor concentration on substrate loading was investigated. The rate of palladium deposition increases at high Pd concentrations. The resulting membrane was characterized by XRD and SEM-EDX analysis. Furthermore, permeation fluxes of the as-synthesized membrane were evaluated for various gases at different H₂ Pressure differences. The membrane permeance was determined to be 6.8×10^{-7} mol/m².s.Pa at 798 K and 1 bar under pure hydrogen. The hydrogen permeance and selectivity of hydrogen relative to other gases (CH₄, CO₂, CO, and N₂) were evaluated at 773 K. All gases exhibited dilution and inhibiting (especially CO) effects on hydrogen permeation. The prepared membrane does not seem damaged as the permeability recovered after treatment with pure hydrogen.*

KEYWORDS: *Hydrogen purification; Pd composite membrane; Wet impregnation; Electroless plating.*

INTRODUCTION

Recently, the ultra-high quality hydrogen demand has increased substantially because of its essential role in several kinds of technological applications as a clean “green” fuel of interest [1]. It can be applied in petroleum refining, petrochemical industry, semiconductor manufacturing, hydrogen fuel cell vehicles, etc. Currently,

hydrogen has been obtained with many by-products, such as the electrolysis of water, reforming process of hydrocarbon sources, gasification of coal, etc. The hydrogen produced by natural gas reforming processes is most associated with impurities such as CO, CO₂, O₂, N₂, H₂O, CH₄, etc. So, the separation of hydrogen is necessary

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for various applications. The diverse types of membranes are one of the main techniques used to separate and produce high-purity hydrogen [2-4].

Unique advantages such as high hydrogen permeability and infinite theoretical hydrogen perm-selectivity caused to Pd composite membranes have been much studied [5]. Among the possible techniques for preparation, the ElectroLess Plating (ELP) technique to date is the best one for the Pd-based composite membrane produced. In the ELP technique, Pd species are commonly reduced from the plating solution and then grow on the Pd nucleus. The Pd nuclei act as a catalyst site for Pd complexes reduced. This procedure is called pre-seeded on the substrate surface which leads to uniform coverage of Pd film on the target surface. Hence, before the Pd plating, the substrate surface is required to activate by seeding the Pd nucleation sites [6].

The sol-gel process is one of the methods for activation of the substrate surface that has been investigated recently. In this procedure, γ -AlOOH sol is modified by adding a Pd solution and then deposited by a dip-coating process for activation of the substrate surface. The advantages of this activation method are surface smoothing of the last Pd layer due to the uniformity distribution of Pd particles with high dispersion, increase of the deposition rate of Pd film on the activated substrate and increase of cohesion between the thin Pd film, and the porous substrate because of the Pd nucleus tightly adsorbed on the γ -Al₂O₃ layer [7-9]. The Pd- γ -Al₂O₃ layer was also coated on the alumina substrate. In this procedure, γ -Al₂O₃ suspension in an acidic PdCl₂ solution was employed for coating on the substrate [10]. The palladium-alumina layer was prepared using a combined sol-gel process and the electroless plating technique [11].

The deposition of metal complexes on mineral oxides (γ -Al₂O₃ layer) by the wetness-impregnation method is also investigated. In this procedure, Pd particles were coated *via* the wet impregnation method after the deposition of the γ -Al₂O₃ layer on the substrate surface. The impregnation of Pd particles in the γ -Al₂O₃ layer can be considered as an adsorption process based on the Langmuir-type model. The pH value of the impregnation solution is a vital variable in the adsorption process of metal complex ions on mineral oxides. The results displayed that the best conditions for Pd impregnation were pH 1.5-2.0 and 1.2 wt. % Pd concentration [12-14]. It seems that all the used Pd particles in this procedure can exist on the activated surfaces and be active as a catalyst site for the reduction of the Pd salt

complexes in the ELP technique. To the best of our knowledge, the adsorption Pd complex on the γ -AlOOH layer was not investigated for the activation process.

In this work, the ceramic substrate is activated by the deposition of Pd particles *via* the wetness-impregnation method. The effects of Pd particle concentration and type of layer (γ -AlOOH or γ -Al₂O₃) were investigated. Characterization of the prepared Pd composite membranes was analyzed utilizing SEM and XRD. Additionally, hydrogen flux behavior through the Pd-based composite membrane has been evaluated in the presence of several gases, such as N₂, CH₄, CO₂, CO in the feed side of the membrane module.

