Separation of Hydrogen and Carbon Dioxide Using a Novel Membrane Reactor in Advanced Fossil Energy Conversion Process

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Principal Author(s): Shamsuddin Ilias

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Name and Address of Submitting Organization:
North Carolina A&T State University
Department of Mechanical and Chemical Engineering
Greensboro, NC 27411
E-mail: ilias@ncat.edu
Tel: (336) 334-7564  Fax: (336) 334-7904
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ABSTRACT

Inorganic membrane reactors offer the possibility of combining reaction and separation in a single operation at high temperatures to overcome the equilibrium limitations experienced in conventional reactor configurations. Such attractive features can be advantageously utilized in a number of potential commercial opportunities, which include dehydrogenation, hydrogenation, oxidative dehydrogenation, oxidation and catalytic decomposition reactions. However, to be cost effective, significant technological advances and improvements will be required to solve several key issues which include: (a) permselective thin solid film, (b) thermal, chemical and mechanical stability of the film at high temperatures, and (c) reactor engineering and module development in relation to the development of effective seals at high temperature and high pressure.

In this project, we are working on the development and application of palladium and palladium-silver alloy thin-film composite membranes in membrane reactor-separator configuration for simultaneous production and separation of hydrogen and carbon dioxide at high temperature. From our research on Pd-composite membrane, we have demonstrated that the new membrane has significantly higher hydrogen flux with very high perm-selectivity than any of the membranes commercially available. The steam reforming of methane by equilibrium shift in Pd-composite membrane reactor is being studied to demonstrate the potential application of this new development.

A two-dimensional, pseudo-homogeneous membrane-reactor model was developed to investigate the steam-methane reforming (SMR) reactions in a Pd-based membrane reactor. Radial diffusion was taken into consideration to account for the concentration gradient in the radial direction due to hydrogen permeation through the membrane. With appropriate reaction rate expressions, a set of partial differential equations was derived using the continuity equation for the reaction system. The equations were solved by finite difference method. The solution of the model equations is complicated by the coupled reactions. At the inlet, if there is no hydrogen, rate expressions become singular. To overcome this problem, the first element of the reactor was treated as a continuous stirred tank reactor (CSTR). Several alternative numerical schemes were implemented in the solution algorithm to get a converged, stable solution. The model was also capable of handling steam-methane reforming reactions under non-membrane condition and equilibrium reaction conversions. Some of the numerical results were presented in the previous report.

To test the membrane reactor model, we fabricated Pd-stainless steel membranes in tubular configuration using electroless plating method coupled with osmotic pressure. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) were used to characterize the fabricated Pd-film composite membranes. Gas-permeation tests were performed to measure the permeability of hydrogen, nitrogen and helium using pure gas. The membranes showed excellent perm-selectivity for hydrogen. This makes the Pd-composite membrane attractive for selective separation and recovery of H2 from mixed gases at elevated temperature.
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EXECUTIVE SUMMARY

Inorganic and composite membranes are being considered as potential candidates for use in membrane-reactor configuration for effectively increasing reaction rate, selectivity and yield of equilibrium limited reactions. To investigate the usefulness of palladium-ceramic and palladium-stainless steel composite membrane in membrane-reactor configuration, we are investigating the steam reforming of methane by equilibrium shift for simultaneous separation and recovery of hydrogen and carbon dioxide. To have a better understanding of the membrane reactor, we developed a two-dimensional pseudo-homogeneous reactor model for steam reforming of methane by equilibrium shift in a tubular membrane reactor. Parametrically we studied the performance of the reactor and the simulation results show that under appropriate operating conditions, the membrane reactor outperforms the conventional packed-bed reactor. We also fabricated Pd-stainless steel composite membrane by electroless deposition coupled with osmotic pressure. From gas permeability study, it was observed that the membrane has excellent H2-permselectivity.
Energy from coal-fired power plants will continue to play a major role as dominant energy source for foreseeable future. For sustained fossil fuel utilization to meet the world’s energy demands while addressing the concern over global climate change, it is imperative to develop cost-effective technologies to capture and sequester the resulting CO₂. The conventional technology for removal of CO₂ from dilute gas streams emanating after fossil fuel combustion is expensive and incurs substantial energy penalty. According to a recent DOE report, for coal-based power systems, the energy penalty may vary from as much as 27% to 37% depending on the selection of CO₂ removal process and operating conditions [1]. For natural gas-based power plants, the penalty may vary from 15% to 27%. The relatively lower penalty is due lower carbon content in the fuel.

Because of concerns over the effect of CO₂ emissions from the combustion of carbon-based fossil fuels, hydrogen has become potentially the fuel of the future [2, 3]. The demand for cleaner fuels will continue to increase with increased demand for hydrogen. The processes that remove sulfur from petroleum fuels or coal consume hydrogen and the new generation of cleaner fuels (with alcohols and ethers), all have high H/C ratios. In addition, hydrogen has become an increasingly important chemical feed stock for wide range of industries including metal processing, chemical and polymer synthesis, microelectronics. Conventional wisdom suggests that the demand for hydrogen would continue to grow as we move towards cleaner environment through the use of cleaner fuels. Under the auspices of Vision 21, advanced coal gasification power plants such as an IGCC power plant offer new opportunities for integrating CO₂ capture [4, 5]. Carbon dioxide separation from hydrogen is important in the separation of the water gas shift reaction products. First syngas is produced by removing hydrogen sulfide and carbon dioxide from other gasification products, mainly CO and H₂.

Conventional technologies for removal of CO₂ from syngas streams include low temperature absorption by mono-ethanol amine (MEA), glycol, and methanol; hot potassium carbonate and sodium carbonate process; and separation by polymeric membranes at ambient temperature. Recovery of CO₂ by absorption requires gas cooling and heat recovery leading to inefficient use of energy. Furthermore, significant amount of energy is also required for regeneration in solvent-and reagent-based systems. Polymeric membranes are useful at relatively low temperatures for selective separation of hydrogen, and are quickly degraded by condensation of components such as water, carbon dioxide, ammonia and hydrocarbons. Whether it is steam reforming of methane or water gas shift reaction in the IGCC power plant, the major challenge regarding CO₂ and H₂ recovery and separation technology is to reduce the overall costs by lowering both the energy penalty and the capital costs. In this context, membrane-based technology for simultaneous separation and recovery of CO₂ and H₂ appears very attractive.

The use of membrane as membrane-reactor separator is not new. Inorganic membrane reactors allow simultaneous reaction and separation, and therefore offer the possibility of combining reaction and separation in a single operation at high temperatures to overcome the equilibrium limitations experienced in conventional reactor configurations. Such attractive features can be advantageously utilized in a number of potential commercial opportunities, which include dehydrogenation, hydrogenation, oxidative dehydrogenation, oxidation and catalytic decomposition reactions. However, to be cost effective, significant technological advances and improvements will be required to solve several key issues which include: (a) permselective thin solid film, (b) thermal, chemical and mechanical stability of the film at high
temperatures, and (c) reactor engineering and module development in relation to the development of effective seals at high temperature and high pressure.

In our laboratory, we developed a new class of palladium-ceramic composite membranes by depositing thin-film palladium on microporous ceramic substrate. Laboratory tests at elevated temperature and pressure indicated that the new membrane has both high permeability and selectivity for hydrogen [6]. We believe this new membrane will be an excellent candidate for hydrogen separation and applicable in membrane-reactor configuration for separation of hydrogen by equilibrium shift when the reaction product (H₂) thermodynamically limits the equilibrium conversion. In IGCC application, the clean syngas or natural gas can be steam reformed to produce H₂ and CO₂ in an H₂-selective membrane reactor. Since, these reactions are thermodynamically equilibrium-limited, the membrane reactor offers an opportunity for H₂ separation and CO₂ capture in a single unit. This method will have several technological advantages over other hydrogen-purification methods, including the following:

- Reforming reaction is not limited by chemical equilibrium. As soon as product hydrogen is formed, hydrogen is transported across the membrane.
- Reforming and separation will be carried out in a single unit, thereby eliminating the need of hydrogen separation and recovery units.
- The membrane reactor-separator is modular and compact in size.

