



CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Gases

- 10% carbon monoxide in helium from Thai Industrial Gas Public Co., Ltd.
- 20% carbon dioxide in helium from Praxair (Thailand) Co., Ltd.
- 5% Oxygen in helium from Thai Industrial Gas Public Co., Ltd.
- Ultra high purity hydrogen (99.9%) from Thai Industrial Gas Public CO., Ltd.
- High purity nitrogen from Thai Industrial Gas Public Co., Ltd.
- High purity helium from Thai Industrial Gas Public Co., Ltd.
- Ultra high purity helium from Thai Industrial Gas Public Co., Ltd.

3.1.2 Chemicals

- Hydrogen tetrachloroaurate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), ACS, 99.99% purity from Alfa Aesar A Johnson Matthey Company.
- Titanium dioxide (TiO_2) P25 Anatase AR grade of 99.0% purity from Sigma-Aldrich Company
- Sodium carbonate (Na_2CO_3)

3.2 Equipment

The experimental setup for simulate reformatte, as shown schematically in Figure 3.1, was divided into 3 main parts

3.2.1 Gas Blending system

The reactant gas mixture is composed of CO , H_2 , CO_2 , and O_2 . The carrier of the reactant gas is He. Every stream line was passed through micro-filter to remove particles and check valve to prevent the reverse flow. Mass flow controller

was used to control the flow rate. After that the reactant gases were mixed before sending to the reactor.

3.2.2 Catalytic Reactor

The PROX reaction was performed in a single-stage and a double-stage reactor at atmospheric pressure and the temperature was monitored and controlled by a PID temperature controller equipped with a thermocouple (type K). For the reactor part, it was made of glass U-tube with an inside diameter of 6 mm. The catalyst was packed between glass wool plugs in the middle of the reactor.

3.2.3 Analytical Instrument

The outlet gas from the reactor was analyzed and the composition was analyzed qualitatively and quantitatively by auto-sampling with a Agilent Technologies 6890N series the gas chromatograph equipped with a thermal conductivity detector (TCD). The gas column utilized in the chromatograph was carboxsphere, 80/100 mesh, 10 ft × 1/8 inch stainless steel packed column. The temperature of oven, injector, and detector was maintained at 55, 110, and 175°C, respectively.

3.3 Methodology

3.3.1 Catalyst Preparation Process

The Au/TiO₂ catalysts were prepared by deposition-precipitation. The Au amount was varied in the range of 1–2 wt% for studying the effect of metal loading. HAuCl₄·3H₂O (Acros) was used as the Au precursor. HAuCl₄ aqueous solution was prepared with 4.2×10^{-3} M. Then, the solution was stirred while the temperature was increased to 80°C. After that, the pH of solution was adjusted to 7 by dropping Na₂CO₃ (APS Finechem). Then, 2 g of TiO₂—75% anatase and 25% rutile—was added into the HAuCl₄ solution. Then, pH and temperature were maintained under vigorous stirring for 2 h. The precipitate was filtered and washed carefully until the disappearance of Cl⁻ ions. The Au catalysts were dried at 110°C overnight and calcined in air at the desired temperatures for studying the calcination effect (uncalcined, calcined at 200 and 300°C).

3.3.2 Catalytic Activity Testing

The catalysts were tested with two cases in order to find the optimum operating temperature with the simulated reformat system for the best CO oxidation conversion and selectivity.

The first case, the single-stage reactor testing was investigated with all oxygen. The second case, the PROX reactors were serially connected, as shown in Figure 3.1. The effluent from the first reactor was passed directly to the second reactor. The reaction mixture is composed of 1%CO, 1%O₂, 40% H₂ and balanced being in He without H₂O and CO₂ in the stream with a total of flow rate of 50 ml/min. The temperature and oxygen in each stage was individually controlled. The temperature was varied in the range of 30–120°C and the amount of O₂ entering each stage was varied at split at ratios of 80:20, 60:40, 50:50, 40:60, and 80:20.

Many parameters affecting the activity and selectivity of the Au/TiO₂ catalysts, which are studied in this research such as the effects of calcination temperature, Au loading, and the presence of CO₂ and H₂O in the feed stream.

3.3.2.1 Effect of Calcination Temperature

The effect of calcination temperature on the catalytic performance of 1% Au/TiO₂ are studied (uncalcined, calcined at 200, and 300°C) in the simulated reformat gas. The suitable calcination temperature is chosen for the next study.

3.3.2.2 Effect of Au Loading

The effect of Au loading on the Au/TiO₂ catalyst is studied on the CO conversion and CO selectivity in the PROX reaction. The percentage Au loading is varied with 1%, 1.5%, and 2%.

