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A Comparison of the Inhibiting Effect of CO and CO$_2$ to Hydrogen Permeation and *n*-Value in Pd and Pd/Ag Membranes Prepared on Alumina Support

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Abstract

The mitigation of the CO inhibition effect in palladium membranes is necessary due to its significance in the efficiency of membrane reactors and hydrogen production systems. In this work, the hydrogen separation performance of a Pd and Pd/Ag membrane both of thickness 2 μm is investigated using a mixed gas with composition (H$_2$ = 50%, CO = 28%, CO$_2$ = 10%, CH$_4$ = 8%, N$_2$ = 4%) at temperature 623 - 873 K and pressure (0.05 - 0.4 bar) was investigated. The component gases CO and CO$_2$ were observed to inhibit hydrogen permeation through the membrane and lead to deviations from Sievert's law for *n* values 0.55 and 0.62 for the Pd membrane and unity for the Pd/Ag membrane. For the Pd/Ag membrane, the concentration of CO in the permeate stream was reduced as a result of the addition of Ag. The effect of the component gases to hydrogen permeation was observed to be lower for the Pd/Ag membrane. Annealing the membrane in hydrogen at high temperature decreased the inhibition effect and enhanced hydrogen permeation through the membrane.

Keywords

1. Introduction

The future of the global energy system is hugely dependent on how the challenges posed by fossil fuels (energy security and environmental security) are ad-

dressed. These challenges are based on the need to address energy shortages, ensure environmental suatainability and make energy more affordable to the communities [1] [2]. The indefinite exploitation of fossil fuels for energy purposes is not sustainable as they cause environmental pollution through emission of greenhouse gases particularly CO_2 which necessitates global action to develop environmentally friendly and sustainable energy technologies [2]. Global efforts are ongoing on alternative and unconventional sources of energy to prepare the world towards the impending energy vacuum as oil and gas resources deplete and continue to cause environmental concerns. However, it is very important to note that fossil fuels are still expected to be the major source of energy in the next 25 - 30 years or even more. Within this period, there will be spike in research and development in renewable and alternative sources of energy [3]. Membrane technology for hydrogen separation and production from Syngas is in demand for industrial applications. The syngas contains component gases CO and CO_2 which could impede hydrogen separation through palladium membranes hence the need to investigate the inhibition effect of CO and CO_2 and how it can be ameliorated [3]. Hydrogen is widely regarded as a very reliable energy carrier as a result of some advantages it has such as high gravimetric energy density (1.43×10^8 J/kg) and its zero carbon emission [3] [4].

The relevance of hydrogen as a reliable route for clean energy is increasing every day because it is renewable, environmentally friendly and affordable. The combustion of hydrogen produces only water vapour with a limited pollution to the environmental impact when produced thorugh renewable sources [2]. Hydrogen is currently widely used in several industries such as petroleum, steel, space, chemical and petrochemical industries but is expected to be increasingly more relevant in transportation and power generation sectors [2] [4] [5]. Everyday, membrane reactors play an important role in shifting the quilibrium during water-gas shift reaction for conversion of CO to hydrogen through the steam methane reforming (SMR) process. The reaction between steam and hydrocarbons using supported Nickel catalysts is represented as follows [6]:

$$CH_4 + H_2O = CO + 3H_2 \tag{1}$$

$$CO + H_2O = CO_2 + H_2 \tag{2}$$
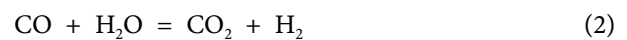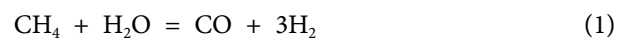
The first reaction is an endothermic reaction requiring high temperatures (above 80°C) due to the instabiltiy of CO_2. The CO produced in reaction (1) further reacts with steam to produce H_2 and CO_2 through the exothermic reaction in reaction (2) commonly referred to as water-gas shift reaction.

High purity hydrogen is necessary for refinery, fuel cell and petrochemical applications. The application of palladium membranes in membrane reactors is significant as high purity hydrogen (>99.99 vol%) is required for maximum efficiency of fuel cells and nuclear purposes. For fuel cell applications, ultra pure hydrogen (>99.99 vol%) is required for maximum efficiency and also for nuclear applications. This makes it imperative that hydrogen is purified and separated from the syngas stream. The technologies commonly used in hydrogen separa-

tion and purification processes include pressure swing absorption (PSA), cryogenic cooling and membrane technology. The membrane technology using H_2-selective membranes such as palladium and palladium-alloy membranes is usually preferred due to some of its advantages such as low energy comsumption and cost effectiveness [2]. These H_2-selective membranes are either in stand alone forms or as composites such as stainless steel, glass and ceramic supports. Since the stand-alone membranes cannot withstand high temperature and pressure, the attention is now on the composites which have high mechanical strength.