We propose to use our newly developed membrane to study the water gas shift reaction and/or steam reforming of methane in a membrane reactor-separator for concentration and recovery of H₂ and CO₂ simultaneously.

**RESEARCH OBJECTIVES**

The objectives of this research are to:

1. Design and fabrication of membrane reactor using thin film Pd-Ag alloy composite membrane in tubular configuration.
2. Conduct water-gas shift reaction and/or steam reforming of methane experiments to study the equilibrium shifts and permeation characteristics.
3. Model the membrane reactor for water-gas shift reaction and steam reforming of methane by equilibrium shift and validate the performance of the reactor.

This report summarizes the work performed under the US DOE Grant No. DE-FG22-99FT40620, covering the period 9/1/1999 to 12/31/2003.

**MATERIALS AND METHODS**

In the development of hydrogen selective inorganic membrane for hydrogen separation and to capitalize the membrane selectivity in membrane reactor-separator configuration to enhance productivity of equilibrium-limited reactions, there is still a great deal of technical challenges that needs serious research efforts. In this section, the efforts to meet some of the
challenges have been discussed. The preparation of hydrogen selective palladium membrane that has high hydrogen flux and good thermal and mechanical stability is the major challenge that is being researched and investigated at laboratory scale. In this section, the fabrication of palladium membrane on porous stainless steel substrate (inside and outside surface) using electroless plating method combined with osmosis has been discussed.

**Fabrication of Pd-Stainless Steel Membrane**

The palladium membrane on porous stainless steel was developed using electroless plating with osmosis. Electroless plating is based on the controlled autocatalyzed decomposition or reduction of metallic salt complexes on substrate surfaces. This method has several advantages over other deposition processes:

1. Both conducting (metal) and non-conducting (ceramic, polymer) surfaces can be coated
2. Uniform, thin dense films can be formed on bodies with complex shape
3. Relatively simple apparatus is required
4. The method is relatively inexpensive

There are several different types of substrate available commercially for the deposition of palladium. Porous Vycor-glass, ceramic are the main two substrates over which much work has been done. The membranes made with these substrates have very low mechanical and thermal stability. Considering this, other supports that have better thermal and mechanical stability is desirable. Stainless steel is a good candidate because of its resistance to cracking and simplicity to module construction [7-9]. They are expected to have good thermal stability due to the relatively small difference in thermal expansion coefficients between palladium and stainless steel.

In the lab palladium was deposited first on the inside surface of the asymmetric microporous stainless steel (SS) tubes purchased from Mott Metallurgical corporation. The inside and outside diameter of the SS tubes are 1/4 and 3/8 inch, respectively. The average pore size of the tube is 0.2µm. The tubes purchased in lengths of 12 inch were first cut to the desired length of 2.5-4.0 inch using diamond saw. Several samples have been prepared changing some parameters such as pump speed, hydrazine concentration etc. All the samples were prepared according to the following three basic steps:

- Substrate cleaning
- Sensitization and activation
- Electroless plating

**Substrate cleaning**

An important characteristic of plating palladium on porous stainless steel is the strength of the bond that can develop between the base stainless steel and the palladium layer. Metal to metal bonds with high adhesion values require thorough surface preparation to present a clean and optimally rough surface structure. Foreign contaminants like grease, oil, dirt, corrosion products and others should be completely removed from the stainless steel surface. The cleaning of the 0.2µm stainless steel substrate was performed according to the following sequential steps:
1. At first the porous tube was cleaned with a commercial cleaner supplied by ALCONOX in an ultrasonic bath at 60°C for two hours.

2. Then the tube was cleaned ultrasonically with carbon tetrachloride supplied by Aldrich Chemicals at 23°C for one hour.

3. It was then cleaned with deionized water at the same temperature for one hour, followed by drying at 120°C for two hours.

Sensitization and activation

The membrane went through surface sensitization and activation prior to electroless plating. The purpose of the surface activation was to seed the stainlesssteel (SS) surface with palladium nuclei, which during the electroless deposition would initiate the autocatalytic process of reducing the metastable Pd salt complex on the target surface. The sensitization and activation procedure consisted of successive immersions in an acidic SnCl₂ bath (sensitizing) followed by an acidic PdCl₂ bath (activating). After immersion in each bath a gentle rinsing in deionized water was used. The typical composition of the activation and sensitization bath is given in Table 1. Measure was taken to prevent the activation of the outer surface by covering the outer surface with Teflon tape. The sensitization and activation steps reduce the induction period of the palladium deposition, promote complete coverage of the surface and improves coating quality [10]. Therefore it is the key step for electroless plating. Sensitization is the adsorption of a reducing agent on the target surface and activation occurs when the catalytic material is adsorbed on the substrate. The oxidation/reduction mechanism for this step is:

$$Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^0$$

During rinsing with deionized water after immersion in the acidic SnCl₂ bath, the partial hydrolysis of Sn²⁺ takes place to form little poorly soluble product, Sn(OH)₁.₅Cl₀.₅ and other more complicated hydroxy-chlorides [11]. It is replaced by Pd⁰ via the redox step shown in Eqn. (1). The mechanism of sensitization and activation was established, involving the concept of an equilibrium shift towards formation of complex palladium anions and predominance of the number of palladium ions over tin ions on the surfaces.

An excess of Sn²⁺ on the target surface of porous stainless steel can create a loose (crumbly), easy-to-peel layer, while a deficiency of Sn²⁺ can lead to non uniform seeding of the palladium nuclei [9]. The distribution of catalytic centers for autocatalytic Pd²⁺ reduction must be dense and uniform at an optimum concentration of Sn²⁺ on the surface. Depending on the intensity of the activation, the two step immersion sequence in SnCl₂ and PdCl₂ was generally repeated 8-10 times. A perfectly activated layer has a uniform dark brown color and smooth surface. After 10 sensitizing and activating cycles the activated surface was dried at 120°C for 2 hours before dipping it into the plating solution.

Electroless plating with osmosis

Palladium was deposited on the activated surface using electroless plating technique with osmosis. Electroless plating is defined as the deposition of metallic coating by a controlled autocatalytic chemical reduction that is catalyzed by the metal or alloy being deposited. Plating was performed combined with osmosis that was originally developed by Yeung and co workers [9]. Osmosis is the spontaneous flow of solvent, from a dilute to a more concentrated solution, when the two liquids are separated from each other by a suitable membrane [12]. For osmosis to
occur, the membrane should be semipermeable, i.e. allow free passage of the solvent but not of
the dissolved solute. The composite membrane was prepared using a plating bath that contained
EDTA stabilized palladium metal complex with hydrazine as reducing agent and ammonia to
stabilize the bath and maintain the pH value. Table 2 shows the plating bath composition and the
plating conditions along with the composition of the osmotic solution. The palladium films were
deposited on the inside surface of the metal tube by circulating the plating solution through the
SS tube using a peristaltic pump. Tygon tubing with ¼ inch ID and 3/8 inch OD was used giving
a constant volumetric flow rate of about 500 ml/min. The SS tube was immersed in the osmotic
solution and the whole bath was placed in a constant temperature water bath from Fischer
Scientific along with the plating solution bath. The temperature of the bath was kept at 60°C. The
experimental setup is presented in Figure 1. The osmotic solution used for this experiment is a
high molecular weight polyethylene glycol (PEG) solution. PEG was supplied by FLUKA
Chemicals and has a molecular weight of 17500. A concentration of 2.857x 10⁻³ M solution of
PEG was used as an osmotic solution to allow the osmotic flux to pass through the pores of the
tube from the plating solution into the osmotic solution.

In electroless plating, metal ions are reduced to metal by the action of chemical reducing
agent, which is simply electron donor. The metal ions are electron acceptors, which react with
electron donors. The catalyst is the metal surface, which accelerates the electroless chemical
reaction allowing oxidation of the reducing agent. Palladium deposition occurs according to the
following two simultaneous reactions:

Anodic reaction:

\[ \text{NH}_2\text{H}_4 + 4\text{OH}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4e^- \]  \hspace{1cm} (2)

Cathodic reaction:

\[ 2\text{Pd}^{2+} + 4e^- \rightarrow 2\text{Pd}^0 \]  \hspace{1cm} (3)

Autocatalytic reaction:

\[ 2\text{Pd}^{2+} + \text{NH}_2\text{H}_4 + 4\text{OH}^- \rightarrow 2\text{Pd} + \text{N}_2 + 4\text{H}_2\text{O} \]  \hspace{1cm} (4)

The cathodic deposition of palladium catalyzes the anodic oxidation of hydrazine thus
resulting in an autocatalytic process. Pre-seeded palladium nuclei on the substrate at the
sensitization/activation step reduce the induction period of the autocatalytic process at the
beginning of the deposition.

