

CHAPTER III

EXPERIMENTAL

3.1 Materials, equipment, and instruments

3.1.1 Materials

- 1 Porous stainless steel tube from Mott Metallurgical Corporation porous stainless steel, 316L, O.D. – 9 mm, length – 70 mm, and wall thickness– 1 mm. The average pore size was 0.1 μm . The porosity was 17%
- 2 Palladium (II) chloride (PdCl_2), 99.9% from Alfa Aesar
- 3 Tetraamminepalladium (II) chloride monohydrate ($\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$), 98% from Alfa Aesar
- 4 Tin (II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), 98% from Carlo Erba
- 5 Hydrazine anhydrous (N_2H_4), 99.5% from Aldrich
- 6 Hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), 99.5% from BDH chemical
- 7 Disodium ethylenediaminetetraacetate (Na_2EDTA), 99.5% from Carlo Erba
- 8 Platinum on alumina ($\text{Pt}/\text{Al}_2\text{O}_3$), 0.5%wt from Alfa Aesar
- 9 Platinum on alumina ($\text{Pt}/\text{Al}_2\text{O}_3$), 1.0%wt from Alfa Aesar
- 10 Ruthenium on alumina ($\text{Ru}/\text{Al}_2\text{O}_3$), 0.5%wt from Alfa Aesar
- 11 Quartz wool from Alltech
- 12 Helium gas, 99.999% from Bangkok Industrial Gas Co., Ltd. (BIG)
- 13 Argon gas, 99.999% from Thai Industrial Gas Co., Ltd. (TIG)
- 14 Hydrogen gas, 99.999% from Bangkok Industrial Gas Co., Ltd. (BIG)
- 15 Standard hydrogen in argon, 10% from Thai Industrial Gas Co., Ltd. (TIG)
- 16 Standard mixed gas from Bangkok Industrial Gas Co., Ltd. (BIG):
 - 16.1 methane: carbon dioxide (50%:50%, 1:1)
 - 16.2 methane: carbon dioxide (33%:67%, 1:2)
 - 16.3 methane: carbon dioxide (25%:75%, 1:3)

3.1.2 Equipment

- 1 Home-made reaction apparatus

- 2 Digital flow meter from Alltech
- 3 Flow meter
- 4 Capillary flow meter

3.1.3 Instruments

- 1 Scanning Electron Microscope (SEM), JEOL model JSM-5800LV with Electro Dispersive Spectrometer (EDS)
- 2 Gas Chromatography (GC) with Thermal Conductivity Detector (TCD), Perichrom model PR2100

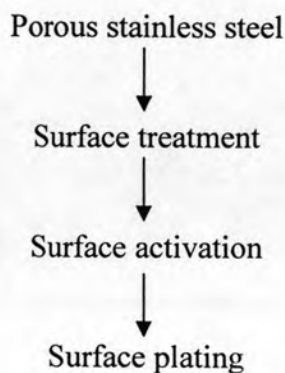
3.2 Experimental procedure

In this chapter the experimental procedure was divided into 5 parts

- 3.2.1 Preparation of single layer plating on porous stainless steel
- 3.2.1 Preparation of multilayer plating on porous stainless steel
- 3.2.3 Palladium membrane characterization
- 3.2.4 Dry reforming reaction
- 3.2.5 Instrument analysis

3.2.1 Preparation of single layer plating on porous stainless steel

The general procedure for metal plating was shown in Scheme 3.1.



Scheme 3.1 General procedure for metal plating.

3.2.1.1 Surface treatment

There were two steps for surface treatment, *i.e.*, surface cleaning and surface oxidation in air as following:

3.2.1.1.1 Surface cleaning by using alkali solution

Before plating, the foreign contaminants deposited on the stainless steel surface like grease, oil, dirt, corrosion products, and others was perfectly eliminated by cleaning the porous stainless steel in an ultrasonic bath with alkaline solution at 60°C followed by rinsing in tap water, deionized water, 18 M Ω -cm and isopropanol.

The alkaline cleaning solution consisted of a combination of alkali sodium compounds in Table 3.1.

Table 3.1 Chemical composition of alkali cleaning solution

Chemical	amount
Sodium hydroxide, NaOH	45 g/l
Sodium carbonate, Na ₂ CO ₃	65 g/l
Sodium phosphate, Na ₃ PO ₄ ·12H ₂ O	45 g/l
Liquid detergent	5 ml

Then the cleaned porous stainless steel was dried at 120°C for 4 hours.