EXPERIMENTAL SECTION

Preparation of Pd composite membrane

In this work, the tubular alpha-alumina substrate with an average pore size of 570 nm, porosity 48%, and length 50 mm was purchased from Nanofanavar Company (Iran). Introducing an intermediate layer caused to suppression of the penetration of activated layer material into the substrate's pores. The intermediate layer was obtained by dipping the substrate in the TiO₂-Boehmite suspension for 30 seconds. The system was dried for 24 h at ambient temperature and sintered vertically at 1273 K for 3 h in an electric furnace. This procedure was repeated two times [15].

The γ -AlOOH sol was achieved by adding aluminum tri-sec butoxide (purity 97%, Merck Co.) and PEG solution dropwise to distilled water at 80°C under vigorous stirring. Stabilization of sol was obtained by the addition of nitric acid (pH~3-4). The sol was refluxed for 16 h to form a stable γ -AlOOH sol. The porous substrate was coated by the dip-coating method in the prepared γ -AlOOH sol for 10 s. Then, the system was dried at ambient temperature at least for 24 h.

For the preparation of wetness impregnation solution, PdCl₂ particles (59 wt. % purity, Merck Co.) by difference concentrate (2.8×10^{-3} & 5.6×10^{-3} M) were added to distilled water. The hydrochloric acid (37%, Merck) was added to the PdCl₂ solution as a complex agent. Two procedure was applied by wetness impregnation of Pd particles including:

(I) The coated substrate by γ -AlOOH layer was calcined at 873 K for 3 h to obtain the γ -Al₂O₃ layer. Then, the formed γ -Al₂O₃ layer was immersed in an impregnation cell by Pd concentrate about 2.8×10^{-3} M (M₁) at 3 h at ambient temperature.

(II) The coated substrate by γ -AlOOH layer was immersed in the impregnation cell by Pd concentrates about 2.8×10^{-3} M (M_2) and 5.6×10^{-3} M (M_3) at 10 min at ambient temperature.

Following the impregnation method, the substrate was dried in an electric furnace for 10 h at 343 K. All of the cases were calcined at 873 K for 3 h and reduced in hydrogen atmosphere during 10 h at 773 K to form the catalytically active Pd species.

For depositing the Pd layer by the ELP method, the activated substrate was immersed in a well-stirring bath vessel containing plating Pd solution. The plating solution consisted of Pd chloride (PdCl_2 , 3.6 g/L, Merck) as a metal source, ethylene diamine tetraacetic acid disodium salt (Na_2EDTA , 76 g/L, Merck) as a chelating agent, and hydrazine (N_2H_4 , 10 ml/L, Acros Organics Co.) as the reducing agent. To adjust the pH value, ammonia (NH_3 25%, 650 ml/L, Merck) was added to the plating solution to maintain it in the range of 10-11. The ELP bath temperature was kept at 343 K with a water jacket. Pd particles were normally prepared by reduction of the plating solution containing Pd complexions with a reduction agent. The as-deposited Pd film was rinsed with ammonia solution and deionized water in sequence. Then, it was dried overnight in an oven at 393 K for 12 h. Finally, the formed Pd film is annealed under the hydrogen stream. The annealing treatment helps the Pd species to agglomerate together to form a denser film. The ELP procedure was repeated to achieve the gas-tight permeation of the prepared Pd composite membrane.

Membrane characterization

X-Ray Diffraction analysis (XRD, Siemens D5000) was used to determine the crystallinity of Pd particles in the activated layer and the structure of the Pd composite membrane. To study the surface morphology of the activated substrate, the prepared Pd membrane, and estimate the thickness of the Pd membrane, scanning electron microscopy (SEM, Can Scan MV2300 Check Republic) was used. The distribution of Pd particles in the activation layer was determined by SEM-EDX analysis.

Gas permeation measurements

The prepared Pd composite membranes were mounted in a homemade stainless steel module. The Ar leak measurements were carried out at a pressure 3 bar and

ambient temperature to determine possible pinholes in the Pd film.

For high-temperature application, the membranes were sealed using graphite packing that could withstand temperatures up to 873 K. It was heated to the desired temperature in flowing Ar. The performance of Pd composite membrane was measured by introducing H_2 pure gas at different temperatures at 1 bar. The hydrogen and Ar selectivity (pure gas flux ratio) was determined in the range of 0.5-3 bar at 773 K. Finally, the volumetric flow rate of permeated hydrogen from the experiments of separation H_2 - N_2 , H_2 - CH_4 , H_2 - CO_2 , and H_2 - CO gas mixture was measured as a function of trans-membrane pressure. The pressure of the permeate side was always at the atmospheric pressure and the permeate flow was measured using a bubble flow meter at the desired temperature.

