CHAPTER IV
EXPERIMENT

In the research of dehydrogenation of propane in palladium membrane reactor, both simulation and experiment are considered. In order to model a membrane reactor, an accurate reaction rate data of the dehydrogenation of propane and permeation rate data of hydrogen through the membrane are necessary. This chapter is categorized in four parts: catalyst preparation, kinetic studies, permeation studies and membrane reactor studies.

4.1 Catalysts preparation

Three types of propane dehydrogenation catalysts were used in catalyst selection section of kinetic study part.

1. (0.3 wt%)Pt/γ-Al_2O_3
2. (0.3 wt%)Pt-(0.3 wt%)Sn/γ-Al_2O_3
3. (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6 wt%)K/γ-Al_2O_3

4.1.1 Preparation of catalyst support.

Alumina support (obtained from Sumitomo Aluminium Smelting Co., Ltd., Japan) which was grounded to the required mesh size of 60/80 was washed with distilled water 3-4 times to remove the very fine particles and other impurities, and dried at 383 K for overnight. Subsequently, the support was calcined in air at 573 K for 3 hours.

4.1.2 Preparation of platinum catalysts

- *Preparation of impregnation solution*

The impregnating solution for two grams of support was prepared by calculating the amount of the chloroplatinic acid (manufactured by Wako Pure Chemical Industries Co., Ltd., Japan.) stock solution (1 gram of chloroplatinic acid in 25 ml de-ionized water) to the required metal loading (see Appendix A for detials of calculation of amount of metal required). Hydrochloric acid, 5 wt% of alumina support, was then added to the solution. De-ionized water was finally added until 2 ml of the solution was obtained.

- *Preparation of platinum catalyst*

Two grams of alumina support was impregnated with the impregnation solution and then the mixture was left for 6 hours to obtain good distribution of metal complex. After that the impregnated support was dried at 383 K in air overnight. Consequently, the dried material was calcined in air (100 ml/min.) at 773 K for 3 hours with heating rate 283 K/min.

4.1.3 Preparation of platinum-tin catalysts

- *Preparation of impregnation solution*

Impregnation solution was prepared using the same method for preparation of platinum catalyst but stannous chloride dihydrate ($SnCL_2.2H_2O$ manufactured by Fluka Chemie AG, Swizerland) was added to the impregnation solution before impregnating with the support. This is called “Co-impregnation method”.

- *Preparation of platinum-tin catalyst.*

The same preparation method for preparation of platinum catalyst, was employed for the preparation of platinum-tin catalyst.

4.1.4 Preparation of platinum-tin-potassium catalyst.

- Preparation of impregnation solution.

Preparation of impregnation solution used the same method as preparing platinum-tin solution. Re-impregnation potassium solution was prepared by mixing potassium nitrate (KNO_3 manufactured by E.Merck, Federal Republic of Germany) which calculated to the desired amount with water into 2 ml.

- Preparation of platinum-tin-potassium catalyst

The preparation of Pt-Sn-K catalyst used co-impregnation method, the same method as preparing Pt-Sn catalyst but followed by re-impregnation. After calcination of co-impregnated platinum-tin catalyst, the calcined material was re-impregnated by potassium solution. The calculation of potassium loading was shown in Appendix A. The re-impregnation material was calcined again with the same condition.

4.2 Kinetics study

4.2.1 Reaction of propane dehydrogenation

The reaction system consisted of a microreactor installed in an electrical furnace. The furnace temperature was controlled by a temperature controller. The microreactor was constructed from a quartz tube. A gas mixture (3% or 20% propane balanced in nitrogen) is used as a reactant gas. The experimental conditions of the dehydrogenation reaction are shown in Table 4.1. Concentration of the exit gas at each time on stream was measured using a gas chromatograph, the operating condition for the gas chromatography is shown in Table 4.2. The experimental procedures are as follows :

