



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Catalyst Preparation Materials

All of chemicals used in the catalyst preparation are shown as follows:

- $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ of 99.5% purity was obtained from ACROS Organics.
- $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of 99.9% purity was obtained from Merck.
- Na_2CO_3 buffer solution was prepared from Na_2CO_3 of 99.9% purity precursor, which was obtained from UNIVAR.

3.1.2 Gases

All of reactant gases were supplied from Thai Industrial Gas Public Co., Ltd. The reactant gases composed of carbon monoxide (CO , 99.99 % purity), hydrogen (H_2 , 99.99 % purity), and oxygen (O_2 , 99.99 % purity) balanced by helium (He). H_2O was also used in this work.

3.1.3 UV lamp

The UV lamp specifications are 11 Watt (power), 253.7 nm (wavelength), G23, 2 pin-Stecksocket, 89 Volt, and 0.16 A. It was supplied from Phillips Company. The lamp measures 236×28×13 mm.



Figure 3.1 UV lamp image.

3.2 Experimental Setup

The experimental setup is shown schematically in Figure 3.1 and it can be divided into three main parts.

3.2.1 Gas Blending Section

The reactant gas mixture was composed of 1 % carbon monoxide (CO), 1 % oxygen (O₂), 40 % hydrogen (H₂), and balanced in He. Each stream was passed through the micro filter to remove particles before it entered the mass flow controllers and checked valve to prevent reverse flow. After that, all reactants were sent to the mixing chamber and mixed there before going to the reactor with a total flow rate of 50 ml/min under atmospheric pressure.

3.2.2 Catalytic Reactor

The preferential oxidation of CO was conducted under atmospheric pressure in a Pyrex glass U-tube micro-reactor with an inside diameter of 6 mm. The catalyst was packed between glass wool plugs in the middle of the reactor. The temperature of catalyst bed was monitored and controlled by PID temperature controller equipped with a thermocouple (Type K).

3.2.3 Analytical Instrument

The effluent gas from the reactor will be qualitatively and quantitatively analyzed by auto-sampling into on-line gas chromatograph equipped with a packed carbosphere column, 80/100 mesh, and 10 ft x 1/8 inch and a thermal conductivity detector (TCD).

3.3 Experiment

3.3.1 Catalyst Preparation Procedure

3.3.1.1 *Support Preparation*

Zn(NO₃)₂·6H₂O was used as a precursor to prepare ZnO, which Zn(NO₃)₂·6H₂O was dissolved by deionized water, after that heated and stirred

the solution simultaneously at 80°C, while the pH of was maintained at 8 by using Na₂CO₃. The mixture was aged and the precipitate was washed with warm deionized water. After being dried at 110°C overnight, the precipitate was calcined at 300 °C for 3 hours.

3.3.1.2 Au Loading

Photodeposition (PD) technique was used in order to deposit Au over ZnO supports, for which HAuCl₄.3H₂O was employed as a gold precursor. The precursor solution—including dissolving water, support, and gold precursor—was regulated to pH 8 by using Na₂CO₃ as a precipitant agent. After that the UV lamp was plugged in the photoreactor to irradiate the suspension. During irradiation, the suspension was stirred at the speed of 770 rpm for a period of time. The temperature of suspension was maintained at room temperature and thereafter the residual ions were removed by washing with deionized water. The sample was dried overnight. And only in case of calcined catalysts, after being dried at 110°C overnight, the precipitate was calcined at 300 °C for 3 hours.

3.3.2 Experimental Procedure

All series of catalysts were tested the catalytic activity to study the appropriate conditions of irradiation time, calcination, and precipitant agent concentration. In addition, the different color of catalysts of each catalyst was observed.

3.3.2.1 Catalytic Activity Testing

The reaction was carried out in a fixed bed U-tube micro-reactor by packing with 0.1 g catalyst of 80 mesh inside. The activity was investigated at varied temperatures in the range of 30 to 120°C. The CO conversion (X_{CO}), O₂ conversion (X_{O_2}), and CO selectivity (S) are calculated as follows:

$$X_{CO} = \frac{[CO]_o - [CO]}{[CO]_o} \times 100 \quad (10)$$

$$X_{O_2} = \frac{[O_2]_o - [O_2]}{[O_2]_o} \times 100 \quad (11)$$

$$S = \frac{[O_2]_{CO}}{[O_2]_{CO} + [O_2]_{H_2}} \times 100 \quad (12)$$

where:

X = CO conversion (%),

S = selectivity towards CO (%),

$[CO]_o$ = concentration of CO in the reactant gas,

$[CO]$ = concentration of CO in the product gas,

$[O_2]_o$ = concentration of O₂ in the reactant gas,

$[O_2]$ = concentration of O₂ in the product gas,

$[O_2]_{CO}$ = amount of O₂ for CO oxidation, and

$[O_2]_{H_2}$ = amount of O₂ for H₂ oxidation.