3.2.1.1.2 Surface oxidation

The cleaned porous stainless steel was oxidized at 450°C with heating rate 4°C/min in air by using muffle furnace. Then the oxidized porous stainless steel was weighed and activated later.

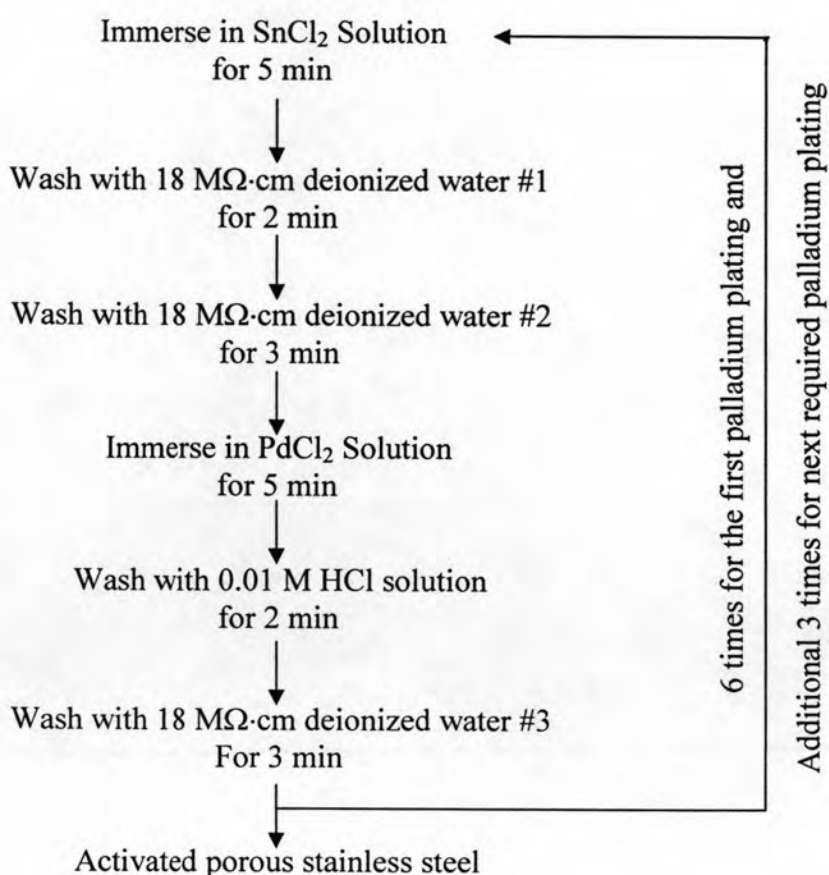
3.2.1.2 Surface activation

The typical composition of the activation bath is presented in Table 3.2. The sequence of surface activation steps were shown in Scheme 3.2. It consisted of the successive immersions of the PSS supports in the acidic SnCl₂ bath, the 18 M Ω -cm

deionized water, and followed by the acidic PdCl₂ bath. Then the activated porous stainless steel was rinsed with 0.01 M HCl 18 MΩ·cm deionized water to prevent hydrolysis of the Pd²⁺ ions. A two-step immersion sequence in SnCl₂ and PdCl₂ solution was generally repeated 6 times. In case of porous stainless steel tube, surface activation must be repeated but only 3 times were required if the tube was found to be not dense. A perfectly activated layer had a dark-brown color and smooth surface.

Table 3.2 Chemical composition of activation bath

	Chemical	Amount
Sensitization step	SnCl ₂	1.0 g/l
	HCl (37%)	1.0 ml/l
Activation step	PdCl ₂	1.0 g/l
	HCl (37%)	1.0 ml/l



Scheme 3.2 The procedure for surface activation step.

3.2.1.3 Palladium electroless plating [27]

The typical palladium plating solution composition was shown in Table 3.3. The freshly prepared plating solution was necessarily left for more than one day in order to form the stable palladium complex. The porous stainless steel was kept in the palladium plating solution at pH 10 and at temperature 60°C for 90 min. It was then cleaned with the warm deionized water and let it at room temperature. Plating and cleaning was then started over again for the next 3 times. Finally, it was dried at 120°C for 4 hours. The layer thickness was measured using gravimetric method. The palladium layer composition was analyzed quantitatively and qualitatively by scanning electron microscope. The plating bath was used for porous stainless steel disk shown in Figure 3.1. For porous stainless steel tube, it was performed in plating cell exhibited in Figure 3.2.