3.3.2.3 Effect of the Presence of CO₂ and H₂O in the Feed

The CO₂ and H₂O are fed into the reactor with other reactant gases. The catalytic activity of Au/TiO₂ is investigated for the PROX with the presence of CO₂ and H₂O.

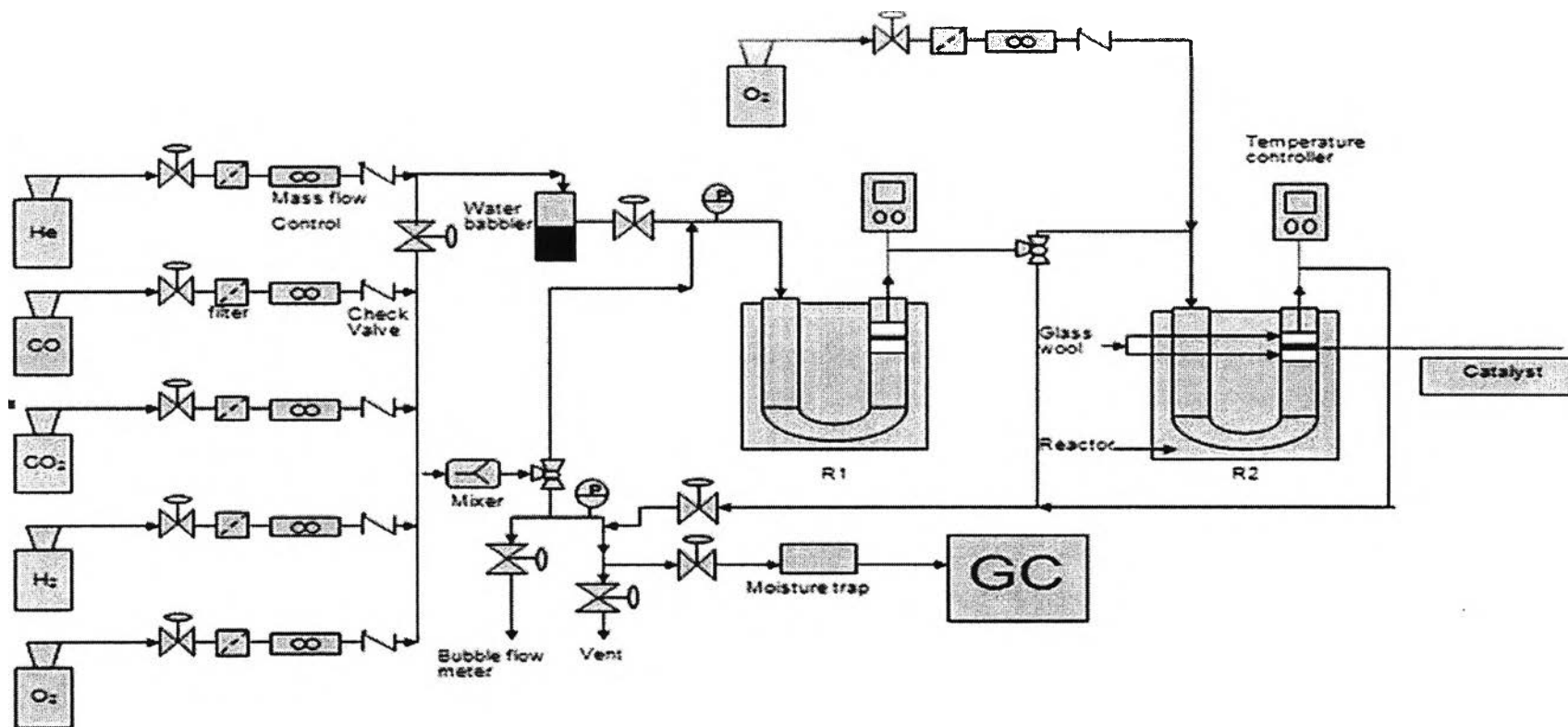


Figure 3.1 Experimental setup for preferential CO oxidation reaction using the double-stage reactor.

3.3.3 Real Reformate Stream Experiment

The data and result from the simulated reformate system should be applied with the real reformate unit (Oxygen feed ratio and the reaction temperature of both reactors), in order to confirm the result that it is practical for the real application unit. The real stream catalytic reforming unit composes of:

- Catalytic reforming unit
- PROX

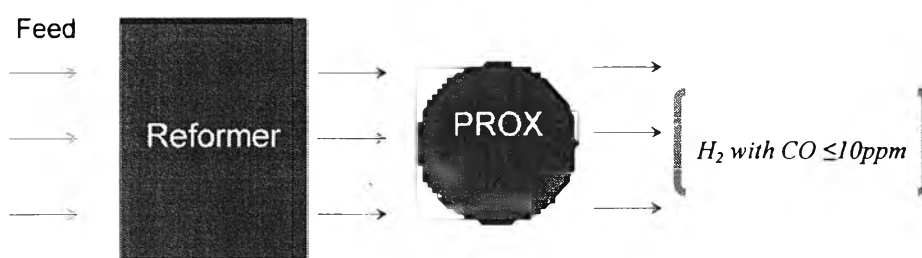


Figure 3.2 Real catalytic reformates system.