RESULTS AND DISCUSSION

Characterization of Pd composite membrane

The impregnation effect of Pd complexes ($(\text{PdCl}_4)^{2-}$ on γ - Al_2O_3 (M_1) and γ -AlOOH (M_2 and M_3) layers was investigated. The surface polarization of boehmite is a function of the pH due to its amphoteric nature. The adsorption of cation or anion is possible if the pH of the solution is higher or lower than the isoelectric point of boehmite (around 7.5). Tetrachloropalladate ($(\text{PdCl}_4)^{2-}$) is an anionic complex and adsorption of Pd(II) complex on the boehmite can be performed at a $\text{pH} < 7.5$. So, the acidic medium was applied in this work.

The morphology of the activated substrates was studied by SEM images (Fig.1). There was no obvious structure difference among all cases. In addition, the EDX spectra show that Pd is distributed on the membrane surface and Pd loading was relatively low in M_1 substrate

After Pd plating on M_1 , M_2 , and M_3 substrates, the experimental results showed that no dense Pd layer was formed on the M_1 substrate. However, the Pd plating process was successfully done on the M_2 substrate for 15 h. It was concluded that the M_1 substrate sufficiently was not activated. Generally, the Pd complex was adsorbed on the hydrated γ - Al_2O_3 layer. The results showed that a lyogel layer on the γ - Al_2O_3 layer (M_1) could not be formed after 3 h immersing while the interaction between the Pd(II) complexes and the γ -AlOOH layer (M_2) was appropriate after 10 min immersing.