The plating was carried out at a constant temperature of 60°C. The plating solution was
prepared at a temperature of 50°C so that when it was placed in the water bath it quickly reached
the temperature of the bath. The osmotic solution was also kept in the water bath to attain
the temperature. When the temperature of the osmotic bath and plating bath reached equilibrium
with the water bath then hydrazine was added along with the substrate tube. Before plating, the
pump and tubing were rinsed three times with deionized water by circulating it through the loop.
Then water was substituted by plating solution in the container, the pump was open to the
maximum rate to mix the plating solution with the rinse water which is left in the pump and
tubing. After ten minutes of mixing, the solution was considered uniform. Then the flow rate was
reduced to 500 ml/min.

After plating, the deionized water was again circulated in the loop twice to clean the
pump and tubing, making sure that no plating solution was left in the loop. Otherwise the pump
and tubing would be plated with palladium. At the beginning of the plating, the plating solution passing though the inside of the tube can be seen coming out to the PEG solution. The streams were seen moving upwards. Because of the loss of the plating solution to the PEG solution, both the solutions were changed every hour with fresh solutions to maintain the osmotic pressure difference. The plating was continued until a desired film thickness was obtained. The tube was rinsed in deionized water after plating and then dried at 120°C overnight. After drying, small pieces were cut from both ends for SEM images. The Pd-plated stainless steel tube was tested for leaks and pinholes at room temperature with nitrogen. In the leak tests, at a set pressure of 20 psi, the pressure drop was about 1-1.5 psi per 10 minutes.

Another sample was made changing the pump speed and the hydrazine concentration. From the work of Yeung and Varma [12], it was found that the pump speed should be around 120 ml/min so that a laminar flow region establishes between the plating solution and the inside of the tube. Moreover, the hydrazine concentration was also changed. This time hydrazine was bought from Aldrich chemicals with a composition of 35wt% hydrazine in solution of water. The amount of hydrazine added to the solution was very critical and was calculated based on the stoichiometric requirement of the reaction. The composition of the hydrazine initially used was more than the amount required so the bath was not stable for more than half an hour. Now the concentration of hydrazine in the plating solution was same as mentioned in Table 2 but the composition of the hydrazine solution was changed. This sample went through the same leak test as the one mentioned previously and the pressure was dropping very slowly. It was found that it was not leaking from the membrane surface but from the ends of the tubes.

Modification and repair of a damaged membrane

In the lab, several samples were made and discarded because of their leak or damage caused by plating procedure or inappropriate sensitization and activation procedure or damage by cutting the membrane edges for SEM. This way, a great amount of money was being wasted not only on the tubes but also for expensive palladium precursor. A new approach, to minimize the cost associated with the research was found by modifying the existing membrane using the electroless plating with osmosis.

From the SEM image of one of the sample that was already leaking, it was found that it had a thin layer of coating but pinholes and defects were also seen. This sample was repaired and densified successfully with the electroless plating with osmosis. The plating bath composition is same as Table 1 except for the new hydrazine (35 wt%) from Aldrich chemicals. In this case, it was made sure that damaged membrane had proper activation and sensitization. After the sensitization and activation and after plating for some few hours if SEM image of a membrane shows very thin layer of deposit then that membrane can be repaired. If the membrane had no proper sensitization and activation then that could not be repaired.

Membrane Reactor Design

The major objective of this project was to set up a new tubular membrane module, which can perform high-temperature chemical reaction and should be compatible to the membranes supported on different materials, for instance, ceramic or stainless steel. During the time of designing the membrane reactor, the emphasis was given to following interests:
1. The membrane reactor should be able to operate at high temperature (at least 500-600°C), since most of the chemical reactions occur at high temperature.

2. The membrane reactor should be flexible for testing membranes of different sizes

3. Easy assembly and disassembly

The membrane reactor is shown in Figure 2. The outer shell of the membrane reactor was a stainless steel pipe with 1 inch outer diameter, (OD) obtained from Greensboro Plumbing Supply Co (GPSC). The Two pairs of stainless steel flanges, also from GPSC, were welded on the pipe to make a gas tight chamber. Round graphite sheets (CGR Products, Greensboro) were used as the seals for the flanges due to the high temperature performance. Two 1/4 inch Ultra-Torr fittings from Swagelok (No.1 in Figure 2) were welded on the flanges. Two 1/4 inch tubing inserted in to the chamber through the Ultra-Torr fittings were connected with the membrane tube by two reducing unions. The size of the reducing unions can be changed depending on the outer diameter (OD) of the membrane tube. The OD of the membrane tube can reach up to 3/4 inch to connect to 1/4 inch tubing. For a membrane with larger size, the tubing has to be changed to a larger size; otherwise there is no commercial reducing union available to connect the membrane and the tubing.

Each of the other end of two 1/4 inch tubes were connected with a tee made by welding three Ultra-Torr fittings together (No.2, 3 and 4, Figure 2). The tee consisted of two 1/4 inch (No. 2 and 3) and one 1/8 inch (No. 4) Ultra-Torr fittings. One of the 1/4 inch fitting (No. 2) was used to seal the 1/4 inch tubing coming out from the chamber and the other one (No. 3) was connected with gas line coming out of the reactor. The 1/8 inch one was to seal the K-type thermocouple in the system.

A 2 inch IDx15 inch wide ceramic band heater from Industrial Heater Corporation was used by the previous students to maintain the reactor temperature at some desired level. But this heater was not compatible for the high temperature application. So a new temperature controller from Omega (Micromega CN 77333) was used to maintain a constant temperature of the membrane reactor. Two K-type thermocouples were there in the system. One thermocouple was fixed at the middle of the membrane tube and the other one was inserted into the membrane tube to detect the temperature distribution. It can be placed at any place desired. One of the two thermocouples was connected with the heater. The other one was connected to the digital temperature display. A heating tape (420W, 120V and 8-ft long) connected to output-1 of the temperature controller was used around the permeator to maintain a constant temperature of the permeator. Another similar heating tape connected to the output-2 of the temperature controller was used to preheat the inlet gas stream.

The experimental setup for membrane reactor is shown in Figure 3. The setup was configured with the pressure gauges and plug valves and control valves in such a way that any membrane with a coating on inside/outside surface can be used to perform any experiment. The set up for the membrane with palladium coating on the outside surface should be different from the membrane with inside palladium coating. The present setup was made in such a way so that any membrane tube with outside or inside coating can be used successfully.

Three digital mass flow controllers from Aalborg, model DFC 3600 were used in three different inlet lines and all of then were calibrated with respect to nitrogen for a maximum flow of 2.0 slpm. These mass flow controllers were connected to a personal computer through a RS
232 to RS-422/485 converter obtained from Telebyte (model 9365). The controllers were operated from the personal computer using software provided by Aalborg. To measure the permeate flow rate from shell side and tube side two mass flow transducers (Matheson, model 8143) were placed in the outlet lines from the chamber. These transducers were able to measure flow rates greater than 1000 cm$^3$/min. A digital soap-bubble flow meter (J & W Model ADM2000) was used for flow rates 0.1-1000 cm$^3$.min.

The shell side and tube side had two outlets each. One outlet from shell side was connected through 1/8 inch stainless steel tubing to the GC (HP 6890 plus) and the other outlet was opened to atmosphere to measure permeate flow rate. The tube side also had the same configuration. Needle valve was used in the shell side or tube side outlet lines opened to the atmosphere, depending on the permeation side. The permeate as well as the retentate gas composition could be measured using GC by simply opening the plug valves of the two outlet lines from shell and tube side.