Table 3.3 The composition of electroless Pd plating solution

Chemical	Amount
Tetraaminepalladium (II) chloride, Pd(NH ₃) ₄ Cl ₂ ·H ₂ O	4.0 g/L
Ammonia solution, NH ₄ OH (28%)	198 mL/L
Disodium ethylenediaminetetraacetate, Na ₂ EDTA	40.1 g/L
Hydrazine anhydrous, N ₂ H ₄ (1M)	5.6 – 7.6 mL/L



Figure 3.1 Plating bath for porous stainless steel disk.

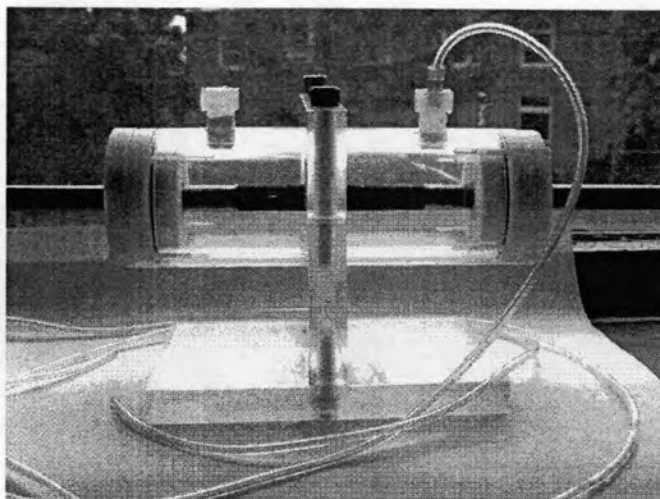
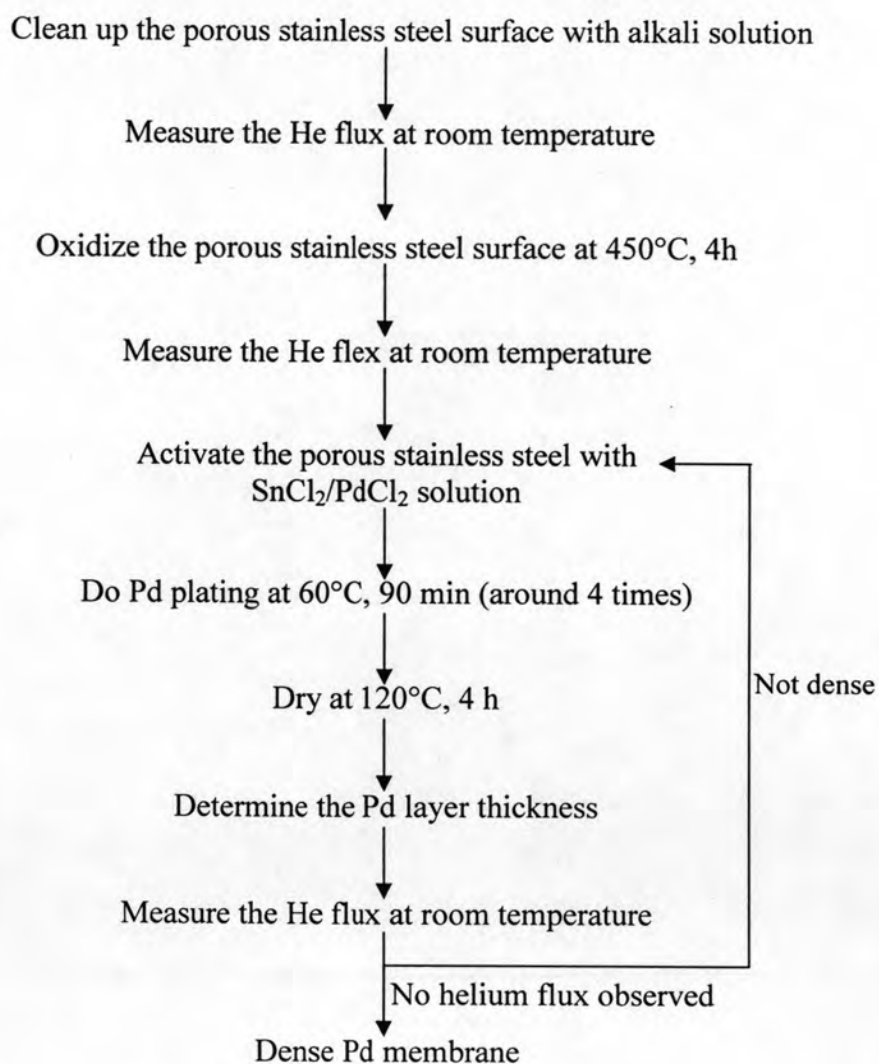