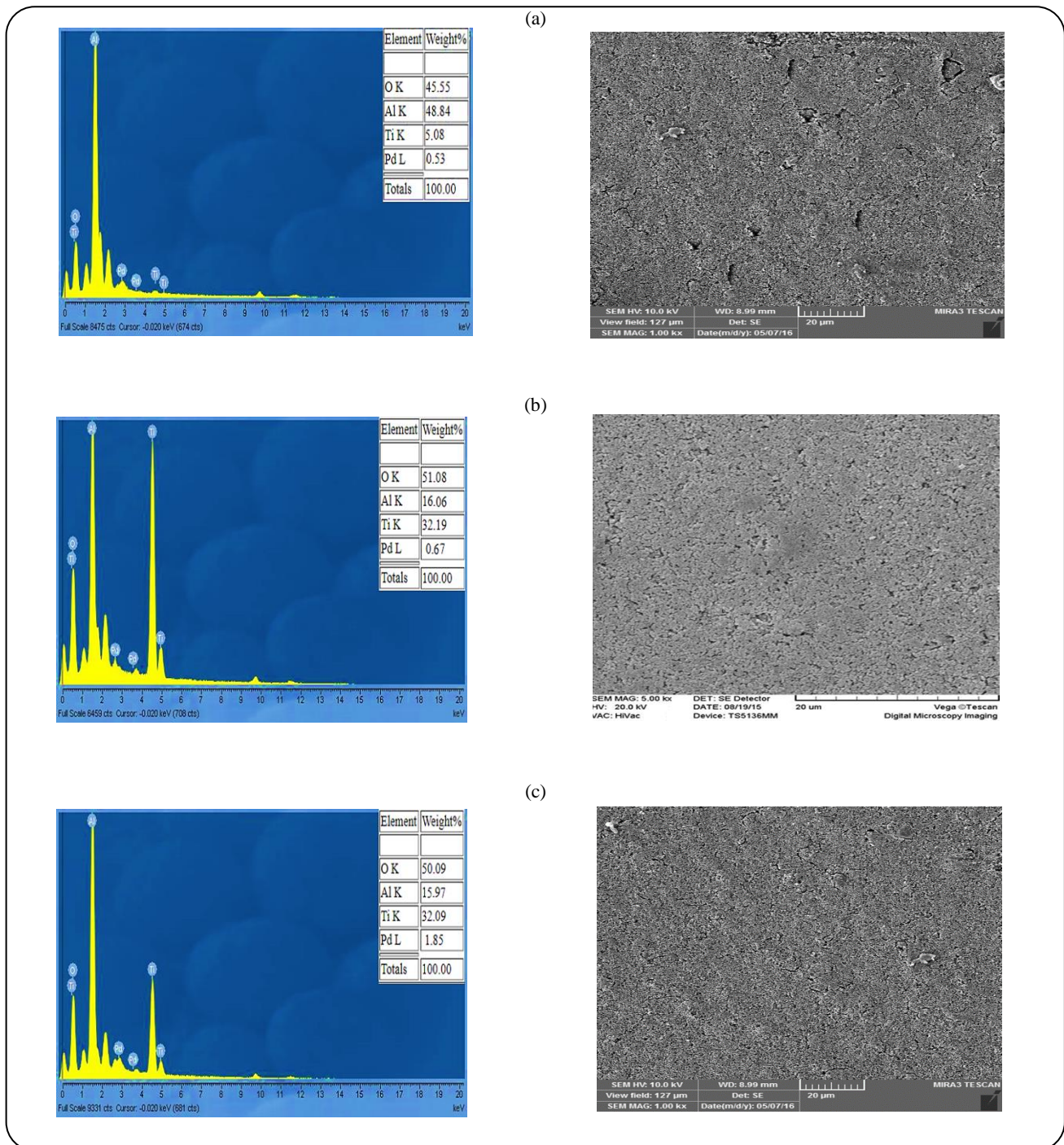


Fig. 1. SEM image and the corresponding EDX spectrum of (a) M₁, (b) M₂, and (c) M₃ substrate.

To reduce plating time, a higher concentration of Pd particles was used on γ -AlOOH layer (M₃). The dense Pd layer was plated for 5 h for the M₃ substrate. It was shown that the adsorption of the Pd complex was improved at high Pd concentrations. Therefore, the Pd plating only was done twice on M₃ substrate to characterize and

perform an investigation of the final prepared Pd composite membrane.

Surface and cross-sectional SEM images of a final synthesized Pd composite membrane (M₃) were presented in Fig. 2. As shown in Fig. 2, the smooth and no visible defects or pinholes on the Pd membrane surface were observed