**STEAM REFORMING OF METHANE: MEMBRANE REACTOR MODEL**

In order to develop a model for a membrane reactor, one needs to consider the reaction kinetics and the transport mechanism through the membrane as well as through the catalyst bed. The present work is to study a Pd-ceramic or Pd-stainless steel membrane reactor for methane-steam reforming reaction. Nickel catalyst pellets are assumed inside the membrane tube, i.e. tube is the reaction side.

**Kinetic Parameters**

The three major reactions in steam reforming of methane are:

\[
CH_4 + H_2O \rightleftharpoons CO + 3H_2; \quad \Delta H = 206 \text{ kJ.mol}^{-1}
\]

\[
CO + H_2O \rightleftharpoons CO_2 + H_2; \quad \Delta H = -41 \text{ kJ.mol}^{-1}
\]

\[
CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2; \quad \Delta H = 165 \text{ kJ.mol}^{-1}
\]

A number of kinetic rate expressions have appeared in the literature to describe the steam reforming of methane. These rate expressions vary from empirical expressions to ones based on fundamentals. In this work, kinetic parameters are taken from work of Xu and Forment [13], where they studied steam reforming of methane in a tubular reactor without membrane. The steam reforming of methane was carried out using nickel catalyst supported on magnesium pellets. The reaction rate equations for three main reactions are given as:

\[
r_1 = \frac{k_1 p_H^2 \left( p_M p_S - \frac{p_H^3 p_C}{K_1} \right)}{p_H^2 \kappa^2}
\]

(8)

\[
r_2 = \frac{k_2 p_C p_S \left( p_C p_S - \frac{p_H p_D}{K_2} \right)}{p_H \kappa^2}
\]

(9)
where \( \kappa = 1 + K_c \rho_c + K_H \rho_H + K_M \rho_M + K_S \frac{\rho_S}{\rho_H} \)

Here \( k_1, k_2 \) and \( k_3 \) are the rate constants for three reactions and corresponding equilibrium constants are denoted by \( K_1, K_2 \) and \( K_3 \) respectively. The adsorption equilibrium constants of the species are denoted as \( K_i \), where \( i=M \) for methane, \( S \) for steam, \( C \) for carbon monoxide, \( D \) for carbon dioxide and \( H \) for hydrogen. The numerical values of the rate constants, equilibrium constants and adsorption equilibrium constants were taken from literature [13]. We write the rate of production or depletion of the species \((i=M, S, C, D \) and \( H)\) as:

\[
\begin{align*}
    r_M &= r_1 + r_3 \\
    r_S &= r_1 + r_2 + 2r_3 \\
    r_C &= r_1 - r_2 \\
    r_D &= r_2 + r_3 \\
    r_H &= 3r_1 + r_2 + 4r_3
\end{align*}
\]

Hydrogen Transport through Membranes

An ideal Pd-ceramic/SS membrane is nonporous. No pore space is available for diffusion. The transport of gases through nonporous membranes occurs by an activated solution-diffusion mechanism. The permeation of hydrogen through the membrane can be described by Sievert’s law as:

\[
N_H = \frac{Q_H}{h} (P_H^p - p_H^p) \tag{16}
\]

where \( P_H \) and \( p_H \) are the hydrogen partial pressures of feed side and separation side, \( Q_H \) is the permeability and \( h \) is the membrane thickness. The values for \( n \) range from 0.5 to 1. The value of 0.5 implies that the transport of hydrogen through the bulk of metal is rate determining and that equilibrium is established at the surface, i.e. an equilibrium between hydrogen molecules in gas phase and hydrogen atoms dissolved in the metal.

Membrane Reactor Model

The membrane reactor shown schematically in Figure 4 is a packed-bed catalytic tubular reactor. Catalyst pellets are inside the Pd-ceramic membrane tube. Hydrogen produced by the steam reforming of methane permeates through the membrane into the shell side. Argon is used as the carrier gas in the feed side and as sweep gas in the shell side to remove the permeated hydrogen. Concentration of hydrogen near the membrane wall is depleted due to permeation. Hence, a concentration gradient occurs in the radial direction. A two-dimensional model is suitable to describe the transport mechanism through the catalyst bed.
Two-dimensional heterogeneous model requires the knowledge of effectiveness factor. For a first-order reaction, it can be evaluated easily. Steam methane reforming is a complex reaction and defining the effectiveness factor is complicated. In order to avoid this complexity, two-dimensional pseudo-homogenous model is assumed to describe the transport mechanism through the catalyst bed. Based on some simplifying assumptions, argon \((A)\), methane \((M)\), hydrogen \((H)\), carbon monoxide \((C)\), carbon dioxide \((D)\) and steam \((S)\) can be written as:

\[
u \frac{\partial \hat{C}_i}{\partial Z} = (D_{\infty}) \frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial \hat{C}_i}{\partial R} \right) + r_i \tag{17-22}
\]

where \(i=A,M,H,C,D,S\) and since argon is non-reactive, \(r_A=0\).

The boundary conditions are given as:

**BC 1:** At \(R = 0\) and \(0 \leq Z \leq L_0\),

\[
\frac{\partial \hat{C}_i}{\partial r} = 0 \tag{23}
\]

**BC 2:** At \(R = R_f\) and \(0 \leq Z \leq L_0\)

\[
\frac{\partial \hat{C}_i}{\partial r} = 0; \quad i = A, M, H, C, D, S \tag{24}
\]

and

\[
(D_{\infty}) \frac{\partial \hat{C}_H}{\partial R} = \frac{Q_{\infty}}{h} \left( p_H^n - \hat{p}_H^n \right) \tag{25}
\]

The inlet conditions on the reaction and permeation sides are:

**IC 1:** at \(Z=0\) and \(0 \leq R \leq R_i\)

\[
C_i = C_i^o; \quad i = A, M, S \tag{26}
\]

\[
C_i = 0; \quad i = H, C, D \tag{26}
\]

**IC 2:** at \(Z=0\) and \(R_2 \leq R \leq R_3\) for cocurrent and at \(Z = L_o\) and \(R_2 \leq R \leq R_3\) for countercurrent flow configurations,

\[
c_A = c_A^o, \quad c_H = 0 \tag{27}
\]

Expressing the concentration of the species in partial pressures, the governing equations, Eqns. (17-22) and the boundary conditions, Eqns. (23-27) were normalized for numerical solutions. The equations were solved by finite difference method. An iterative scheme was used to get converged solution. The details are reported elsewhere [14].

**RESULTS AND DISCUSSIONS**

In this work, a thin film palladium-stainless steel composite membrane was developed using electroless deposition technique. This section consists of the results of thin film deposition of palladium on both the outside and inside surface of the stainless steel membrane. Effect of different parameters on the deposition process was examined. The surface morphology and microstructure of the composite membrane were also examined and described in details. Finally, the separation behavior of the composite membrane with outside palladium coating was
investigated at different temperature and pressure and is discussed in great length in the following section.

**Pd/SS Composite Membrane Characterization**

Figure 5, 6 and 7 show SEM micrographs of the inside surface and cross-sectional image SS tube (0.2µm). Figure 8 and 9 show the same but with palladium coating. This sample was made with a pump speed of 500 ml/min and a hydrazine composition 99%. From Figure 8 and 9 it can be seen that the deposition is not dense and the thickness of the film, obtained from the SEM images was 4-5µm. Figure 10 and 11 show a slightly different picture. This sample was made with a pump speed of 120 ml/min and a hydrazine composition of 35 wt%. These images show a dense film with a considerable thickness of 10µm. The plating bath for this sample was becoming unstable with the 99% hydrazine. However, after changing the hydrazine composition to 35 wt% the plating bath becomes stable.

During electroless plating, palladium was deposited by reduction-oxidation reactions involving Pd-amine/metal complex and hydrazine reducer. On an activated support the reduction-oxidation occurs preferentially around the Pd-seeds. They were initiated by the reaction of hydrazine with hydroxide ions producing nitrogen gas and water with simultaneous release of electrons. The electrons are transferred across the Pd island and used for the decomposition of the Pd-amine complex into Pd metal and ammonia gas. The palladium metal is deposited onto the nuclei resulting growth. Nitrogen and ammonia gases are evolved as bubbles during the plating process.