Hydrogen permeation through palladium membranes can be decribed through the process below [5] [6] [7]:

1) External mass transfer where the hydrogen molecules undergo internal diffusion from the bulk of the gas phase onto the membrane surface on the high pressure side.

2) The hydrogen molecules are dissociated into atoms through a reversible dissociative adsorption also on the high pressure side.

3) The hydrogen atoms are dissolved into the bulk palladium layer through a reversible dissolution process.

4) The hydrogen atoms undergo diffusion into the bulk metallic layer.

5) The hydrogen atoms undergo reversible movement from the bulk metallic layer to the membrane surface.

6) The hydrogen molecules undergo reversible recombination desorption at the low pressure side.

7) External mass transfer of hydrogen molecules on the membrane surface at the low pressure side.

A challenge in hydrogen separation and purification from syngas stream using Pd-based membranes is the inhibition effect caused by some co-existing gases such as CO and CO_2. In particularly, CO is known to be a major inhibitor to hydrogen permeation in Pd-based membranes.

2. Background

2.1. CO Inhibition to H_2 Permeation through Pd-Based Membranes

CO inhibition refers to the decrease in hydrogen flux as a result of competition for permeation sites on the membrane surface. The inhibition effect is essentially different from mass transfer resistance due to the competitive adsorption phenomena which differs from concentration polarization in mass transfer resistance [8]. The inhibition effect is more commonly explained based on two mechanisms: One is that H_2 molecule slow hydrogen permeation through the membrane by blocking hydrogen adsorption sites. The second is that the activation barriers in steps (2) and (5) of hydrogen permeation through Pd membranes described above are enhanced by the presence of CO on the membrane surface [5] [6] [7] [8] [9]. One molecule of CO can block several sites on the pal-

ladium membrane surface and lead to severe decrease in the rate of hydrogen permeation through the membrane [5]. The inhibition effect is dependent on several factors including temperature, pressure, membrane thickness and composition of the gas mixture [9] [10]. It has been reported that deviation from Sievert's law could be due to several factors including membrane defects, poisoning of the membrane surface by carbonaceous elements/impurities, mass transfer resistance etc. [2].

$$J = \frac{Q}{L}\left(P_{high}^{n} - P_{low}^{n}\right) \tag{1}$$

The value of the pressure exponential n in Equation (1) indicates the rate limiting step for hydrogen permeation through the membrane [10] [11]. If bulk diffusion of atomic hydrogen is the rate limiting step, $n = 0.5$. If the surface processes $i.e.$ either hydrogen dissociative adsorption on the high pressure feed side or the atomic hydrogen recombination and desorption at the low pressure permeate side controls hydrogen permeation, then $n = 1$. However, when both surface processes and bulk diffusion control hydrogen permeation through the membrane, then n will vary between 0.5 and 1 [10] [11] [12] [13].

2.2. Experimental

The membranes used in this investigation were prepared using the electroless plating method in which a thin palladium layer was deposited over the porous support. The porous ceramic a-alumina support of 30 nm pore size was supplied by ceramiques techniques et industrielles (CTI SA) France. The specification of the support is shown as follows: O.D = 10 mm, I.D = 7.34 mm, Effective length = 340 mm.

2.3. The Electroless Plating Method

Prior to the plating of the metallic layer, there is the need to seed the support with Pd nuclei. This involves a two-step process of sensitization and activation to create catalytic sites for deposition of the Pd layer. This is a standard practice in electroless plating of palladium over porous support. The sensitization and activation processes stimulate the adsorption of the metal ions, enhance strong adhesion of the Pd nuclei on the substrate and eliminate induction period of the metal to ensure better uniformity of coating and improved membrane quality. The support was dried in an oven at 65°C for 2 hours to remove any moisture and later calcined at 1100 K for 10 hours at a rate of 2°C per minute after which it was stored overnight in the laboratory at room temperature.