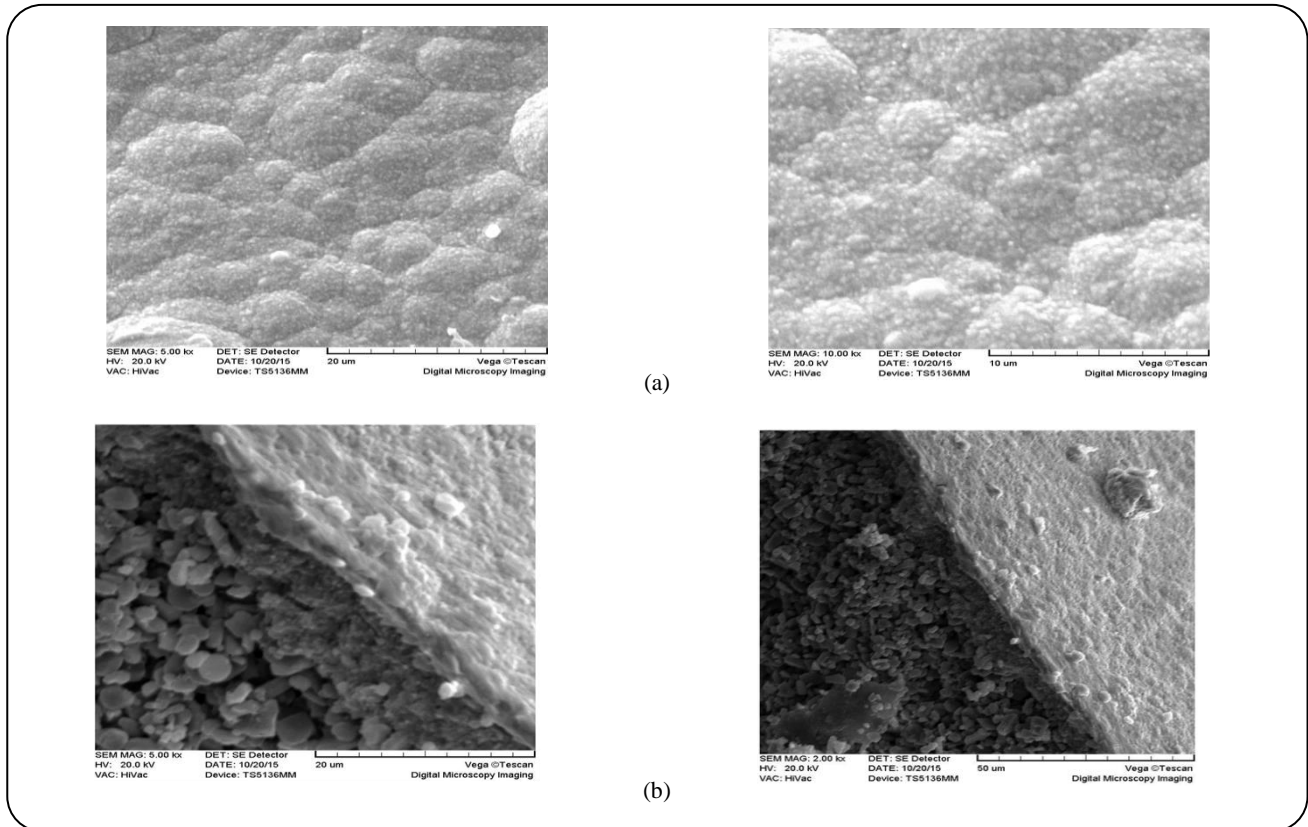


Fig. 2: SEM images of the (a) top and (b) cross-section of M₃ membrane.

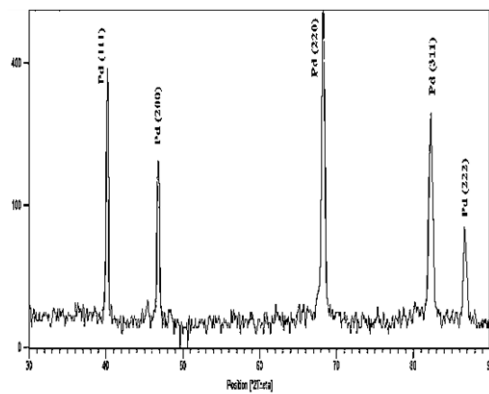


Fig. 3: XRD Analysis of M₃ membrane after Pd plating.

observed for the M₃ membrane. Fig. 3 gives the XRD pattern of the M₃ membrane after Pd plating via ELP method. The presence of a pure Pd layer in FCC structure was observed after Pd plating.

Performance investigation of Pd composite membrane

Ar leak was measured to determine possible pinholes at $\Delta P=3$ bar. The prepared membrane was gas-tight for Ar

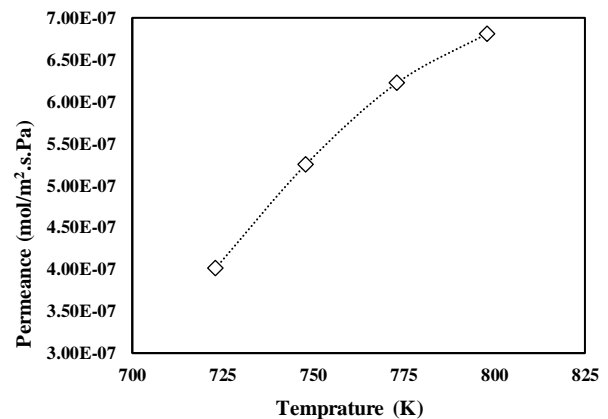


Fig. 4: H₂ flux of Pd membrane as a function of temperature.

and suitable for performance study. Fig. 4 exhibits the pure H₂ flux of the membrane at various temperatures and $\Delta P=1$ bar. The H₂ flux increased at high temperatures that were consistent with the solution-diffusion mechanism of H₂ transferring through the Pd layer.

Sievert's law was used for the explanation of H₂ flux through Pd film (J_{H_2}) so that the equation can be written as follows:

