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Palladium composite membrane with high reversibility of CO_2 poisoning

Zeinab Darabi[1], Ali Akbar Babaluo[1,*], Sona Jamshidi[2]

[1] Chemical Engineering Faculty, Sahand University of Technology, Tabriz, Iran.
[2] Chemical Engineering Faculty, Islamic Azad University, Tabriz Branch, Iran.

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Abstract

A palladium membrane was prepared using the electroless plating technique (ELP) for the separation and purification of hydrogen from a gas mixture. Depending on operating conditions, hydrogen flux from the membrane was in the range of 0.012-0.023 $mol.m^{-2}.s^{-1}$. The membrane performance in the presence of CO_2 was investigated. The results of the GC analysis showed that at a feed concentration of 10% CO_2 and a difference pressure of 1-2 bar, no traces of CO_2 was observed in the permeate side. However, hydrogen permeation through the membrane decreased due to the occupation of the catalytic active sites by CO_2. At the concentration of 20% CO_2 and a difference pressure of 1-2 bar, a peak of methane was detected in the permeate side by the GC analysis, this is related to the diffusion of carbon from the feed side to the permeation side. Study on the topography of the membrane surface showed short height hills and wide valleys on its surface. This topology of the surface conduced high chemical resistance of the membrane, so that the effect of CO_2 poisoning was reversible without defect creation on the membrane. Recovery of the poisoned membrane was done by exposing it to hydrogen atmosphere at 500 °C for an hour. The obtained results show that the recovery of hydrogen permeation was up to 99%.

1. Introduction

Global demand for energy is increasing day by day. Fossil fuels are the main source of energy used and it produces major environmental concerns [1]. Hydrogen, as a clean energy carrier, plays an important role in future energy supply. IEA* and EIA** express that although renewable and nuclear energy

*Corresponding Author's Fax: 04133444355
E-mail address: a.babaluo@sut.ac.ir

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* International Energy Agency
** Energy Information Administration

is growing, fossil fuels still remain as basic energy sources [2]. One of the most important applications of hydrogen is in fuel cells. Fuel cell efficiency is around 50-60%; whereas, the efficiency of steam plants and internal combustion motors are relatively 35% and 15-20%, respectively. Therefore, hydrogen usage as an energy carrier can lead to increasing the life of the available fossil fuel. Other applications of hydrogen are the synthesis of ammonia, methanol, pure metals, and semiconductors, as well as refining crude oil [3]. Common methods of hydrogen production include electrolysis, biological methods, partial oxidation and reforming of hydrocarbons; the meantime reforming of hydrocarbons is the most important methods of hydrogen production and about 48 percent of hydrogen produced in the world is achieved from natural gas reforming [4, 5]. Various technologies are used for isolation and purification of hydrogen such as absorption by the solvent, absorption by the pressure swing, cryogenic method and membrane separation processes. Among these methods membrane separation, as a new technology, has high potential in reducing operating costs, systems simplicity and energy consumption reduction [6].

Due to their high permeability coefficient (at least one order more than other metals with FCC structure) and high surface activity needed for the separation of hydrogen molecules into atoms, palladium and its alloy are widely used for separation and purification of hydrogen [2]. One of the problems of palladium membranes is membrane poisoning during palladium surface contact with hydrogen sulfide, thiophene, arsenic, unsaturated hydrocarbons, mercury, chlorine compounds and coke. Coke is created when the membrane comes into contact with CH4, CO_2 and CO. Permeability and selectivity of palladium membranes are reduced after exposure to coke at high temperatures. This phenomenon may be due to the influence of carbon atoms penetrating into the palladium lattice, whereby the palladium lattice expands. Palladium lattice expansion leads to membrane efficiency drop [5]. The height of hillocks on the palladium surface increased after CO_2 exposure. Increasing of hillock height caused the increasing of defect sizes and allowed other gases, except H_2, to permeate through the membrane [7]. It must be noted that both CO and CO_2 formed a bond to the palladium surface and decreased the palladium surface sites for H_2 adsorption and blocked available dissociation sites for hydrogen, resulting in a decrease in hydrogen permeation [8, 9]. Hence, in this work the surface topology of the membrane synthesized via electroless plating using the organic-inorganic activation method was studied to evaluate the influence of CO_2 on membrane surface poisoning. To the best of our knowledge, the poisoning of CO_2 on palladium membranes synthesized via organic-inorganic activation method has not been investigated. Also, the influence of CO_2 on the performance of these membranes and their poisoning reversibility has been investigated for the first time.