Figure 3.2 Plating cell for porous stainless steel tube.



Scheme 3.3 The procedure of Pd membrane preparation.

3.2.1.4 Preparation of intermetallic diffusion barrier

Followings were the procedure for depositing a certain metal on cleaned and oxidized porous stainless steel before palladium plating.

3.2.1.4.1 Silver tungsten eletroless plating [59]

The plating bath composition is presented in Table 3.4.

Table 3.4 Silver-tungsten plating solution composition

Chemical	Amount
Silver nitrate, AgNO ₃	5 g/L
Sodium tungstate, Na ₂ WO ₄	20 g/L
Benzoic acid, C ₆ H ₅ COOH	40 g/L
Hydrazine hydrate, N ₂ H ₄ H ₂ O	0.45 mL/L
Ammonium acetate, CH ₃ COONH ₄	20 g/L

Prior to activation of surface of porous stainless steel, the surface treatment step was applied as explained in section 3.2.1.1. The surface activation as described in section 3.2.1.2 was applied to initiate film deposition on the porous stainless steel. All deposition was performed at pH 9 at room temperature. Finally, the plated porous stainless steel was washed in iso-propanol followed by drying in nitrogen. The layer thickness was measured using gravimetric method. The Ag-W thin film composition was analyzed qualitatively and quantitatively by scanning electron microscope (SEM).

3.2.1.4.2 Silica deposition by sol-gel method [62]

Colloidal silica sols were prepared under base-catalyzed condition *via* hydrolysis of tetraethyl orthosilicate (TEOS). The concentration of NH₃ and distilled water based on TEOS of 0.28 M were 3.3 M and 10 M, respectively. The volume of reaction mixture was adjusted to 500 mL with ethanol. Prior to the addition of NH₃/H₂O mixture, TEOS/ethanol mixture was stirred vigorously in an oil bath of

50°C. The addition of the $\text{NH}_3/\text{H}_2\text{O}$ was carried out drop-wise followed by refluxing the mixture for 3 hours at vigorous stirring resulting in the stable colloidal silica sol. The porous stainless steel oxidized at 450°C for 6 hours was modified with the colloidal silica sol by dip-coating. Finally the coated porous stainless steel was dried at 120°C for 4 hours and calcined at 800°C for 4 hours, respectively. The silica layer composition was analyzed qualitatively and quantitatively by scanning electron microscope (SEM).

3.2.1.4.3 Chromium electroplating [63]

After surface cleaning, the porous stainless steel was oxidized at 800°C for 6 hours. Then chromium plating bath was applied as shown in Figure 3.3.

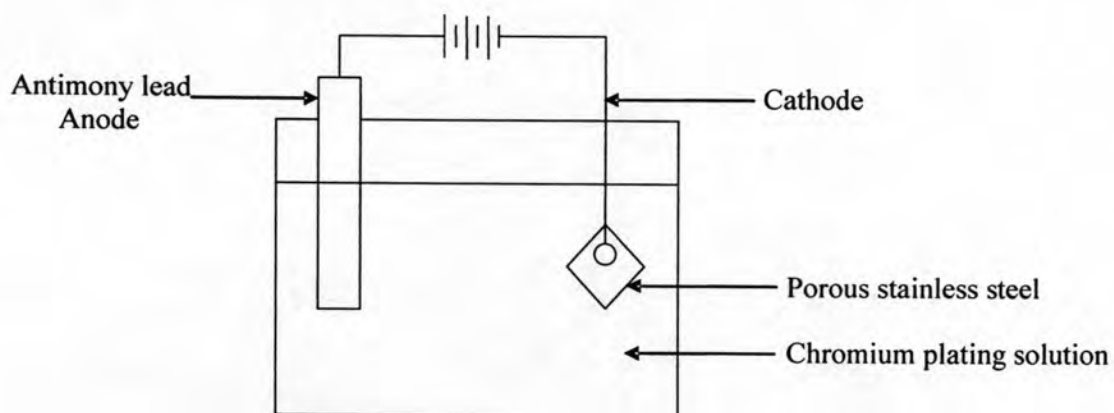


Figure 3.3 The chromium plating bath.