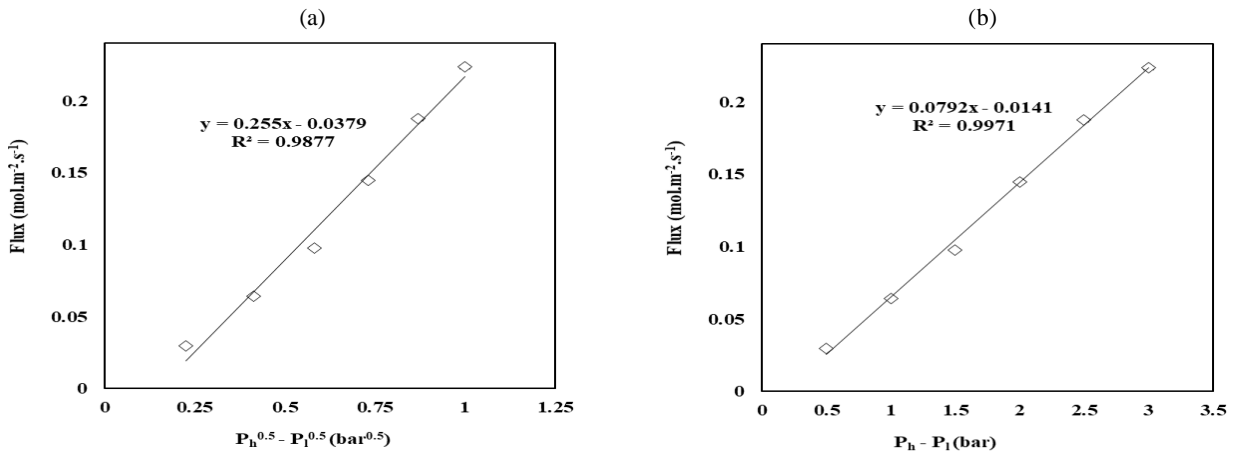


Fig. 5: H₂ flux versus pressure difference at various pressure exponents (a) $n=0.5$ and (b) $n=1$ at $T=773$ K..

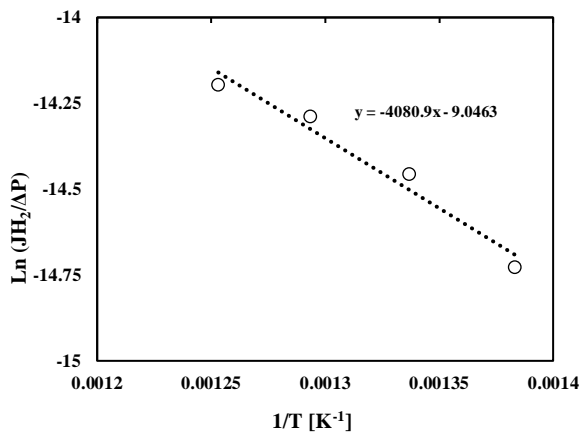


Fig. 6: Logarithmized pure H₂ permeance vs. reciprocal temperature and the linear fit for determination of the apparent activation energy.

$$J_{H_2} = P_0 \exp\left(-\frac{E_A}{RT}\right) [P_h^n - P_l^n] \quad (1)$$

In this equation, three constants can be determined: the pre-exponential factor (P_0), the apparent activation energy (E_A), and the exponent (n). In Fig. 5, the hydrogen permeation flux was measured as a function of trans-membrane pressure at $n=0.5$ and 1. It can be seen that the H₂ flux increased at high trans-membrane pressures. With the experimental data in Fig. 5, the optimal value of n was derived by linear curve fit with R^2 above 0.9971 according to Eq. (1).

The relationship between the H₂ flux and the temperature can be described by an Arrhenius law as follows:

$$\ln\left(\frac{J_{H_2}}{\Delta P}\right) = \ln(P_0) - \frac{E_A}{RT} \quad (2)$$

Fig. 6 shows an Arrhenius plot of the H₂ flux versus the reciprocal temperature. The apparent activation energy (E_A) was achieved from the slope of the fitted graph and equal to $E_A=33.93$ kJ/mol. Also, with the H₂ flux measured at four different temperatures, four pre-exponential factors were derived with the fitted E_A of 33.93 kJ/mol. The obtained pre-exponential factors (P_0) were averaged leading to the value of 1.179×10^{-5} mol/m².s.Pa.

Mixture gas experiments

The separation behavior of the prepared Pd composite membrane was examined by feeding by H₂/CH₄, H₂/CO₂, H₂/CO, H₂/Ar, and H₂/N₂ mixtures. The permeation measurement apparatus is described in section 2.3. The Pd composite membrane was used in the permeation apparatus with gas mixture as a feed. The permeation was studied at the constant temperature 773 K. The pressure at the retentate side was set with a pressure control valve in the pressure range 1-3 bar, and the permeate side was kept at atmospheric pressure. No sweep gas was used in the measurement apparatus. The total feed gas flow rate was set at 100 ml/min and thus kept practically constant. The effect of different concentrations on the H₂ permeance through Pd composite membrane were investigated between 1-3 bar at constant temperature and total feed flow rate. After each series of tests, the membrane was fluxed with H₂ stream before starting the new test to Pd membrane surface be regenerated. The flow rate of either permeate was measured by a soap-bubble flow meter, and

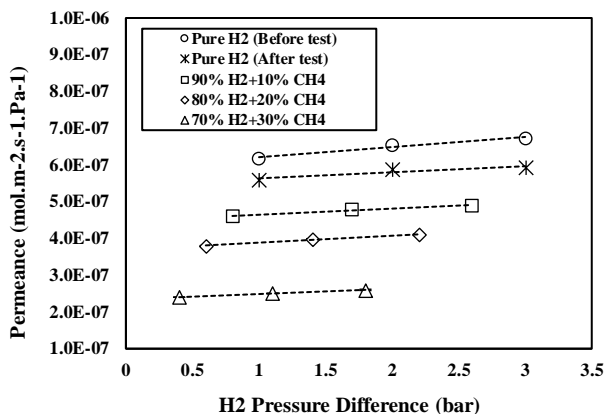


Fig. 7: H_2 permeance vs. H_2 pressure difference for different ratios of H_2/CH_4 at 773 K.

feed mixture and permeate compositions were analyzed using gas chromatography.