Sensitization and Activation

The two-step sensitization and activation procedure was carried out using a 0.005 M Sn (11) and a 0.005 M Pd (11) solutions respectively. Both ends of the support were sealed to ensure that only the outer section of the support comes in contact with the solution (Table 1).

Both the sensitization and activation processes were carried out simultaneously

Table 1. Composition of sensitization and activation solutions.

Sensitization Solution	$SnCl_2$ = 0.36 g
	Distilled Water = 320 mL
	0.1 HCl = 10 mL
Activation Solution	Pd $(NH_3)_4(NO_3)_2$ = 1.0 mL
	Distilled water = 320 mL
	0.1 Hcl = 10 mL

and the two solutions placed in the cupboard. A glass cylinder containing distilled water was placed in the fume cupboard to rinse the support after each step. In the sensitization and activation step, the support was dipped into the sensitization solution for 5 minutes and rinsed with distilled water. It was then dipped into the activation solution for another 5 minutes and rinsed in distilled water. This procedure was repeated 10 times in order to obtain a uniformly seeded support. After each dipping, the support was rinsed for 10 seconds in distilled water and immersed immediately back into the solution. The 10 seconds time in-between each dip for 10 dips gives a total time of 1 minute 40 seconds. In practice, the time in-between during the sensitization and activation will be more than 10 seconds because there is always a time lag of a few seconds before the support is dipped back into the solution or while placing the support upright vertical position in the glass cylinder.

The total time spent on the 2 step sensitization and activation process is as follows:

$$\text{Sensitization step} = 5 \text{ minutes} \times 10 \text{ dips} = 50 \text{ minutes}$$

$$\text{Activation step} = 5 \text{ minutes} \times 10 \text{ dips} = 50 \text{ minutes}$$

$$\text{Rinsing with distilled water} = 90 \text{ secs} \times 2 = \underline{3 \text{ minutes}}$$

$$\text{Total} = \underline{1 \text{ hour } 43 \text{ minutes}}$$

Deposition of the Pd layer

After the two-step sensitization and activation steps, the support is now ready for deposition of the palladium layer. The composition of the 2 plating solutions for the Pd and Pd-Ag membranes is as follows.

After the 2 step sensitization and activation, the support is now ready for deposition of the palladium layer. The composition of the electroless plating bath is presented in Table 2. A Hydrazine based bath was used to deposit the Pd layer onto the activated support. The support was again sealed at both ends with a plastic protector to prevent internal deposition. The plating solution was stabilised with Na_2EDTA and heated in a water bath. Initially, the water bath was prepared and the glass tube containing the plating solution placed into the water bath. The plating solution was heated to a temperature of 60˚C. The temperature of the plating solution was monitored using a thermometer and maintained at 60˚C. The activated support was then immersed into the plating solution at a constant plating time of 30 minutes. The plating solution was prepared and

Table 2. Composition of Pd and Pd/Ag electroless plating baths.

Plating bath composition	Pd plating bath	Pd/Ag Plating bath
Pd precursor	$PdCl_2$ 2.2 g	$PdCl_2$ 2.1 g
Ag precursor		$AgNO_3$ 0.7 g
Complexing agents	Na_2EDTA 25.0 g	Na_2EDTA 31 g
	NH_4OH 220 mL	NH_4OH 200 mL
Reducing agent	1M N_2H_4 10 mL	1M N_2H_4 10 mL
Plating temperature	333 K	333 K

placed into the water jacket without the hydrazine reducer. However, the 1M N_2H_4 reducer was added just before the support was inserted into the plating solution.

The point at which the hydrazine reducer was added signals the commencement of the electroless plating process and the plating time starts at that point.

After the preparation, the membranes were dried overnight at room temperature and prior to the permeation test, the membrane was reduced in flowing hydrogen at 350°C for 10 minutes to activate the palladium layer. The permeation tests for hydrogen were carried out above the critical temperature of 300°C to avoid hydrogen embrittlement for the Pd membrane.

2.4. Permeation Test Equipment and Procedure

The permeation tests were carried out in a stainless steel shell and tube membrane reactor module. Graphite O-rings were fitted tightly at both ends of the membrane reactor module to prevent gas leakages. Gas flow rates were measured using a digital flow meter and the separation data collected online using a Varian HP 3800 Gas Chromatograph interfaced with a PC and equipped with a T.C.D and F.I.D detectors in series. Inlet and exit pressures were controlled using back-pressure regulators. The temperature and pressure were monitored using thermocouples and pressure gauges and characterization carried out using a scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA) to identify both the morphological features and elemental composition. The key components of the gas permeation test rig are shown in Figure 1.