The hydrazine oxidation is considered to be the rate limiting step. This refers the dissociative chemisorption of hydrazine to form adsorbed atomic hydrogen and an adsorbed anion radical. Therefore, it is expected that the effective adsorption and dehydrogenation of hydrazine on catalytic sites is the rate controlling step in electroless plating. Therefore changing the hydrazine composition but keeping the same concentration achieved a better coating. Yuen and coworkers [8] have shown that, higher concentrations of hydrazine favor the deposition of palladium. However, excessive amount of hydrazine results in bulk precipitation and poor coating. Plating rate of palladium also depends on the ammonium hydroxide concentrations. It had been shown that plating rate of palladium increases with decreasing ammonium hydroxide concentrations. But at very low concentration, the plating bath can become unstable resulting in bulk precipitation. To maintain the bath stability the ammonium hydroxide concentration was kept unchanged but the hydrazine composition was changed. It is obvious that the stoichiometric quantity for the reaction, with 99% hydrazine was more than the quantity with 35 wt% hydrazine. This resulted in a more stable bath and a denser film. The pump speed also played a significant role. It has been found that with a pump speed of 500ml/min the flow region inside the tube became turbulent. As a result the solution inside tube never had enough time to create stable plating condition to exchange water molecules with the osmotic solution. Souleimanova, et al [15] used a pump speed of 120 ml/min. Keeping the pump speed at 120 ml/min yielded a better adhesion of the film with the support since it created a more stable region for plating palladium.

The leak test for this sample shows that the gas starts leaking from the end of the tube. This indicates that the membrane is dense but the ends are porous. The reason for this is not known yet. Both the ends were covered with Tygon tube during the plating period to a certain extent. These ends were cut since they had no deposition. Moreover, the tubes were cut again in
order to take the SEM images. The reason of the leakage may be due to the rupture of the film or any crack formed during cutting. The other probable reason for this leakage from the ends may be the improper end seal. This needs further research.

Figure 12, 13, 14, and 15 show the SEM images of a membrane that is damaged and leaky and is being repaired and made dense, without any defects. Palladium is an expensive metal. During preparation of a defect free membrane several samples had been prepared and discarded for their defective characteristics. As a result a large number of stainless supports are being wasted along with huge amount of palladium. To balance this huge cost associated with the preparation of a defect free membrane a new approach has been found. After a few number of attempts, it has been found that some samples that are suffering from the leakage of gases can be made defect free by using the electroless plating with osmosis. The defective or damaged membrane is caused by that could be a result of cutting the edges for SEM which forms cracks or excessive heat treatment or improper sensitization and activation procedure or unstable bath condition resulting from inappropriate concentration of the plating bath components, etc could be successfully repaired. In this method the membrane is heat treated after each five hour of plating. Heat treatment is carried out at 120ºC in a furnace for whole night. Figure 12 and 13 show the cross section of the membrane with respect to inside surface with a thickness of 10-12 µm. The deep penetration proves that palladium is depositing on the defects and cracks and also the channels inside the support are also being filled up with palladium. With time the thickness of the film is increased and most of the defects or pores are repaired. The plating is continued until the thickness reaches to 20 µm. Figure 12 shows that all the new palladium particles are deposited on the large particles making the film denser. This membrane also suffered from the same end leakage problem.

Figure 16 and 17 show the SEM images of the as-deposited Pd/SS composite membrane with a palladium deposition on the outside substrate surface. From the images, it is clear that the palladium film was dense and all the deposited palladium particles are spherical. Small particles are deposited among the large particles and hence minimize the defects. Figure 17 shows uniform coating and deep penetration of the palladium onto the support pores. These results demonstrate that a defect free palladium composite membrane can be prepared by the electroless plating with osmotic field.

The membrane samples were further characterized by EDX analysis, one of them is shown in Figure 18. EDX analysis has been conducted to determine the elemental composition of the deposited film. Analysis has confirmed the deposition of pure palladium on the surface of SS tube. Pressure hold test for this membrane proves that there is no leak from membrane as well as from the ends. Permeability and selectivity tests are performed with this membrane and the details of the tests are described in the following section.

Permeation Characteristics of the Composite Membrane

For the hydrogen permeation study, an 18µm thick Pd/SS membrane (corresponding to calculated weight gain of 21.22 mg/cm²) has been. The effective membrane surface area is 18.0 cm²). Gas permeability experiments are performed for three different pure gases: hydrogen, nitrogen and helium. Experiments are conducted at five different temperatures and eleven different pressures differentials.
Figure 19 shows the dependency of the hydrogen permeation flux on the transmembrane pressure difference for different temperatures. The value of hydrogen pressure exponent, n was found to be 0.650, determined by regression analysis. The regression coefficients were found around 0.989 for all temperatures tested. The hydrogen permeances and the regression coefficient values are given in Table 6.1 for all the temperatures.

The value of the pressure exponent n, is routinely used as an indication of the rate limiting step of the hydrogen permeation through the Pd layer. If the value of n is equal to 0.5, Sievert’s law is assumed to be followed. In that case the rate determining step is the diffusion of hydrogen through the bulk of palladium. If the value of n is greater than 0.5, then the permeation rate is influenced by the surface process, leakage of the hydrogen through defects in the Pd layer, transport resistance of the support, poisoning of the palladium surface and so forth. However, it was suggested that for a thin palladium membrane the hydrogen transport could be controlled by a surface process of hydrogen i.e. adsorption and dissociation of molecular hydrogen.

From Figure 19, it is clear that hydrogen permeation flux increases with increase in the differential pressure as expected. Increase in temperature also results in higher hydrogen flux which can be clearly seen from Figure 20. Figure 21 shows that nitrogen permeation flux also increases with the pressure differentials. After the heat treatment of the as-deposited membrane there is a strong possibility of formation of pinholes. As seen, in the case where pinholes exist in the metal layer, the hydrogen gas can permeate through the metallic part and the pin-hole region of the membrane, whereas the nitrogen gas can only pass through the pinholes using Knudsen mechanism. The increase of nitrogen flux with differential pressure proves the presence of pinholes. From Figure 22, it can be seen that nitrogen flux decreases with temperature. It is assumed that with continuous exposure to high temperature, but under nitrogen atmosphere these leaks in the palladium layer disappear again.

A permeation experiment performed with pure helium also shows the same result as nitrogen. Figure 23 demonstrates that the helium permeation flux is greater than nitrogen permeation flux. The kinetic diameter of helium molecules is 2.6 Å whereas the kinetic diameter for nitrogen molecule is 3.64 Å. As a result the helium permeation flux is larger than nitrogen permeation flux. The pressure exponents for nitrogen and helium gases at 450ºC have been found to be 1.26 and 1.03, respectively. Figure 24 shows the dependency of nitrogen and helium on their pressure exponents with pressure differentials at a temperature of 450ºC. From this figure, for a permeability flux of $6.4249 \times 10^{-4}$ moles/m².s the pressure differential for nitrogen permeation is 45 psi and helium permeation is 20 psi. This difference in pressure differentials explained the difference in pressure exponents. Since kinetic diameter of nitrogen is larger than helium so it needed higher-pressure differentials than helium to pass through the pinholes of the membrane. As a result the pressure exponent for nitrogen is greater than that is for helium.

Figure 25 shows hydrogen selectivity with respect to nitrogen. Hydrogen selectivity is defined as the ratio of hydrogen flux to nitrogen /any other less permeable gas flux. It can be seen from Figure 25 that hydrogen selectivity increased with the temperature but decreased with transmembrane pressure difference. Mathematically, the hydrogen permeation flux, $J_{H_2}$, is related to the mass transfer resistance of the support, $R_s$, of the deposited dense metallic film $R_m$ and of the pin holes, $R_p$ as follows:
To increase $J_{H_2}$, one has to reduce $R_m$ and/or increase $R_p$, the resistance of the metallic film $R_m$ is determined by temperature, film thickness (if the surface reaction is not rate-limiting) and microstructure. The resistance of pinholes, $R_p$ can be increased by reducing the number of pinholes and the pinhole size. Hydrogen permeates through both the pinholes and dense metallic films. The hydrogen permeance through the dense metallic film would increase substantially with temperature, as was seen from Figure 20, but that through the pinhole would decrease slightly with temperature. At higher temperatures number of pinholes decreases. As a result, the selectivity would increase with increasing temperature. Since nitrogen gas can permeates through only the pinholes so at a higher temperature when the pinholes are decreased the nitrogen flow also decreased. Thus the selectivity of hydrogen increased with temperature but decreased with increasing transmembrane pressure.