The experimental results indicated that the hydrogen permeability of the membrane is reduced by increasing the other gases in the feed. Decreasing hydrogen flux can be described by the dilution and inhibition effect of other gases. when hydrogen dilution in the feed increases, the hydrogen driving force and hence permeation rate decreases. The dilution effect was observed in all mixture gas experiments. In the following, the possible inhibition effects of gases were described in detail.

H_2/CH_4 mixture permeation measurement

Fig. 7 shows the dependency of the Pd membrane permeance on the feed composition and H_2 pressure difference. As shown in Fig. 7, the experimental results indicated that the hydrogen permeability of the membrane is reduced by increasing the CH_4 concentration. It can be concluded that the CH_x species ($x = 1-3$) has been created on the Pd surface at high-temperature operation and the effective Pd membrane surface was reduced. In other words, concentration polarization increased with CH_4 concentration which could block H_2 dissociation sites. The composition of the permeate gas was monitored by gas chromatography. H_2 purity on the permeate side at different trans-membrane pressures at feed mixture gas was more than 98%. The permeate H_2 concentration through Pd film has been reduced by increasing of CH_4 concentration. This is attributed to the decomposition of some CH_4 on the Pd surface and goes to the permeate side. The hydrogen permeance is almost constant after testing

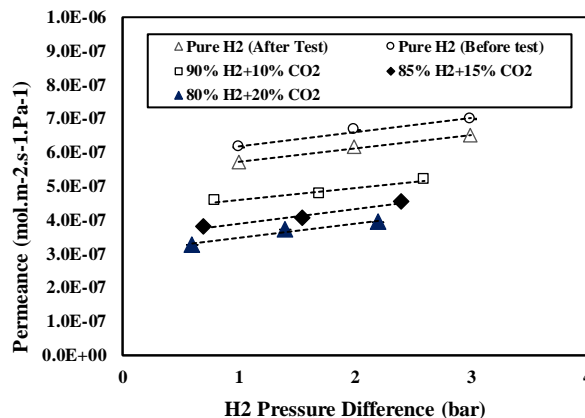


Fig. 8: H_2 permeance vs. H_2 pressure difference for different ratios of H_2/CO_2 at 773 K.

by using the H_2/CH_4 gas mixture. This indicates the good chemical stability of the Pd composite membrane.

H_2/CO_2 mixture permeation measurement

The H_2/CO_2 measurements were performed at different conditions at $T=773$ K. Fig. 8 reports the results obtained using a feed with the following composition: 10, 15, and 20 mol% of CO_2 in H_2/CO_2 mixture gas. The permeance of Pd composite membrane was significantly reduced for 20% CO_2 -80% H_2 Mixture gas.

Carbon atoms accumulate over the Pd membrane surface at high temperatures and lead to blocking some of the sites of H_2 dissociation, thus causing a H_2 permeability reduction to another side. After these tests, the Pd composite membrane was first regenerated in H_2 atmosphere for 3-4 hours at the same temperature. The permeate compositions were analyzed using gas chromatography. The obtained results showed that H_2 purity on the permeate side was more than 99% in all cases.

H_2/CO mixture permeation measurement

In this section, the influence of CO gas was studied on the Pd membrane permeance. Thus, the Pd membrane was fed using H_2/CO mixture by different concentrations containing 5 and 10 % of CO. The report of the experimental results obtained was shown in Fig. 9 at the different H_2 pressure and $T=773$ K. Increasing the CO concentration to 10 % leads to a reduction of Pd membrane permeance. It can be concluded that CO has been dissociated on the Pd catalytic surface and the trace of C atoms diffuses through the Pd film and recombine with diffused