In this step, the fuel processing system is used to produce hydrogen, which compose of steam reformer, and PROX. Steam reforming of methanol has been selected as the primary reforming process. The catalyst used in PROX reactor, from previous step is performed, whereas the catalysts used in reformer are the commercial catalyst.

In this step, the commercial Cu-Zn/Al₂O₃ catalyst was carried out in a fixed-bed reactor loaded with 0.2 mg of the catalyst. The commercial catalyst was tested the catalytic activity by feed stoichiometry water to methanol mole ratio (H₂O/CH₃OH = 1.3/1) at the total flow of the most experiment is about 110 ml/min. Then, the reformate gas was sent to the PROX reactor in order to reduce the CO concentration by using the Au/TiO₂ catalyst in the double-stage pack-bed reactor.

For the simulated reformate gas and real composition of reformate gas case, the outlet gas was analyzed by a Gas Chromatograph (Agilent Technologies 6890N). The temperature of reactor was controlled by K-type thermocouple. The performance of catalyst was measured by %CO conversion, %O₂ conversion, and %PROX selectivity.

$$\%CO \text{ conversion} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100$$

$$\%O_2 \text{ consumption} = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100$$

$$\%PROX \text{ selectivity} = \frac{1/2 \times ([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} \times 100$$

3.3.4 Catalyst Deactivation Experiment

An Au/TiO₂ sample was tested for the storage that affect on the catalytic activity. The sample was separated into two main groups, which were exposed and unexposed to light. The container for the exposed to light sample are transparent glass bottles, as shown in Figure 3.3. On the other hand, the unexposed to light sample was kept in the container, which was wrapped with black tape to avoid the light. Then, both samples were measured the activities for the PROX of CO reaction for four times (fresh catalyst, 1 month, 2 months, and 3 months).



Figure 3.3 Containers for exposed and unexposed to light samples.

3.3.5 Catalyst Characterization

Various methods will be used to characterize the prepared catalysts, there are:

3.3.5.1 *Atomic Absorption Spectroscopy (AAS)*

The AAS, VARIAN model 300/400, was used to determine the concentration of a metal in the sample. This technique uses to evaluate the concentration of an element. The standard solution was diluted from the stock solution of 1000 ppm to establish a calibration curve. The sample solutions were diluted to measure the actual metal loading, which could be obtained from the absorbance of the prepared solution.

3.3.5.2 *X-ray Diffraction (XRD)*

The crystalline size and the relative content of Au on the surface is estimated by using a X-ray diffractometer (IDX-3530). X-ray diffraction (XRD) is based upon the fact that the X-ray diffraction pattern is unique for each crystalline substance. The identity of the crystalline phases can be found by matching the pattern of the unknown and standard.

3.3.5.3 *UV-visible Spectrophotometry (UV-vis)*

The spectrophotometer is used measure the amount of light absorbs. The instrument operates by passing a beam of light pass through a sample. Then, the intensity of light reaches the detector. The intensity of light relates with quantity and type of element in the sample. The amount, metallic stage of Au can be measured by UV-visible spectrophotometer (UV 2550 SHIMADZU).

3.3.5.4 *Scanning Electron Microscopy (TEM)*

TEM was employed to investigate the average particle size of metals and identify the microstructure of prepared catalysts, such as metals dispersion and the crystalline size of the Au on the support. Catalysts were prepared in a thin form appropriate for TEM, that it was dispersed in pure water and a drop of the suspension was deposited on a copper grid. TEM was carried out in a JEM 2100 operating at an accelerating voltage of 200 kV in bright field modes. A beam was passed through a series of lenses to form a magnified image of a sample that has been inserted in the area of the objective lens. The image from selected area was viewed through projection onto a viewing screen. However, electron beams are easily

scattered by air molecules and TEM columns must be kept under high vacuum. Additionally, the electromagnetic lenses were used for focus the electron beam.

3.3.5.5 Temperature-Programmed Reduction (TPR)

Temperature-Programmed Reduction (TPR) was employed for evaluating the number and quantity of the reducible species present in the sample and the temperature at which the reduction itself takes place as a function of the temperature. The gas used for analysis is a mixture of reactive gas with an inert gas, as hydrogen in argon or nitrogen at 5–10%. The prepared catalyst sample was submitted to a linear increase of temperature and to a constant flow of the gas mixture. The reaction generally starts at room temperature. At a certain temperature, the reaction speed becomes considerable and the hydrogen consumption can be monitored through the TCD detector.