The experimental values of the hydrogen permeances, which are calculated from the slopes of plots of Figure 19 at different temperatures, are used to calculate the activation energy for hydrogen permeation through the 18.0 µm thick palladium membrane. An Arrhenius plot of permeability data is shown in Figure 26. The activation energy for this composite membrane is calculated as 16.5769 kJ/mol. This value is in good agreement with those reported by other groups [7, 9].

**Membrane Reactor Results**

Membrane reactor model was investigated in a tubular reactor with following dimensions
- Total reactor length, $L_0 = 0.01$ m
- Inner radius of inner tube, $R_1 = 5.35 \times 10^{-3}$ m
- Outer radius of inner tube, $R_2 = 5.36 \times 10^{-3}$ m
- Inner radius of shell, $R_3 = 6.00 \times 10^{-3}$ m

Catalyst Properties:
- Radius = 0.11 mm.
- Composition of Ni in the catalyst = 15.2%
- BET surface area = 58 m$^2$.
- Catalyst surface area = 9.3 m$^2$/g_{cat} (fresh catalyst)
- Void fraction = 0.528

Permeation parameters used in this investigation were:
- Power index, $n = 0.5$
- Permeability, $Q_{H_2} = 1.618 \times 10^{-06}$ (mol/m.Pa^n.s)
- Permeation constant, $\alpha = 1.824 \times 10^{-08}$ (mol/s)

**Equilibrium, Rate and Adsorption Constants**

Equilibrium constants, reaction rate constants and adsorption constants were evaluated using thermodynamic equations. These are presented in Figures 27a, 27b and 27c, respectively. Figure 27a shows the variation of equilibrium constants with inverse of absolute temperature.
Logarithm of equilibrium constant of reactions (5) and (7) inversely varies with the inverse of absolute temperature and reaction (6) varies proportionally with the inverse of absolute temperature. Figure 27b presents the variation of rate constants with the inverse of temperature. Figure 27c presents the variation of adsorptions constants of the relevant components with inverse of temperature.

**Equilibrium Conversions**

Equilibrium conversions are helpful to compare with conversions the membrane reactor. We developed one model to determine equilibrium conversions and equilibrium compositions at various reaction conditions in a non-membrane reactor as well. At various reaction conditions conversions in a membrane reactor are compared with equilibrium conversions later in this paper.

Equilibrium conversions at various temperatures at a reaction pressure of 5 and 10 atm with a steam/methane molar ratio of 3.0 are presented in Figures 28a and 28b, respectively. These two figures indicate that total conversion of methane increases exponentially with temperature. The conversion curve of CH$_4$ to CO is concave upward and the conversion curve of CH$_4$ to CO$_2$ is convex upward. It indicates that at higher temperatures, the equilibrium conversion of CH$_4$ into CO is relatively high. Figure 28c presents equilibrium yields of hydrogen with respect to the molar amount of methane in the feed.

**Effect of Temperature on Conversions**

Temperature plays an important role in the conversion of steam-methane reforming reactions. Figures 29a to 29c show the influence of temperature on the conversion of methane, conversion of methane into carbon monoxide and carbon dioxide. In both membrane and non-membrane reactor cases conversion patterns are similar. To show the similarities clearly, conversions at 10 atm in a membrane and a non-membrane reactor are shown separately in Figures 29d and 29e, respectively. Conversion of methane increases exponentially with temperature. Methane conversion into carbon monoxide also increases exponentially at higher temperatures (above 700 K). Conversion of methane into carbon dioxide has a decreasing trend at higher temperatures.

**Effect of Reactor Pressure on Conversions**

Pressure also has an effect on the conversions of steam-methane reforming reactions. As shown in Figures 30a to 30c, both for membrane and non-membrane reactors conversion of methane, steam, methane to CO, methane to CO$_2$ decrease with the increase in pressure at a particular temperature.

**Effect of Space Time on Conversions**

The rate of reactions is dependent on the amount and adsorption properties of the catalyst. This leads to a different definition of space-time. Here space-time is defined as the amount of catalyst (in gm) per mol feed of methane per hour.

\[
\text{Space Time} = \frac{W}{F_{\text{CH}_4}^o} \cdot \frac{\text{gm cat}}{\text{hr/mol CH}_4}
\]  

(29)
Figures 31a and 31b show the effect of space-time on conversion of methane, steam, conversion of methane into CO and conversion of methane into CO\textsubscript{2} at 2 and 10 atm, respectively. These conversions increase with an increase in space-time. At lower values, an increase in space-time causes a significant increase in conversions. As the value of the space-time increases, the conversions approach asymptotic values. Figures 31c and 31d show the effect of space-time on conversion of methane into carbon dioxide at 2 and 10 atm, respectively.

**Effect of Steam to Methane Molar Feed ratio**

Figure 32 shows the effect of steam to methane molar feed ratio on conversions at \(P = 2\) atm., \(T = 773\) K, 4 gm Ni catalyst, \(\text{CH}_4\) feed rate = \(2.77 \times 10^{-3}\) mol/s. As steam to methane molar feed ratio increases conversion of methane increases in both types of reactors. But as before, at any feed ratio conversion of methane significantly higher in the membrane reactor. Conversion of methane to CO, which is undesirable, reduces slightly in a membrane reactor as steam to methane feed ratio increases, whereas it increases slightly in a non-membrane reactor.

**Yield of Hydrogen**

Yield of hydrogen can be defined in two ways. They are yield with respect to molar feed rate of methane (\(Y_{mf}\)) and yield of hydrogen with respect to methane reacted (\(Y_{mr}\)). Thus,

\[
Y_{mf} = \frac{\text{H}_2 \text{ production rate}}{\text{CH}_4 \text{ feed rate}}
\]

\[
Y_{mr} = \frac{\text{H}_2 \text{ production rate}}{\text{CH}_4 \text{ depletion rate}}
\]

Yield with respect to feed methane is the amount of hydrogen production per mole of feed methane. Yield with respect to methane reacted can only signify the extent of the reaction (5) in comparison to the reaction (7). If the only rate of the second reaction is greater or equal to the rate of the first reaction, the product will be carbon monoxide free. It can be viewed as only the third reaction is taking place in the reactor. In this case \(Y_{mr}\) is 4.0. If only the first reaction takes place in the reactor, \(Y_{mr}\) will be 3.0. Therefore, a 3.0 value of \(Y_{mr}\) indicates that no carbon dioxide is present in the output and a value of 4.0 shows that no carbon monoxide is present in the output.

Figures 33a and 33b show the effect temperature on the yield of hydrogen with respect to feed rate of methane (\(Y_{mf}\)). In both membrane and non-membrane tubular reactor, the yield increases greatly at higher temperatures. Figure 8a clearly shows that yield of hydrogen in a membrane reactor is much higher than in a similar non-membrane reactor. At higher temperatures, a membrane reactor can give a yield or conversion greater than the equilibrium yield or conversion. Figures 33a and 33b also indicate that at a particular temperature, a lower reactor pressure favors a higher yield.

Yields of hydrogen with respect to methane reacted are presented in Figure 33b. A sharp fall of the yield at higher temperatures (above 700 K) indicates that at lower temperatures, the extent of carbon monoxide production is very small and at higher temperatures carbon monoxide production is severe. It also shows that higher pressure is favorable for a lower carbon monoxide production.
Effect of Sweep Gas Flow Rate on Conversions

Sweep gas flow rate has a great impact on conversions in a membrane reactor. A higher sweep rate lowers the partial pressure of hydrogen in the permeation side. As a result, the diffusion rate of hydrogen through the membrane increases and hence the conversion. Figure 34 shows the effect of sweep gas flow rate on methane conversion. It also shows that at a very high flow rate of the sweep gas, a change in the flow rate does not affect the conversion significantly. It happens because at higher flow rates of the sweep gas, an increment does not lower the partial pressure of hydrogen significantly.