The chromium plating solution consisted of 250 g/L chromic acid and 1.25 g/L sulfuric acid as a catalyst in 200:1 ratio. The chromium plating was performed at room temperature with current density around 100-150 A/ft².

3.2.1.5 Preparation of Pd/Cr₂O₃/PSS

After chromium plating on porous stainless steel as described in section 3.2.1.4.3, it was oxidized at 800°C for 6 hours in air. It was subjected to surface activation and palladium plating as described in section 3.2.1.2 and 3.2.1.3, respectively.

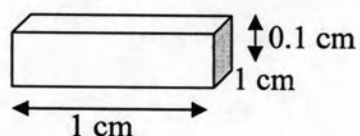
3.2.2 Palladium membrane characterization

3.2.2.1 Determination of plated metal thickness

The plated metal thickness was calculated as follows:

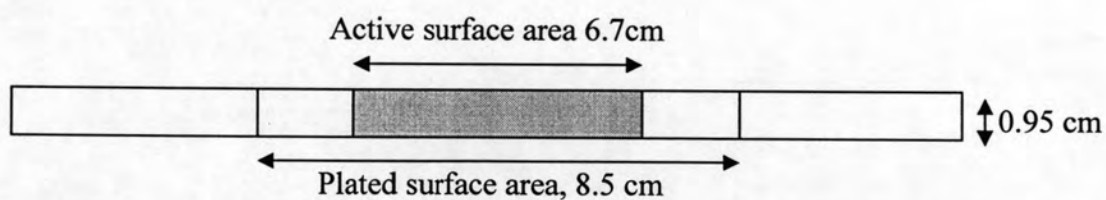
$$\text{Plated metal thickness } (\mu\text{ m}) = \left(\frac{\text{plated PSS weight} - \text{original PSS weight}}{\text{Plated surface area of PSS} \times \text{density of plated metal}} \right) \times 10^4$$

Porous stainless steel of disk



$$\begin{aligned} \text{Plated surface area} &= 2(1 \times 1) + 4(1 \times 0.1) \\ &= 2.4 \text{ cm}^2 \end{aligned}$$

Porous stainless steel tube



$$\begin{aligned} \text{Plated Surface area} &= \pi \cdot d \cdot l \\ &= 3.14 \times 0.95 \times 8.50 \\ &= 25.42 \text{ cm}^2 \end{aligned}$$

3.2.2.2 Helium flux testing

The plated Pd membrane tube was dried at 120°C for 2 hours, then measurement of the helium flux was investigated at room temperature and pressure

difference (ΔP) between shell and tube side at 1 atm, which the tube side was opened to the atmosphere. The apparatus set up of helium flux testing was shown in Figure 3.4. Normally, the flow meter was used for measuring helium flow rate. A soap-bubble capillary flow meter was used for flow-rate less than 1 mL/min; a digital flow meter (Alltech), for flow-rates in the range of 1-500 mL/min; and a wet-test meter for flow-rates greater than 500 mL/min.

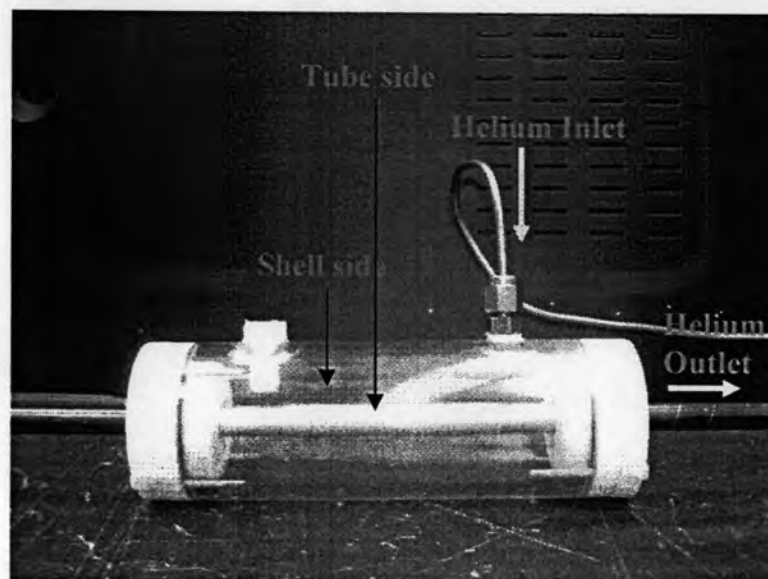


Figure 3.4 Helium flux testing cell.