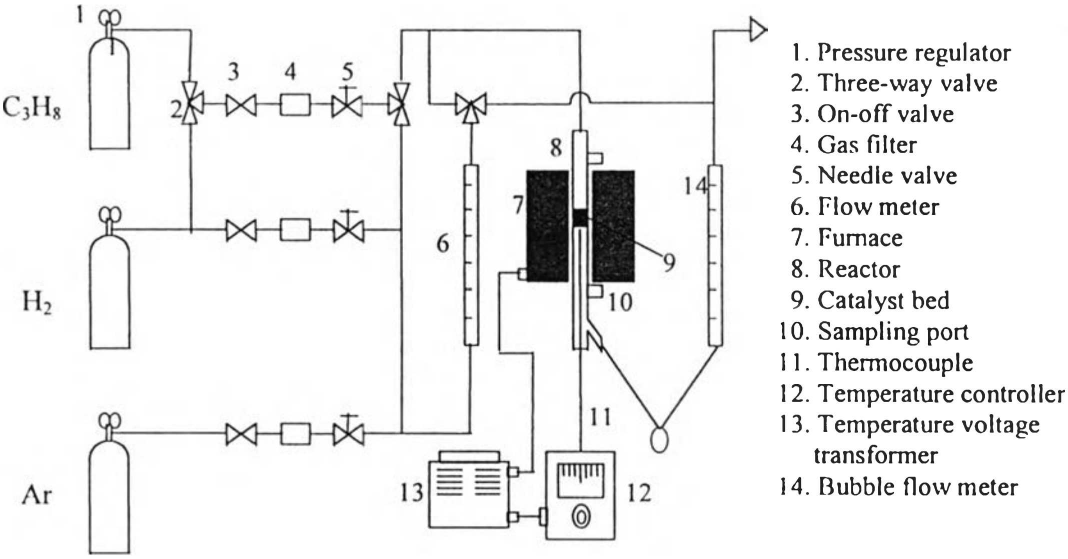


Figure 4.1 Schematic diagram of the kinetic studies experimental set-up.

Table 4.1 Operating conditions of the dehydrogenation reaction

Catalyst reduction temperature	773	K
Reaction temperature	773	K
Operating pressure	1.03×10^5	Pa
Reaction time	3-120	min
Hydrogen/Hydrocarbon ratio	0,1	[-]

Table 4.2 Operating condition of gas chromatograph.

Model	GC 14B	
Detector	FID	
Packed Column	VZ-10	
Nitrogen flow rate	50	ml./min.
Hydrogen flow rate	30	ml./min.
Air flow rate	250	ml./min.
Column temperature	343	K
Injector temperature	373	K
Detector temperature	523	K

1. 0.1 gram of catalyst was packed in the middle of the quartz microreactor. The reactor was then placed in the furnace and ultra high purity argon gas was introduced into the reactor at the flow rate of 30 ml./min.

2. The reactor was heated up at the heating rate of 283 K/min until the catalyst temperature reached 473 K. Then, ultra high purity argon gas was replaced by hydrogen gas at a flow rate of 100 ml/min. followed by heating up the reactor at a heating rate of 283 K/min until the catalyst temperature reached 773 K. The catalyst was reduced at this temperature for 1 hour.

3. When the reduction process was completed, hydrogen gas was changed to high purity argon for 5 minute and then changed to the gas mixture of propane in nitrogen.

4. The gas sampling was taken at 3, 5, 10, 30, 60 and 120 minutes of reaction time on stream..

5. When the desired reaction time on stream was complete, the feed gas was switched to the ultra high purity argon gas. Then, the reactor was cooled down without the holding step.

4.2.2 Determination of coke deposition on metal active site by CO adsorption.

The CO adsorption technique for the measurement of metal active sites of the fresh and spent catalyst was based on the concept that one CO molecule adsorbed on one metal active site (Biswas et.al.,1987). A gas chromatograph equipped with a thermal conductivity detector was used to monitor the amount of CO leaving the reactor. The operating condition of TCD is illustrated in Table 4.3.

Table 4.3 Operating condition of gas chromatograph (GOW-MAC).

Model	GOW-MAC
Detector	TCD
Helium flow rate	30 ml./min.
Detector temperature	353 K
Detector current	80 mA.