Effect of Temperature and Pressure on Hydrogen Separation

Figure 35 shows the effect of temperature on hydrogen separation by the membrane at various reactor pressures. Separation side total pressure is assumed 1 atm in all the cases. The figure shows that with an increase in reaction side total pressure increases the hydrogen removal by the membrane. An increase in the driving force causes this increased efficiency of the membrane. As the temperature increases, the rate of increment in the diffusivity is less than the rate of increment in the hydrogen production. As a result at a particular reactor pressure, as the temperature increases, at first the percentage removal of hydrogen decreases and then increases.

Partial Pressure Profile

Hydrogen diffusion through the membrane causes all the components in the reaction system to diffuse in radial direction. Figures 36a to 36d and 37a to 37d show the variation of partial of CH₄, CO, CO₂ and H₂ in both axial and radial direction at 673 K and 873K respectively with other parameters same. The bottom of the figures is the inlet of the reactor. The right hand side vertical line of a contour represents the membrane and the vertical line at the left hand side represents the centerline of the reactor.

CONCLUSIONS

Electroless plating method combined with osmotic pressure filed proved to be a useful technique in depositing palladium film on inside and outside surface of the porous stainless steel. Surface morphology and microstructure characterization by SEM and EDX demonstrated a strong adhesion of the plated palladium on the substrate and dense coalescence of the film. Characterization of the membrane by conducting permeability experiments with pure hydrogen, nitrogen, and helium gases showed that the membrane had high permeability and selectivity. For example, the hydrogen permeability for a composite membrane with an 18.0µm Pd film was 4.3×10⁻¹ mol/m²⋅s at 450 °C and the H₂/N₂ selectivity was around 1400 at the same temperature. It appears that new membrane is an excellent candidate for membrane-reactor separator application for hydrogen recovery at elevated temperature.

To investigate the potential application of Pd-stainless microporous membrane in membrane-reactor configuration, we investigated the steam reforming of methane. To have a better understanding of the membrane reactor, we developed a two-dimensional pseudo-homogeneous reactor model for steam reforming of methane by equilibrium shift in a tubular membrane reactor. Radial diffusion was taken into account for concentration gradient in the radial direction due to H₂-permeation through the membrane. Simulations results indicated that
due to simultaneous reactions and selective removal of hydrogen, the conversion was significantly higher than a non-membrane, conventional tubular packed-bed reactor and exceeded equilibrium limits. It needs further study to validate the model in a wide range of operating conditions.

REFERENCES


ACKNOWLEDGMENTS

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### Table 1: Composition of the sensitization and activation solutions

<table>
<thead>
<tr>
<th></th>
<th>Sensitization</th>
<th>Activation</th>
</tr>
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<tr>
<td><strong>Solute</strong></td>
<td>SnCl₂</td>
<td>PdCl₂</td>
</tr>
<tr>
<td><strong>Concentration</strong></td>
<td>1.2 g/l</td>
<td>0.1 g/l</td>
</tr>
<tr>
<td><strong>HCl (37%)</strong></td>
<td>2.5ml/l</td>
<td>2.5ml/l</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>Room temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td><strong>Duration</strong></td>
<td>~ 5 min</td>
<td>~ 5 min</td>
</tr>
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</table>

### Table 2: Typical Pd electroless plating bath composition for inside deposition

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
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</thead>
<tbody>
<tr>
<td>PdCl₂ (99.9 % metals basis, Pd content 59.86%)</td>
<td>5 g/l</td>
</tr>
<tr>
<td>Na₂EDTA</td>
<td>70 g/l</td>
</tr>
<tr>
<td>NH₄OH (28%)</td>
<td>500 ml/l</td>
</tr>
<tr>
<td>N₂H₄ (95% min)</td>
<td>10 ml/l</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>10</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>60°C</td>
</tr>
<tr>
<td>Osmotic solution (PEG)</td>
<td>50 g/l</td>
</tr>
</tbody>
</table>

### Table 3: Values of regression coefficients and hydrogen permeances at different temperatures for the composite membrane for n = 0.65

<table>
<thead>
<tr>
<th>Temperature, T (°C)</th>
<th>Regression coefficient (R²)</th>
<th>Hydrogen Permeance, Qₜ/H/t (moles/m.S.Pa⁰.⁶⁵)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0.9879</td>
<td>1.5887045*10⁻⁴</td>
</tr>
<tr>
<td>425</td>
<td>0.997</td>
<td>1.43274238*10⁻⁴</td>
</tr>
<tr>
<td>400</td>
<td>0.999</td>
<td>1.3063437*10⁻⁴</td>
</tr>
<tr>
<td>375</td>
<td>0.999</td>
<td>1.1038264*10⁻⁴</td>
</tr>
<tr>
<td>325</td>
<td>0.987</td>
<td>9.01553157*10⁻⁵</td>
</tr>
</tbody>
</table>
Figure 1: Experimental set-up for electroless plating coupled with osmotic pressure
Figure 2: Membrane Reactor
Figure 3: Experimental Setup for Permeability Study

1 - Pd-SS composite membrane
2 - thermocouple (a is stationary)
3 - carrier gas (Ar)
4, 5, 6 - feed gas H₂, N₂, He
5 - temperature controller
7, 8 - Permeate side flow to GC, Feedside flow to GC
9 - temperature indicator
10 - heater
11 - mass flow controller
12 - Flow read-out box
13 - computer

pressure gauge
on/off valve
needle valve
**Figure 4**: Pd-Ceramic/Stainless Steel Composite Membrane Reactor
Figure 5: SEM image of the inside surface porous SS support.
Figure 6: SEM image of the outer surface of the porous SS support
Figure 7: SEM image of the cross section of the SS support
Figure 8: Inside surface of the membrane after deposition with pump speed 500 ml/min and 99% hydrazine in tetra hydro furan
**Figure 9:** Cross sectional view of the membrane after deposition with pump speed 500 ml/min and 99% hydrazine in tetra hydro furan. Film thickness 4-5 micron
Figure 10: Inside surface of the membrane after deposition with pump speed 120 ml/min and 35 wt% hydrazine in solution of water
Figure 11: Cross sectional view of the membrane after deposition with pump speed 120 ml/min and 35 wt% hydrazine in solution of water. Film thickness 9-10 micron
Figure 12: Inside surface morphology of the repaired membrane after deposition for several hours.
Figure 13: Cross sectional image of the repaired membrane showing the thickness of the film as 10-12 micron.
Figure 14: Cross sectional image of the same membrane from a different angle.
Figure 15: Cross sectional image of the same membrane showing the maximum penetration and final film thickness of 20 micron.
Figure 16: Outside surface morphology of the as-deposited palladium membrane
Figure 17: Cross sectional image of the membrane showing deep penetration with average film thickness of 18 micron
<table>
<thead>
<tr>
<th>Element</th>
<th>Spect. Type</th>
<th>Element %</th>
<th>Atomic %</th>
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<tr>
<td>Cr K</td>
<td>ED</td>
<td>0.61</td>
<td>1.20</td>
</tr>
<tr>
<td>Fe K</td>
<td>ED</td>
<td>3.78</td>
<td>6.91</td>
</tr>
<tr>
<td>Ni K</td>
<td>ED</td>
<td>0.17</td>
<td>0.29</td>
</tr>
<tr>
<td>Pd L</td>
<td>ED</td>
<td>95.44</td>
<td>91.59</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**Figure 18:** EDX analysis of the membrane
Figure 19: Hydrogen permeation flux through a 18 µm Pd/SS composite membrane as a function of the driving force for permeation.
Figure 20: Hydrogen permeation flux as a function of temperature for various pressure differences between retentate and permeate
Figure 21: Nitrogen permeation flux as a function of the differential pressure
Figure 22: Nitrogen permeation flux as a function of temperature at various pressure differences between retentate and permeate.
Figure 23: Nitrogen and helium permeation fluxes as a function of the pressure difference at a temperature of 450°C.
Figure 24: Dependency of nitrogen and helium permeation fluxes on the pressure exponent at 450 °C
Figure 25: H₂/N₂ selectivity coefficient as a function of the pressure difference at different temperatures.
Figure 26: Arrhenius plot of the hydrogen permeance of the Pd/SS composite membrane in a temperature range of 325°C - 450°C
Figure 27.a: Equilibrium constant versus inverse of temperature
Figure 27.b: Rate constant versus inverse of temperature