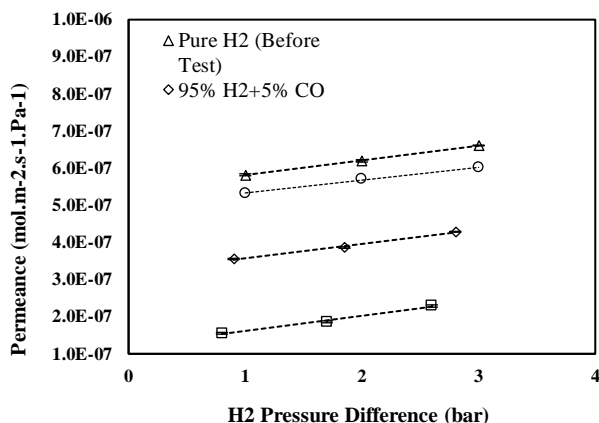


Fig. 9: H₂ permeance vs. H₂ pressure difference for different ratios of H₂/CO at 773 K.

hydrogen on the permeate side to give CH₄. In this case, the purity of permeate H₂ decreases (about 98% at 10 % CO) based on GC results.

H₂/N₂ mixture permeation measurement

For the examination of the influence of N₂ gas on the membrane permeance, experiments were carried out varying the H₂ partial pressure at a constant temperature of 773 K (Fig. 10). It could be seen that the hydrogen permeance increased with increasing H₂ pressure difference and it has been reduced by increasing N₂ concentration in the feed gas mixture. Thus, the Pd composite membrane was deactivated during the exposure to the H₂/N₂ mixture feed at 773 K. The nitrogen atoms adsorbed on the clean Pd surface and readily reacted with hydrogen to produce NH_x-type adsorbate. Consequently, these impurities were divined to be nitrogen-containing species NH_x. The impurities blocking the effective Pd membrane surface that the H₂ could not transport to the Permeate side. The composition of the permeate stream was monitored by gas chromatography and the obtained results showed that the H₂ purity in the permeate side was more than 99%.

The lifetime of the Pd composite membrane is one of the main factors as well as higher hydrogen flux and permselectivity. After each series of tests on the membrane performance, hydrogen permeation fluxes were measured for 12 hours at T=773 K and ΔP=2 bar. The obtained results showed the H₂ flux remained constant over this period. It can be concluded that the Pd clusters of the Pd/γ-Al₂O₃ layer significantly stays on the activation

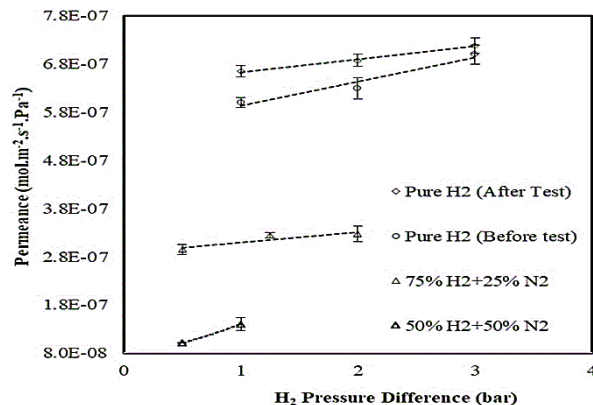


Fig. 10: H₂ permeance vs. H₂ pressure difference for different ratios of H₂/N₂ at 773 K.

layer and the Pd species act as a catalyst site for the reduction of the Pd complexes. The cohesion between the Pd film and the prepared activation layer leads to the high stability of the synthesized membrane on the activated substrate by the wetness impregnation method.

After the permeation test, Ar leak testing was carried out again at T=773 K and ΔP=1 bar. This Ar leak testing definitely that no defects and pinholes were present. After Ar leak testing, the thermal shock was applied to the membrane and again Ar leak testing was measured. It can be seen that no significant change has occurred in the amount of Ar leakage.

CONCLUSIONS

Palladium impregnated alumina layer was prepared directly by coating Pd complexes on the boehmite/ alumina layer. The best palladium membrane was achieved using the Pd- boehmite activated layer with a higher concentration of pd complexes. The Activated layer was very similar to that of the γ-Al₂O₃ layer without palladium particles. This means that the presence of Pd complexes does not change the structure of the alumina layer. Ar leak was not observed in the permeate side during leakage tests. The hydrogen permeation experiments showed that the resulting membrane had hydrogen permeance of 1-7 × 10⁻⁷ mol/m².s.Pa, depending on the operation conditions and different mixture of gases. The permeation test showed that the H₂ purity in the permeate side at different mixture gases was more than 98%. The selectivity of hydrogen to other gases decreased by increasing the CH₄/CO/CO₂/N₂ concentration.

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