$$\text{He Flux (m}^3/\text{m}^2\text{h)} = \left(\frac{\text{Flow rate of He on Tube side (ml/min)}}{\text{Active surface area (cm}^2\text{)}} \right) \times 0.6$$

3.2.2.3 Hydrogen permeation flux testing and selectivity coefficient

The experimental set up diagram for hydrogen permeation flux testing was shown in Figure 3.5. The feed gas was flowed in the shell side of the palladium membrane reactor and the permeated gas was collected on the tube side. The pressure of the feed gas was monitored by a pressure gauge. The gas permeation rate (the volumetric flow rate) was measured in the permeate side at atmospheric pressure and room temperature. A soap-bubble capillary flow meter was used for flow-rate less than 1 mL/min; a digital flow meter (Alltech), for flow-rates in the range of 1-500 mL/min; and a wet-test meter for flow-rates greater than 500 mL/min. Temperature controllers (Omega CN-9000) were used to control the temperature of the furnace and

the palladium membrane reactor. The temperature of the reactor was varied from 350-450°C. Prior to the hydrogen permeation testing. The dense palladium membrane tube was heated in helium at a rate about 1°C/min before subjecting to hydrogen.

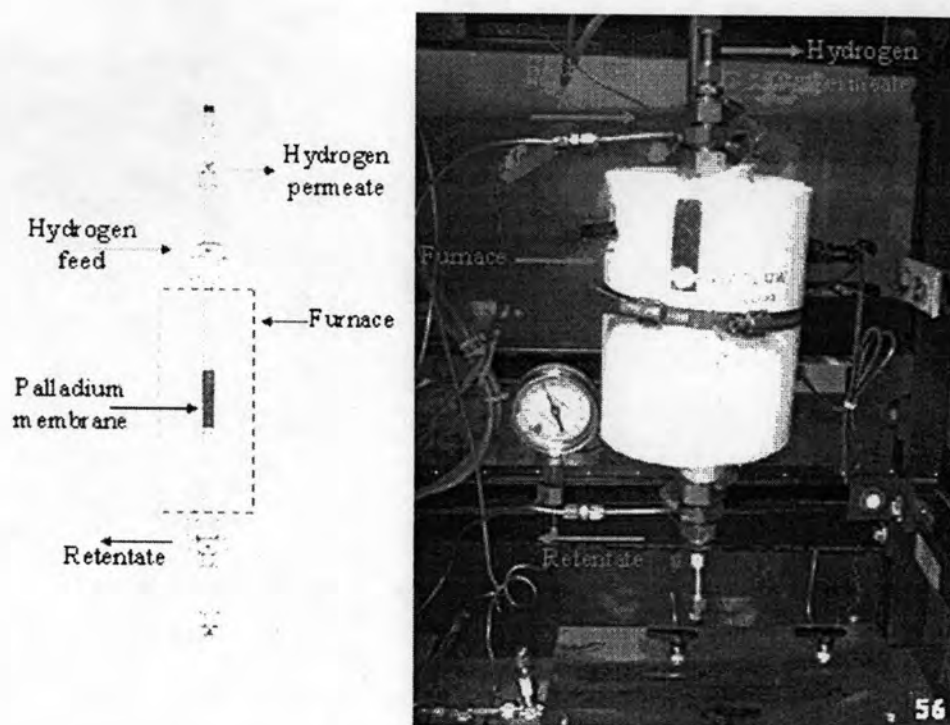


Figure 3.5 The experimental setup for hydrogen permeation flux measurement.