Initially, the composite palladium membrane is inserted into the membrane reactor and the seals at both ends placed tightly to prevent leaks. The reactor bolts and nuts were also fitted appropriately to stop gas leaks. Possible gas leaks through the membrane reactor were investigated using soapy water which shows bubbles if there are any gas leakages. The gas permeation is essentially a cross flow from the feed through the membrane to the permeate while the rejected gas flows out through the retentate. Gases from the cylinder are fed into the reactor through the feed controlled by a pressure regulator. The permeate is analysed through the Gas Chromatograph (GC Varian model 3800) which provides the composition of the permeate in terms of the gases present, their concentration (Peak area counts) and purity levels. The flow meter is placed after the GC to
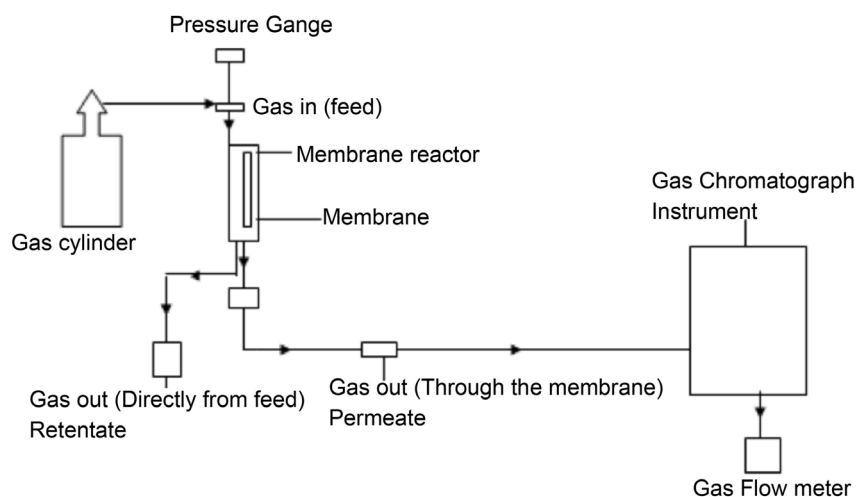
Figure 1. Concept schematic of a gas permeation test plant.

enable the measurement of the permeate flow rate. The flow meter gives the composition from which the separate flow rates of the individual gases can be determined.

3. Results and Discussion

The performance of both the Pd and Pd/Ag membranes was investigated for hydrogen separation and permeation mechanism through the membrane based on Sievert's law from a dry reformate gas mixture with the composition (H_2 = 50%, CO = 28%, CO_2 = 10%, CH_4 = 8%, N_2 = 4%) at temperatures between 623 - 723 K for a transmembrane pressure difference of 0.05 - 0.4 bar. Several studies were carried out on the inhibition effect of CO to hydrogen permeation in palladium membranes. However, most of these studies were at temperatures below 400°C, hence this work investigates this effect 450°C which falls within the relevant temperature range for SMR membrane reactors.

From Sievert's law, the value of the pressure exponential n = 0.5 which indicates that the rate limiting step in hydrogen permeation is bulk diffusion [13]. However, n values of 0.5 are usually observed for thick membranes (>0.5), although several authors have reported n values of 0.5 for thin films (<0.5) [14] [15] n values above 0.5 leading to deviations from Sievert's law occur when the rate of hydrogen reaction on the palladium surface is lower or of same magnitude with the hydrogen diffusion through the bulk [10]. However, membrane thickness of 1 μm has been suggested by many authors as the benchmark thickness when bulk hydrogen diffusion becomes the rate limitng step [8] [9] [10]. The thickness of the membrane is also another determining factor of the inhibiting effect of the coexisting gases CO and CO_2 and it has been reported that the inhibiting effect to hydrogen permeation of a membrane is inversely proportional to its thickness depending on the operating conditions [8], Deviations from Sievert's law were reported for thickness < 1 um thickness and also for low temperatures [10]. As reported by F. Guazzone *et al.* [10], high pressure of hy-

drogen could cause deviation to Sievert's law in membrane with thickness > 1 μm. In fact this group of workers concluded that 1.1 - 2 bara for >1 μm palladium membrane thickness will certainly lead to deviation from Sievert's law [10].