Experimental procedure.

1. 0.1 g. of catalyst was placed in a stainless steel tubular reactor. Helium gas was introduced into the reactor at the flow rate of 30 ml./min. The reactor was heated at the increasing rate of 283 K/min until the temperature reaching 473 K, then the helium gas was changed to hydrogen gas with the flow rate of 100 ml/min. The reactor was heated at the same rate until the temperature reaching 773 K. The reactor was held at this temperature for 1 hour.

2. The reactor was cooled down to room temperature.

3. Now the catalyst was ready for metal active site measurement. Small amount of CO (40 μl) were pulsed through the reactor until saturation was obtained. The saturation point was determined when the integrated area of the successive peak was not changed.

4. The amount of metal active sites of fresh catalyst was calculated by the amount of CO adsorbed (see Appendix B).

To measure the amount of metal active sites of spent catalyst the reactor was heated up to 443 K in helium gas for 30 minnutes to desorb CO gas. After the reactor was heated to 473 K. Helium gas was switched to hydrogen. The reactor was heated to 773 K. Then hydrogen was replaced with high purity argon for 5 minute before being changed to the gas mixture of propane in nitrogen.

When reaching a desired time on stream, the feed gas was switched to helium and the reactor was cooled down to 323 K. High purity helium was changed to hydrogen for 3 hours before being changed back to helium. The reactor was cooled down to room temperature and the step 3 was repeated to obtain metal active sites of spent catalyst.

4.3 Permeation study.

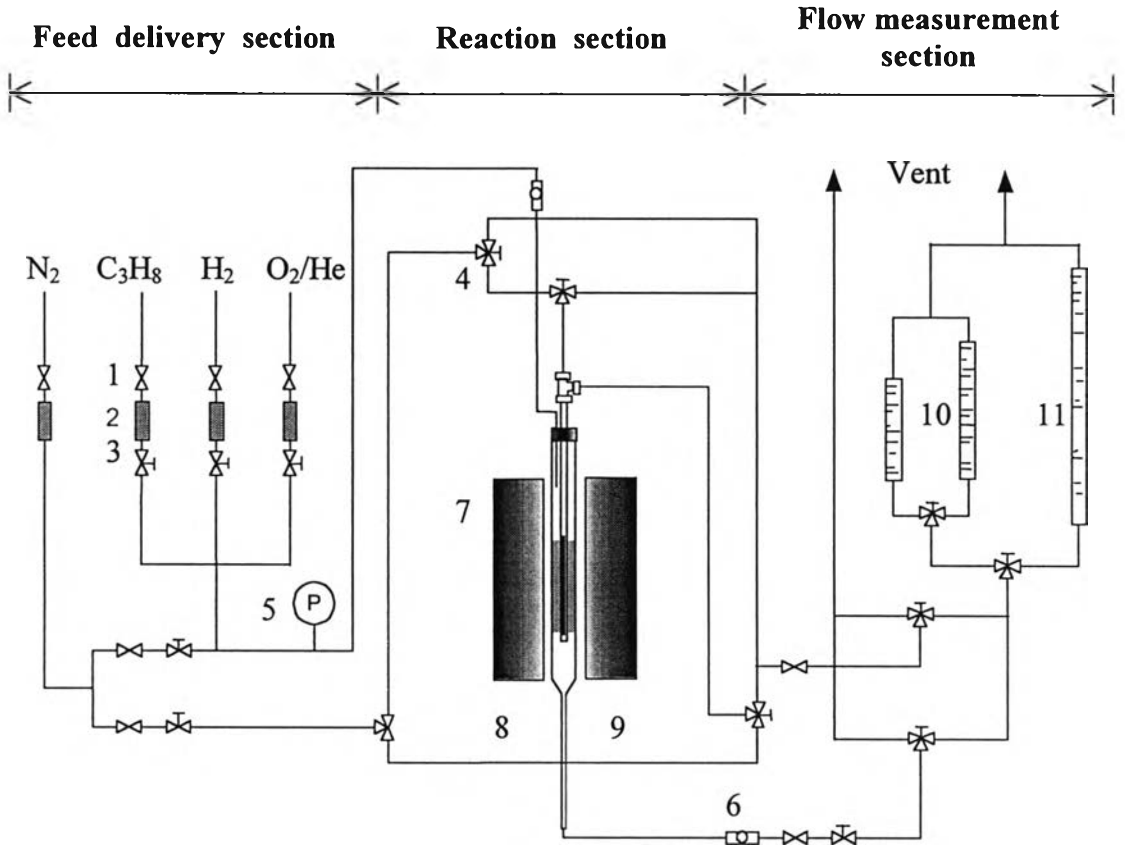
Permeation of hydrogen through the palladium membrane was measured using a membrane reactor apparatus. Then the permeation coefficients can be directly calculated.