3.2.3 Dry reforming reaction test

The experimental set up was shown in Figure 3.5. A catalyst 1.0 g, with a particle size around 500 μ m, was loaded in the shell side around the active surface area of the tube side. It was located in this area by using two quartz wool plugs at both ends of the shell side of the reactor. The catalyst was reduced in pure hydrogen gas 50 mL/min for 4 h at 550°C in a separate apparatus just before use. Helium was flushed and used as a carrier gas for the entire experiment. A thermocouple placed inside the dense palladium tube allowed to control the temperature in the catalytic bed. An equimolar gas mixture of methane and carbon dioxide was fed at flow rate of 30 mL/min. The reaction was monitored by using on-line gas chromatography. Different catalysts 0.5%Ru/Al₂O₃, 0.5% Pt/Al₂O₃, and 1.0% Pt/Al₂O₃ were used. In order to

study the sweep gas effect, Argon gas was fed at different flow rate up to 60 mL/min at the tube side.

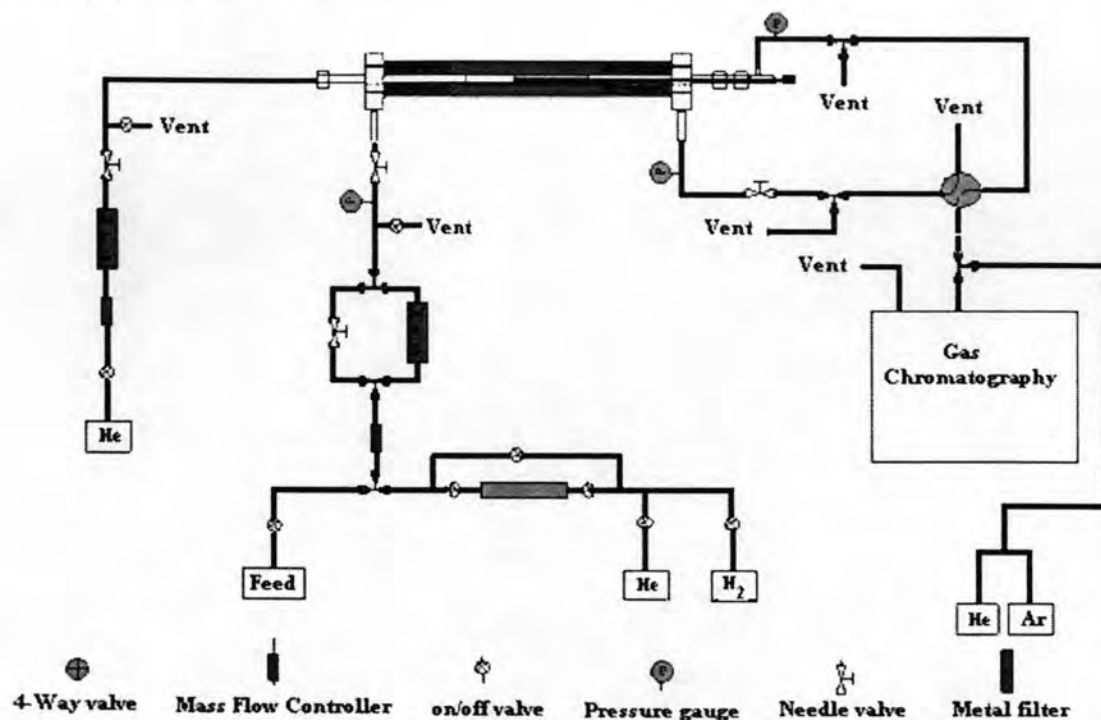


Figure 3.6 The experimental setup for dry reforming reaction.

3.2.4 Instrument analysis

3.2.4.1 Determination of gas composition in dry reforming reaction by means of online GC-TCD

The gas composition from the shell side of palladium membrane reactor was analyzed by the on-line gas chromatography (Perichrom model PR2100) equipped with two automatic valves (Figure 3.7), a sampling valve and a bypass valve. All data were acquired and analyzed by using Clarity computer software. A serial/bypass configuration was arranged for two isothermal columns; Hayesep Q and Molecular sieve 13X, at 40°C. The valve no. 2 was set to “off” during the entire experiment. While the valve no.1 was set to “on” for 19 seconds then “off”. To allow injection of sample gases, the carrier gas, argon gas with pressure 150kPa, directed the mixture of methane, carbon monoxide, carbon dioxide, and hydrogen went through the Hayesep Q column, and then quickly entered the serial-arranged Molecular sieve 13X for separating the hydrogen and carbon monoxide, where those gases were separated and

passed to the Thermal Conductivity Detector (TCD). The temperatures of inlet, oven, and detector were 100 °C, 40 °C, and 150 °C, respectively. The analysis time was 10 min. The amount of permeated gas composition was analyzed by comparing the area under peak with external standard from the calibration curve. The correlation value of accepted calibration curve must be at least 0.995 at 99.5 % confidence level.