From **Figure 2**, it can be observed that for the Pd membrane, hydrogen flux increased with temperature and transmembrane pressure difference reaching a maximum of 17.8 $cm^3 \cdot cm^{-2} \cdot min^{-1}$ at 723 K. It can also be observed that the value of the exponential factor n is 0.62 which indicates a deviation from Sievert's law. In this case, both surface processes and bulk diffusion control hydrogen permeation through the membrane. For the Pd/Ag membrane in **Figure 3**, it can be observed that the membrane was able to separate hydrogen from the gas mixture with the n value at unity. Also, a maximum hydrogen flux of 37.6 $cm^3 \cdot cm^{-2} \cdot min^{-1}$ was observed which is about 2 fold higher than the flux for Pd membrane *i.e.*
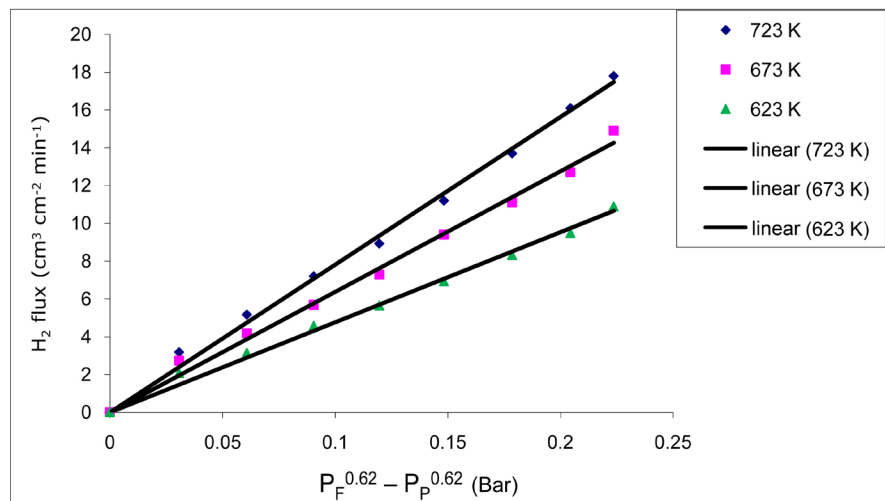

Figure 2. Hydrogen flux against partial pressure difference for hydrogen separation from gas mixture through the Pd membrane.
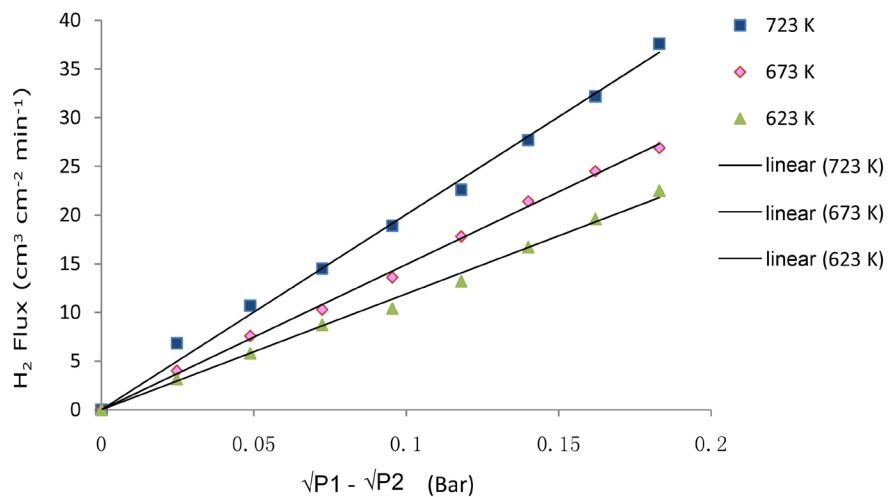

Figure 3. Hydrogen flux against partial pressure difference for hydrogen separation from gas mixture through the Pd/Ag membrane.

17.8 cm^3·cm^{-2}·min^{-1}. This indicates that alloying with silver has enhanced hydrogen permeation and also achieved a Sievert driving force at ($n = 1$) which means surface processes *i.e.* hydrogen dissociative adsorption on the high pressure feed side and/or the atomic hydrogen recombination and desorption at the low pressure permeate side control hydrogen permeation [16], After these tests, both Pd and Pd/Ag membranes were annealed in hydrogen at high temperature to investigate the effect of annealing on both the hydrogen flux and CO inhibition to hydrogen permeation through the membrane.