4.3.1 Membrane reactor apparatus.

The experimental apparatus consists of feed delivery system, membrane module and flow measurement system. The schematic diagram is shown in Figure 4.1. The membrane module is shown in Figure 4.2. It is a shell and tube palladium/silver membrane whose characteristic is shown in Table 4.4.

Table 4.4 Characteristic of Pd/Ag composit membrane.

Separative layer composition	77%Pd / 23%Ag
Separative layer thickness	100 μm
Outer diameter	6.35 mm
Membrane length	150 mm



Component of experimental system.

1. On-off valve
2. Gas filter
3. Metering valve
4. Three-ways valve
5. Pressure gauge
6. Simpling port
7. Electrical furnace
8. Support or catalyst bed
9. Membrane
10. Rotameter
11. Buble flowmeter

Figure 4.2 Schematic diagram of membrane reactor experimental system.

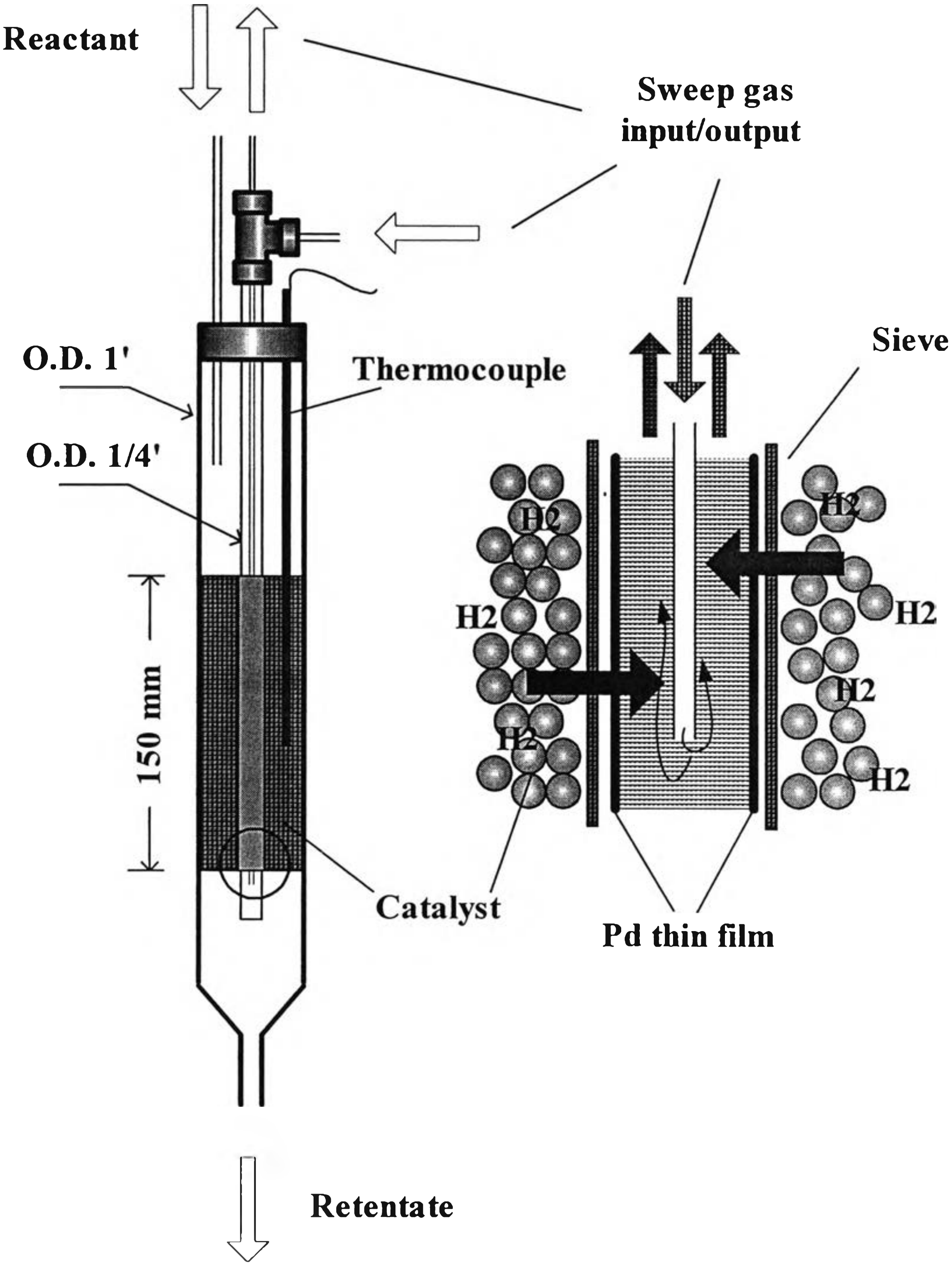


Figure 4.3 Membrane module of the Pd membrane reactor

4.3.2 Permeation of hydrogen through Pd/Ag composit membrane.

For the permeation studies,16 grams of SiO_2 was packed outside the membrane tube (shell side). Before starting an experiment, pretreatment of membrane with hydrogen at 573 K is necessary to prevent defect of Pd surface. Nitrogen gas was introduced in both sides of the membrane at flow rate of 100 ml/min. The reactor was heated at the increasing rate of 283 K/min until the temperature reaching 283 K. Then nitrogen gas in the shell side was changed to ultra high pure hydrogen gas at the flow rate of 100 ml/min and held at this temperature for 1 hour.

In the study of hydrogen permeation through the Pd/Ag membrane, ultra high pure hydrogen was fed though the shell side while nitrogen sweep gas was fed in the tube side. Molar flow rate of hydrogen was fixed at $2.46x10^{-5}$ mol/s and that of nitrogen was varied between $3.35x10^{-5}$ and $1.43x10^{-4}$ mol/s, respectively. Permeate and retentate flow rate were measured using a soap film flow meter.