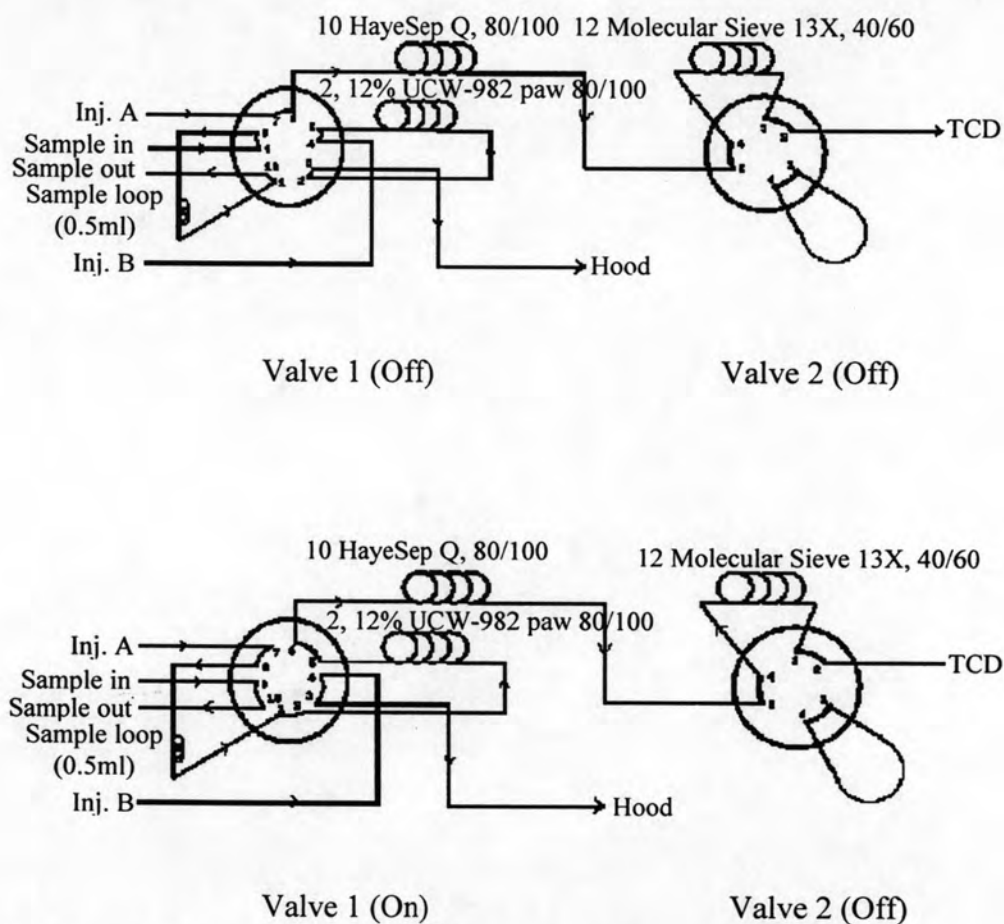


Figure 3.7 The configurations of on-line gas chromatography sampling system.

3.2.4.2 Surface characterization of porous stainless steel and plated porous stainless steel

Surface characterization was performed using JEOL Scanning Electron Microscope (SEM) model JSM 5800LV equipped with Electro Dispersive Spectrometer (EDS) for the qualitative and quantitative analysis. The spatial resolution for SEM-EDX lies between 0.8 and 1.2 μm for the samples we investigated. SEM specimens of the metal deposited porous stainless steel were cut using a SiC saw blade and mounted with phenolic powder in a Smithells II mounting press. The resounding samples were ground with SiC papers with increasing grain fineness from 80 to 400 grit. Grinding was performed by using Metaserv 2000 grinder-polisher. Vibromet I automatic polisher was used to polish the sample to 1 μm over night. Prior to SEM cross-section analysis sample was painted with carbon ink and gold-coated to avoid charging.