3.1. The Inhibition Mechanism in Pd and Pd/Ag Membranes

Figure 4 shows the CO flux in the permeate stream against feed pressure for both Pd and Pd/Ag membranes before annealing the membrane at high temperature. It can be observed that the concentration of CO in the permeate stream decreases with temperature reaching a maximum of 8.28E−03 cm^3·cm^{-2}·min^{-1} at 0.4 bar and 623 K and 2.61E−03 cm^3·cm^{-2}·min^{-1} at the same temperature for the Pd and Pd/Ag membranes respectively. The inhibition effect of CO increases with decreasing temperature and increasing with the concentration of CO in the permeate stream [2] [3] [4] [5]. Lower CO concentration for the Pd/Ag membrane is attributable to the addition of silver which impedes the interaction between the CO and palladium on the membrane surface.

The presence of CO in the permeate stream led to the poisoning of the membrane surface and blocking hydrogen permeation sites through competitive adsorption thus causing deviation from Sievert's law. CO and CO_2 present in palladium-based membranes were found to cause deviations from Sievert's law [2]. These component gases CO and CO_2 impede hydrogen separation because CO can absorb on palladium to cause a sharp drop in hydrogen permeation while CO_2 reacts with hydrogen to produce CO and H_2O thus decreasing the hydrogen partial pressures through the equation [13].
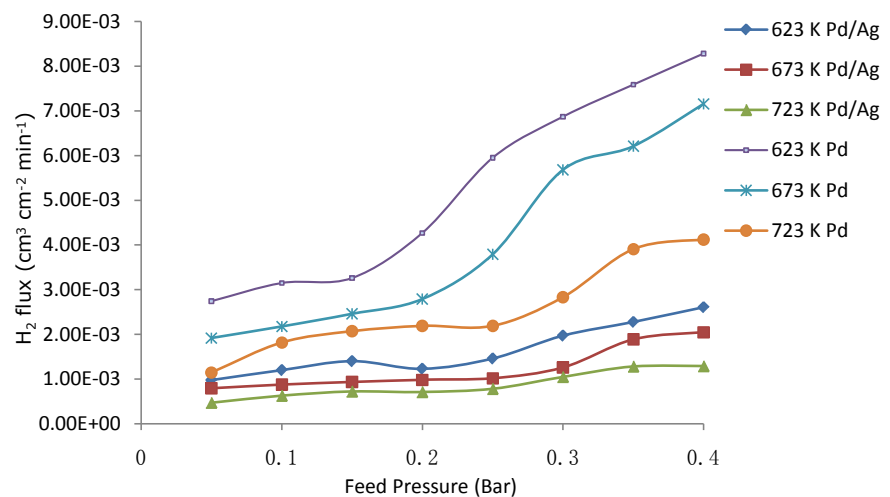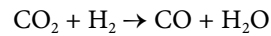

Figure 4. CO flux in the permeate stream against feed pressure before annealing the Pd and Pd/Ag membranes.

$$CO_2 + H_2 \rightarrow CO + H_2O$$

Other authors also reported the same findings [5] [8] [9] [13]. In Cheng's work, annealing the membrane at 923 K increased the hydrogen flux by about 2.5 fold compared to the flux prior to the annealing which suggests that annealing the membrane in hydrogen could enhance hydrogen flux. However, for co-deposited Pd/Ag membrane, annealing could also result in a drop in hydrogen flux. Cheng and coworkers also reported that in co-deposited Pd/Ag membranes, the effect of CO and CO_2 to hydrogen permeation can be reduced or increased depending on the content of silver on the membrane surface and the bulk metal.

Addition of silver in palladium membranes could also have profound effect on the n value and rate limting step to hydrogen permeation across the membrane.

3.2. Effect of Annealing on CO inhibition

The membrane was annealed in hydrogen at 673 K, 773 K and 873 K for 10 hours to investigate the effect of annealing temperature on hydrogen permeation. From **Figure 5** it can be observed that annealing the membrane has reduced the concentration of CO in both the Pd and Pd/Ag membraes to 7.40×10^{-3} cm^3·cm^{-2}·min^{-1} at 673 K and 0.4 bar for the Pd membrane and 1.46E−3 cm^3·cm^{-2}·min^{-1} for the Pd/Ag membrane under same conditions. This shows an appreciable decrease in the concentration of CO in the permeate stream as a result of the annealing process which results in enhanced hydrogen permeation through the membrane.