2. Experimental

2.1 Membrane fabrication

In this work, the ELP method was used to prepare a palladium composite membrane. For this purpose we used a modified ceramic substrate 9mm in diameter with 3-5 mm thickness, 13 cm in length, porosity of 48%, average pore diameter of 570nm and a characteristic surface roughness of 59.6nm (purchased from DPSN Co.). The substrate surface was activated by the organic-inorganic method using palladium nanoparticles in a poly ethylene glycol matrix [10]. After activation of the substrate, palladium deposition on the activated surface was done by the ELP method. The main components of the palladium coating bath included $PdCl_2$ (Merck Co.), Ethylene diamine tetra acetic acid (Na2EDTA, Merck Co.) and hydrazine (Acros Organics Co.). After any deposition of palladium, argon leakage from the membrane was measured and palladium coating was continued until the membrane show no argon leakage.

2.2 Membrane characterization and performance evaluation

Scanning electron microscopy (SEM, Cam Scan MV2300 Czech Republic) was used to study the morphology of the palladium surface.Atomic force microscopy (AFM, Thermo Microscopes) was used to study the surface topology of the membrane. In order to ensure that the membrane is dense, permeation of inert gas through the membrane in the ambient temperature was measured by a soap bubble flow meter. No argon leakage from the permeate side means that the membrane is totally dense.

For high temperature tests, a sealed membrane (by graphite gaskets) was heated to the desired temperature under argon atmosphere then the permeation of pure gases (H_2, Ar) and binary mixtures (H_2-CO_2) was measured over different pressure differences from 1 to 3 bar. An online gas chromatograph (GC) with a thermal conductivity detector (TCD) (Teif Gostar, Ind. Co.) was used to determine the composition of permeate and retentate gases. Gas mixtures were fed to the system by mass flow controllers. Finally, the amount of poisoning recovery was investigated by measuring the hydrogen permeation of the membrane before and after poisoning in the presence of CO_2.

3. Results and discussion

3.1 Argon leakage from membrane during the synthesis

As previously explained, if permeation of inert gas through the membrane at ambient temperature is zero, the palladium membrane can be claimed to be dense. In Fig.1, the argon leakage after deposition of any palladium layer at the pressure difference of 3 bar has been shown. It is obvious that the amount of argon permeation at ambient temperature, after the first palladium deposition on the activated ceramic substrate reduced from 10^{-6} to about 10^{-10} $mol.m^{-2}.s^{-1}.Pa^{-1}$. After the second stage of palladium deposition, permeation of argon decreased one more order (10^{-11} $mol.m^{-2}.s^{-1}.Pa^{-1}$). Finally, after the third palladium layer, with zero argon permeation of the membrane, coating operations have been stopped.

3.2. Morphology of the prepared membrane

A SEM micrograph of the membrane surface is shown in Fig. 2. This figure shows that the prepared palladium membrane has a uniform microstructure and its grains are closely packed together and form a dense Pd layer.