CH₄ + H₂O = CO + 3H₂
CO + H₂O = CO₂ + H₂
CH₄ + 2H₂O = CO₂ + 4H₂
Figure 27.c: Adsorption constant versus inverse of temperature
Figure 28a: Equilibrium conversions at various temperatures, 4.0 gm Ni catalyst, CH₄ feed rate = 2.777×10⁻³ mol/s, steam to CH₄ molar feed ratio = 3.0, P = 5 atm.
**Figure 28b:** Equilibrium conversion at various temperatures. $P = 10$ atm, steam to $\text{CH}_4$ molar feed ratio $= 3.0$
Figure 28c: Yield to H$_2$ with respect to feed methane. 4.0 gm Ni catalyst, CH$_4$ feed rate = 2.777×10$^{-3}$ mol/s, CH$_4$ feed ratio = 3.0
Figure 29a: Effect of temperature on conversion at 2 atm. Ni catalyst loading = 4.0 gm, feed rate CH$_4$ = 2.777×10$^{-3}$ mol/s, steam to CH$_4$ ratio = 3.0, sweep gas flowrate = 3.0×10$^{-3}$ mol/s.
Figure 29b: Effect of temperature on conversion at 5 atm. Ni catalyst loading = 4.0 gm, feed rate $CH_4 = 2.777 \times 10^{-3}$ mol/s, steam to $CH_4$ ratio = 3.0, sweep gas flowrate = $3.0 \times 10^{-3}$ mol/s.
Figure 29c: Effect of temperature on conversion at 10 atm. Ni catalyst loading = 4.0 gm, feed rate $\text{CH}_4 = 2.777 \times 10^{-3}$ mol/s, steam to $\text{CH}_4$ ratio = 3.0, sweep gas flowrate = $3.0 \times 10^{-3}$ mol/s.
Figure 29d: Effect of temperature on conversion at 10 atm in a membrane reactor. Ni catalyst loading = 4.0 gm, feed rate CH₄ = 2.777×10⁻³ mol/s, steam to CH₄ ratio = 3.0, sweep gas flowrate = 3.0×10⁻³ mol/s.
Figure 29e: Effect of temperature on conversion at 10 atm in a non-membrane reactor. Ni catalyst loading = 4.0 gm, feed rate $CH_4 = 2.777 \times 10^{-3}$ mol/s, steam to $CH_4$ ratio = 3.0, sweep gas flowrate = $3.0 \times 10^{-3}$ mol/s.
Curves with cross hairs (+) represent the membrane reactor.
Curves without a cross hair (+) represent the tubular (non-membrane) reactor.

Figure 30a: Influence of pressure on conversion at 473 K. Ni catalyst loading = 4.0 gm, feed rate \( \text{CH}_4 = 2.777 \times 10^{-3} \) mol/s, steam to \( \text{CH}_4 \) ratio = 3.0, sweep gas flowrate = \( 3.0 \times 10^{-3} \) mol/s.
Figure 30b: Influence of pressure on conversion at 723 K. Ni catalyst loading = 4.0 gm, feed rate $\text{CH}_4 = 2.777\times10^{-3}$ mol/s, steam to $\text{CH}_4$ ratio = 3.0, sweep gas flowrate = $3.0\times10^{-3}$ mol/s.
Figure 30c: Influence of pressure on conversion at 723 K. Ni catalyst loading = 4.0 gm, feed rate $CH_4 = 2.777 \times 10^{-3}$ mol/s, steam to $CH_4$ ratio = 3.0, sweep gas flowrate = $3.0 \times 10^{-3}$ mol/s.
Figure 31a: Effect of space time on conversions. $P = 2\text{atm}$, $T = 773 \text{ K}$, steam to $\text{CH}_4$ molar feed ratio = 3.0
Figure 31b: Effect of space time on conversions. $P = 10$ atm, $T = 773$ K, steam to CH$_4$ molar feed ratio = 3.0
Figure 31c: Effect of space time on CH$_4$ conversions. P = 2atm, T = 773 K, steam to CH$_4$ molar feed ratio = 3.0
**Figure 31d:** Effect of space time on CH₄ conversions. P = 10 atm, T = 773 K, steam to CH₄ molar feed ratio = 3.0
Figure 32: Effect of steam to methane molar ratio on conversions. \( P = 2 \, \text{atm}, \, T = 773 \, \text{K}, \, 4 \, \text{gm} \) Ni catalyst, \( \text{CH}_4 \) feed rate = \( 2.777 \times 10^{-3} \, \text{mol/s} \)
**Figure 33a:** Influence of temperature on the yield of H$_2$ with respect to feed CH$_4$. Ni catalyst loading = 4.0 gm, CH$_4$ feed rate = $2.777 \times 10^{-3}$ mol/s, and steam to CH$_4$ feed ratio = 3.0.
Figure 33b: Influence of temperature on the yield of H₂ with respect to feed CH₄ reacted. Ni catalyst loading = 4.0 gm, CH₄ feed rate = 2.777×10⁻³ mol/s, and steam to CH₄ feed ratio = 3.0
Figure 34: Effect of sweep gas flow rate on conversion of CH4. P = 10 atm, T = 773 K, Ni catalyst loading = 4.0 gm, CH4 feed rate = $2.777 \times 10^{-3}$ mol/s, and steam to CH4 feed ratio = 3.0
Figure 35: Influence of temperature on the removal of H$_2$ by the membrane. Ni catalyst loading = 4.0 gm, CH$_4$ feed rate = $2.777 \times 10^{-3}$ mol/s, steam to CH$_4$ feed ratio = 3.0 and sweep gas flowrate = $2 \times 10^{-5}$ mol/s.
Figure 36a: Contour graph of partial pressure of CH₄ in the membrane reactor at T = 673 K, P = 10 atm, Ni catalyst loading = 4.0 gm, CH₄ feed rate = 2.777×10⁻³ mol/s, and sweep gas flowrate = 3×10⁻⁵ mol/s.
**Figure 36b:** Contour graph of partial pressure of CO in the membrane reactor at $T = 673 \text{ K}$, $P = 10 \text{ atm}$, Ni catalyst loading = 4.0 gm, CH$_4$ feed rate = $2.777 \times 10^{-3} \text{ mol/s}$, and sweep gas flowrate = $3 \times 10^{-5} \text{ mol/s}$. 
Figure 36c: Contour graph of partial pressure of CO$_2$ in the membrane reactor at $T = 673$ K, $P = 10$ atm, Ni catalyst loading = 4.0 gm, CH$_4$ feed rate = $2.777 \times 10^{-3}$ mol/s, and sweep gas flowrate = $3 \times 10^{-5}$ mol/s.
Figure 36d: Contour graph of partial pressure of H₂ in the membrane reactor at T = 673 K, P = 10 atm, Ni catalyst loading = 4.0 gm, CH₄ feed rate = 2.777×10⁻³ mol/s, and sweep gas flowrate = 3×10⁻² mol/s.
Figure 37a: Contour graph of partial pressure of CH$_4$ in the membrane reactor at T = 873 K, P = 10 atm, Ni catalyst loading = 4.0 gm, CH$_4$ feed rate = 2.777×10$^{-3}$ mol/s, and sweep gas flowrate = 3×10$^{-5}$ mol/s.
Figure 37b: Contour graph of partial pressure of CO in the membrane reactor at $T = 873$ K, $P = 10$ atm, Ni catalyst loading = 4.0 gm, $\text{CH}_4$ feed rate = $2.777 \times 10^{-3}$ mol/s, and sweep gas flowrate = $3 \times 10^{-5}$ mol/s.
Figure 37c: Contour graph of partial pressure of CO₂ in the membrane reactor at T = 873 K, P = 10 atm, Ni catalyst loading = 4.0 gm, CH₄ feed rate = 2.777×10⁻³ mol/s, and sweep gas flowrate = 3×10⁻⁵ mol/s.
Figure 37d: Contour graph of partial pressure of H$_2$ in the membrane reactor at $T = 873$ K, $P = 10$ atm, Ni catalyst loading = 4.0 gm, CH$_4$ feed rate = $2.777 \times 10^{-3}$ mol/s, and sweep gas flowrate = $3 \times 10^{-5}$ mol/s.