By reducing the concentration of CO, the inhibition effect is reduced hence less resistance to hydrogen permeation through the membrane. The decrease in the CO concentration after annealing implies that the surface reaction rate is faster compared to what it was before annealing the membrane. In **Figure 6**, it can be observed that the hydrogen flux has increased to 21.3 cm^3·cm^{-2}·min^{-1} at
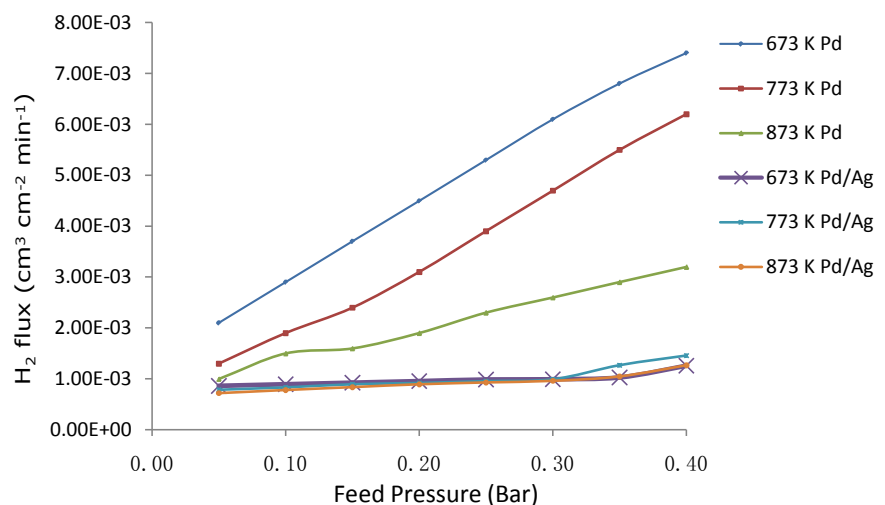
Figure 5. CO flux in the permeate stream against feed pressure after annealing the Pd and Pd/Ag membranes.
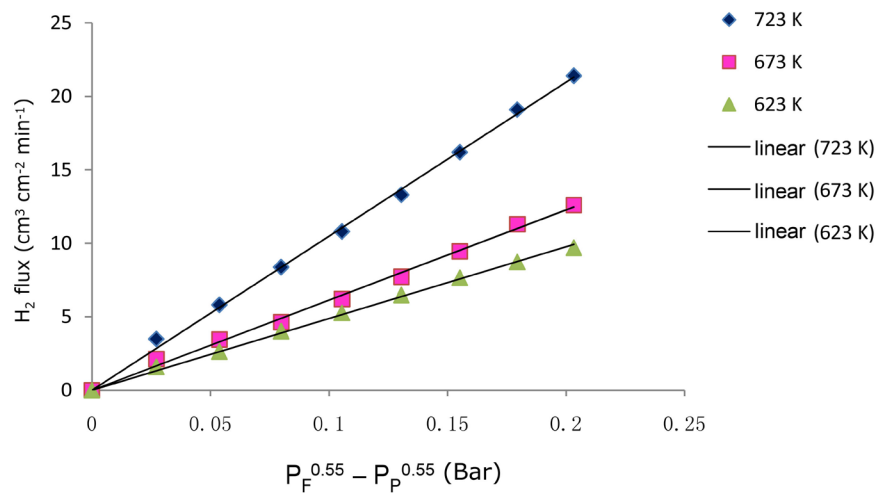
Figure 6. Hydrogen flux against partial pressure difference for hydrogen separation from gas mixture after annealing Pd membrane.

873 K annealing temperature and 0.4 bar from 17.8 $cm^3 \cdot cm^{-2} \cdot min^{-1}$ for the Pd membrane before annealing at same conditions. Also, the Pd/Ag in **Figure 7** shows an increase in hydrogen flux to 40.9 $cm^3 \cdot cm^{-2} \cdot min^{-1}$ after annealing the membrane at 873 K from 37.6 $cm^3 \cdot cm^{-2} \cdot min^{-1}$ at the same temperature. However, the *n* value for the Pd/Ag membrane remains at unity even after annealing the membrane at high temperature. It has been reported that annealing the membrane at high temperature enhanced hydrogen permeation through the membrane by removal of surface contaminants and formation of hydride phases [13]. The *n* value for the Pd membrane decreased to 0.55 signifying deviation from Sievert's law after the annealing as shown in **Figure 6** as against 0.62 before annealing which indicates that hydrogen permeation through the membrane is determined by both surface processes and bulk diffusion.