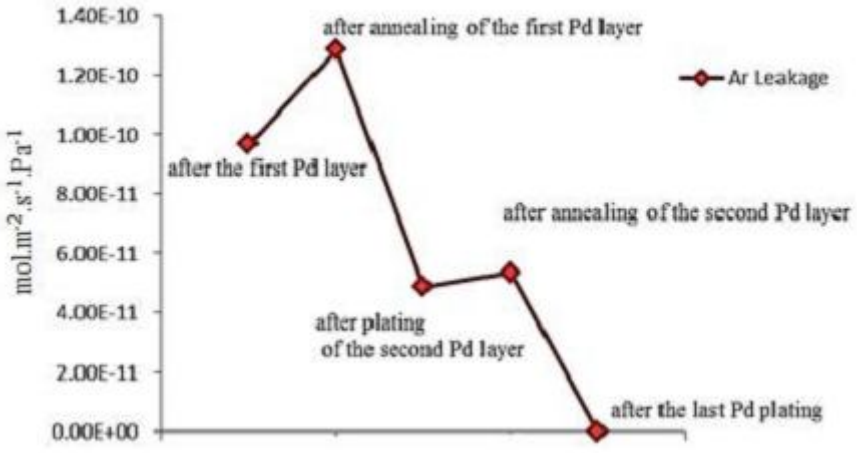

Fig. 1. Ar leakage of the membrane layers at pressure difference of 3 bar

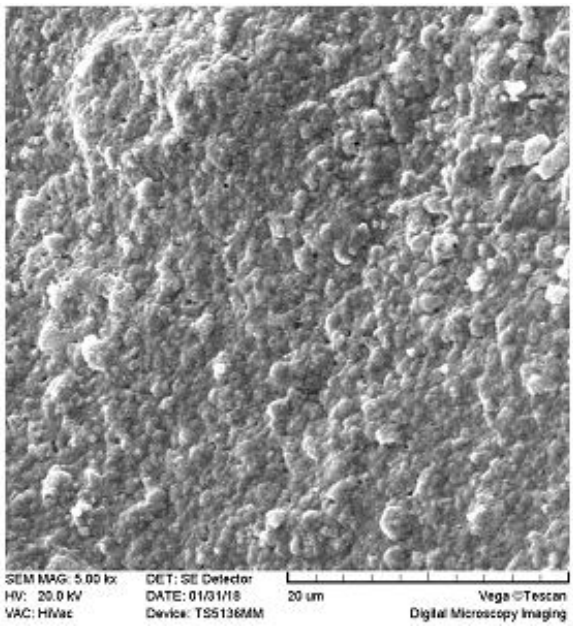

Fig. 2. SEM micrograph of the palladium membrane surface

3.3. Hydrogen flux of the membrane

Fig. 3 shows the hydrogen flux of the membrane in the pressure difference of 1-3 bar during the test. It can be observed that during the first 90 hours the permeation of hydrogen through the membrane is stable, confirming the high stability of the membrane under high temperature operating conditions.

3.2. High temperature CO_2-H_2 binary mixtures tests

For the purpose of investigating the CO_2 poisoning effects on membrane performance, two binary mixtures (10% CO_2-90% H_2 and 20% CO_2-80% H_2) were prepared with mass flow controllers and fed to the permeation test system. The flow of the permeation side was introduced to the GC. At the concentration of 10% CO_2 in the feed and in the pressure difference of 1-3 bar, no characteristic peak of CO_2 was observed in the results derived from the TCD detector for the permeate side. However, at the concentration of 20% CO_2 and pressure differences of 1-2 bar, a characteristic peak was detected related to methane. This phenomenon can be attributed to the diffusion of carbon atoms through the metal matrix. Carbon components can diffuse from the feed side to the permeate side and due to the reaction of hydrogen atoms permeating from the membrane, methane can be formed as reported in the literature [11].

In the pressure difference of 3 bar, there were no traces of CO_2 and CH_4 in the permeate side flow. It can be deduced that there is more competitive diffusion of hydrogen rather than CO_2 in high pressure difference, i.e. in this case there were only the catalytic active sites that were blocked with CO_2 and no carbon was transmitted from the membrane layer. With an increase in the percentage of CO_2 in the feed stream, the hydrogen flux reduced significantly. This decrease is related to the adsorption of CO_2 on the membrane layer and deposition of decomposed carbon atoms on active sites of the membrane surface.