4.4 Membrane reactor studies.

The performance of this reaction in the membrane reactor was carried out by experimental studies and the results were compared with simulation results.

1. The experimental set up in this study is similar to the permeation study but the shell side was packed with catalyst along the membrane length. The reactor was then placed in the furnace and the ultra high purity helium gas was introduced into the shell side of the reactor at the flow rate of 500 ml/min while nitrogen sweep gas flow rate in tube side was adjusted to the desired value.
2. The reactor was heated up at the heating rate of 283 K/min. until the catalyst temperature reached 473 K. Then, ultra high purity herium gas was replaced by hydrogen gas at the flow rate of 500 ml/min followed by heating up the reactor at the heating rate of 283 K/min until the catalyst temperature reached 773 K. The catalyst was reduced at this temperature for 1 hour.
3. When the reduction process was completed, hydrogen was changed to high purity argon for 5 min. and then changed to the gas mixture of propane in nitrogen.
4. The gas sampling was taken at steady state value.
5. When a desired time on stream was reached, the propane was changed to the ultra high purity helium gas. Then, the reactor was cooled down to room temperature.

In case of an experiment with spent catalyst, regeneration of catalyst is necessary. In step two, prior to flow with hydrogen, catalyst was regenerated with 1%O_2 in helium at 773 K for 1 hour and the next step was similar to the above procedure.