The CO reacts with hydrogen on the palladium surface to produce water and CO, the inhibition effect is principally that of CO but the higher the concentration of CO_2, the more CO will be produced leading to enhanced inhibition to hydrogen permeation. The inhibition effect is dependent on the operating temperature as reported by several authors such as K. Hou and R. Hughes [17] who investigated the effect of impurities on hydrogen permeation and reported that CO has a significant adverse inhibiting effect on hydrogen permeation through the Pd/Ag membrane at temperatures less than 623 K [17]. In this work, the findings are different from Hou and Hughes' conclusion because the inhibiting effect of CO and CO_2 on hydrogen permeation was observed at temperatures at and above 623 K (*i.e.* 623 - 723 K). In another investigation, Amano *et al.* [18] reported a significant hindrance to hydrogen permeation through the palladium membrane with addition of CO and CO_2 at temperature below 523 K and 473 K. This corroborates the findings in this work although the temperatures investigated here are higher compared to Amano's. Hara *et al.* [19] also observed significant adverse CO inhibiting effect on hydrogen permeation through palladium
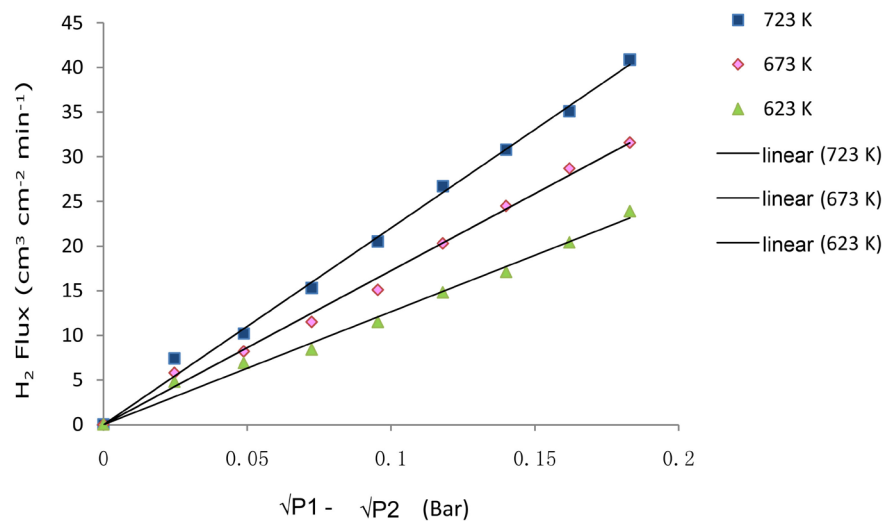
Figure 7. Hydrogen flux against partial pressure difference for hydrogen separation from gas mixture after annealing Pd/Ag membrane.

membranes at temperatures below 573 K. K. Amandusson *et al.* [20] also reported the CO effect to be more pronounced at lower temperatures due to the formation of thicker CO layers at lower temperature.

4. Conclusion

In this work, the inhibition effect of CO on hydrogen permeation and separation through 2 μm Pd and Pd/Ag membranes has been investigated at temperatures between 523 K and 723 K. The electroless plating method was used to deposit thin layers of palladium onto the porous ceramic alumina support. The inhibiton effect of CO was drastically reduced with the addition of the Ag precursor for the Pd/Ag membrane and also through the annealing process. Deviations from Sievert's law were observed as a result of the inhibition effect of CO. However, the deviation was observed to depend on temperature which decreased the concentration of the CO in the permeate stream due to less surface adsorption effect on the membrane. Hydrogen flux through the membrane was also drastically hampered by the inhibition effect of CO which blocked the sites for hydrogen permeation, particularly for the Pd membrane. For the Pd/Ag membrane, about twice the hydrogen flux was observed at same temperature and pressure as a result of the silver enrichment at the surface. This work corroborates with findings in literature that the addition of higher amount of Silver leads to significant improvement in hydrogen permeation. This work has provided a better understanding of the effect of annealing and addition of Silver to the inhibition effect of CO on hydrogen permeation and *n*-value in palladium-based membranes.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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