Clearly, by increasing the concentration of CO_2 in the feed flow the rate of the gas adsorption on the membrane layer is intensified and more catalytic sites are occupied, thus its impact on the hydrogen permeability is highlighted. The impact of CO_2 gas on the flux of the membrane is provided in Fig. 4. According to this figure, hydrogen flux in the presence of different percentages of CO_2 has dramatically decreased compared to that in the pure hydrogen feed. This process reflects the reality that

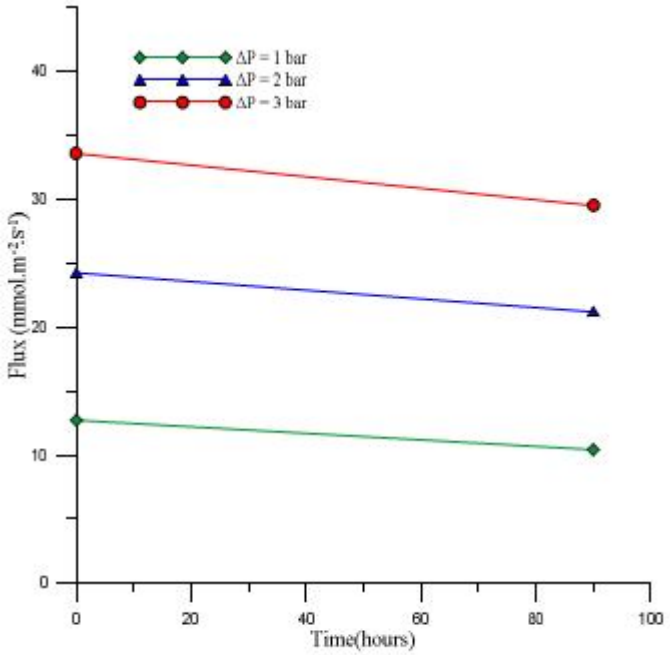

Fig. 3. Hydrogen permeation through the palladium membrane for 90 hours at different pressure differences (ΔPs) and temperature of 450 °C.

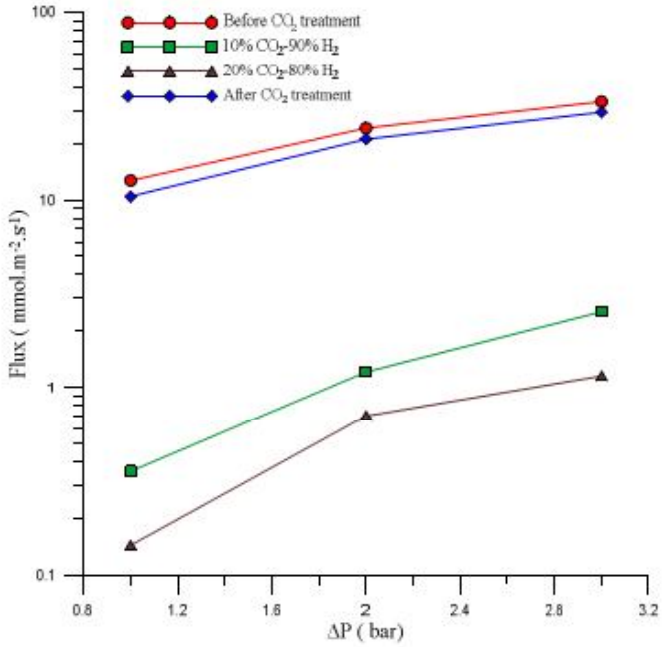

Fig. 4. Hydrogen flux of the palladium membrane at 450ºC and different ΔPs (1-3 bar) in the presence of CO_2, before and after CO_2 treatment

the effect of this gas on membrane performance is perceptible even in low percentages (10 mole %), so that the membrane flux is drastically reduced. In order to restore the level of palladium poisoned with CO_2, temperature of the palladium membrane inside the furnace was raised to 500 °C in hydrogen atmosphere. As expected after putting the poisoned membrane under the hydrogen atmosphere at 500 °C,

the hydrogen permeation achieved the values at the initial time of the test (>99% recovery). This shows that the membrane poisoning is reversible as shown in Fig. 4.

During all these tests, permeation of Ar from the membrane was zero. No argon leakage means that in the presence of CO_2 no defects were created in the membrane.

AFM image of the membrane surface is shown in Fig 5.

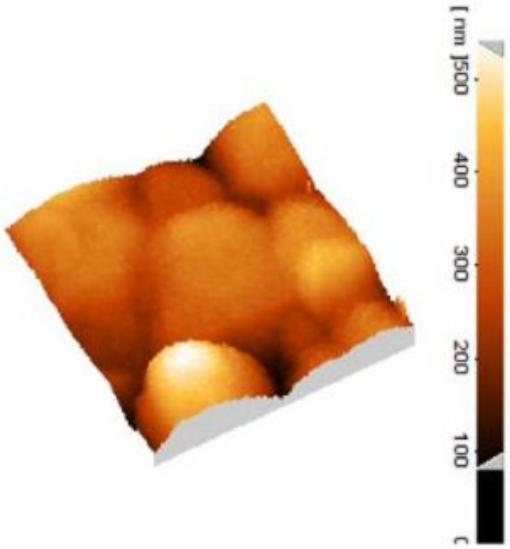

Fig. 5. AFM image of membrane

This image was detected by DME-SPM software. The roughness of the surface was 58.9 nm. As shown in Fig 5, the height of the hills on the membrane surface are low. Because of the short height hillocks and wide valleys, CO_2 has had no effect on the membrane structure, confirming the high chemical resistance of the membrane in the presence of CO_2.

4. Conclusion

In this work a palladium composite membrane was prepared on a modified ceramic substrate via the ELP method. This membrane demonstrated high hydrogen flux in the range of 0.012-0.023 mol.m-2.s^{-1} at different operating conditions. Furthermore, the prepared membrane has good thermal durability in 90 hours and the short height hillocks and wide valleys on its surface means that CO_2 did not affect the membrane performance. The negligible effect of CO_2 on the membrane indicates the high chemical resistance of the membrane. This membrane also showed high reversibility of CO_2 poisoning.

References

[1] R. Bhandari; "The synthesis of Pd-Ag composite membranes for H_2 separation using electroless plating method", Worcester Polytechnic Institute, PhD thesi, 2010.

[2] J. B. Miller, B. D. Morreale, and M. W. Smith,"Pd-Alloy membranes for hydrogen separation", Chapter 5, Elsevier Pub, Amsterdam, 2014.

[3] Ayturk, M. E, "Synthesis, annealing strategies and in-situ characterization of thermally stable composite thin Pd/Ag alloy membranes for H_2 separation", Worcester Polytechnic Institute, PhD thesis, 2007.

[4] M.Yadollahi, M.J.Vaezi and Z.Belbasi,"An overview of the performance of various types of membranes used in the purification of hydrogen", Frayande no, 2013, 40: 68.

[5] L. M. Marcello De Falco Gaetano Iaquaniello, "Membrane Reactors for Hydrogen Production Processes", Springer Pub, New York, 2011.

[6] Yun, S., and Oyama, S. T., "Correlations in palladium membranes for hydrogen separation", Journal of membrane science, 2011, 375: 28.

[7] Kulprathipanja, A., Alptekin, G. O., Falconer, J. L., and Way, J. D., "Pd and Pd–Cu membranes: inhibition of H2 permeation by H_2S", Journal of Membrane Science, 2005, 254:49.

[8] Augustine, A. S., Ma, Y. H., and Kazantzis, N. K, "High pressure palladium membrane reactor for the high temperature water–gas shift reaction", International Journal of Hydrogen Energy, 2011, 36: 5350.

[9] Basile, A., and Gallucci, F. (Eds.), "Membranes for

membrane reactors: preparation, optimization and selection", John Wiley & Sons, 2010.

[10] Jamshidi, S., Kouzegar, Z., Babaluo, A. A., and Haghigi, M., "Preparation of Pd composite membrane via organic-inorganic activation method in electroless plating technique", Iranian Journal of Hydrogen & Fuel Cell, 2015, 2: 151.

[11] H. Li, A. Goldbach, W. Li, and H. Xu, "On CH_4 decomposition during separation from H_2 mixtures with thin Pd membranes", Journal of Membrane Science, 2008, 324: 95.