3.3.2.2 Influence of Irradiation Time

A series of Au/ZnO catalysts, which was prepared by using 0.1 M Na₂CO₃ concentration in both of support preparation and Au loading procedure, was irradiated with the lamp power of 11 watt in the photoreactor and stirred simultaneously for 30, 90, 120, and 240 minutes. All of catalysts were prepared by without calcination. The suitable time was investigated in the PROX, which was evaluated in terms of CO conversion, O₂ conversion, and CO selectivity.

3.3.2.3 Influence of Precipitating Agent Concentration

The effect of precipitating agent concentration under identical conditions on the catalytic activity was studied. The effect of concentration of precipitating agent on the activity, 0.05 and 0.1 M, was varied in both of support preparation and Au loading procedure.

3.3.2.4 Influence of Calcination

The effect of calcination on the catalytic activity of the Au/ZnO catalysts was investigated. For comparison, the Au/ZnO catalyst was further calcined in air at 300°C for 3 hours.

3.3.2.5 Color Observation

Some authors proposed the relationship between the Au particle size and color of the Au catalysts, in this work the color of the prepared catalysts was also observed.

3.4 Catalyst Characterization

The prepared catalysts were characterized by using several techniques as follows:

3.4.1 X-Ray Diffractometry (XRD)

To identify the crystalline structure, chemical composition, and physical properties—the samples are prepared as thin layers on a sample holder—by observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. XRD is non-destructive analytical techniques.

In this work, X-ray diffraction (XRD) patterns were recorded on a JEOL JDX 3530 X-ray diffractometer. The samples were placed over the center of sample holder and they were analyzed by scanning from $2\theta = 25^\circ$ to 75° .

3.4.2 Temperature-Programmed Reduction (TPR)

Temperature-Programmed Reduction (TPR) was carried out in a fixed-bed reactor by packing 50 mg of sample, by increasing the temperature linearly with a rate of $10^\circ\text{C}/\text{min}$, so as to perform the results of reducibility of Au catalysts and interaction between Au and ZnO. Moreover, TPR can be investigated the oxidation of Au. Au^{3+} and Au^+ can be reduced by hydrogen gas, which have a different reduction temperature. For Au^{3+} species, the reduction temperature peak appears at low temperature of around $50\text{--}170^\circ\text{C}$. The other one is the reduction of Au^+ to Au^0 . Au^+ species is more difficult to be reduced than Au^{3+} species; therefore, the reduction temperature will be higher, which is pronounced at about $200\text{--}250^\circ\text{C}$.

3.4.3 Scanning Electron Microscopy (SEM)

This method uses a high energy beam of electrons interacting with the atoms; making up the sample produces signals. SEM characterizes three-dimensional appearance useful for understanding the surface structure of a sample. JEOL, JSM-5410LV Scanning Microscope was carried out in our work in order to examine the morphology and structure of ZnO.

3.4.4 Transmission Electron Microscopy (TEM)

The morphologies and particle sizes of the samples are determined by TEM whereby a beam of electrons is transmitted through an ultra thin specimen. Images are recorded digitally by JEOL, JEM-2100 (200KV) with a resolution point 0.23 nm and lattice 0.14, single tile and double tile ($\pm 30^\circ$) holder.

3.4.5 UV-vis Spectrophotometry

Diffuse reflectance spectra were recorded by UV-vis spectrophotometer-2550 by using light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges, used in the quantitative determination the transition metal ions. The samples were packed in the sample holder and analyzed by limiting wavelength in the range of 800–200 nm. And the data would be converted using Kubelka-Munk formula.

3.4.6 N₂ Adsorption BET Technique

BET method was acquired on an Autosorb-1 to measure the specific surface area. Before analyzing all of samples were degassed. Because of ZnO has a less pore volume, it was evaluated specific surface area with seven points.

3.4.7 Atomic Absorption Spectrometry (AAS)

Actual Au loading was derived from AAS, which is a technique for determining the concentration of a particular metal element in a sample.

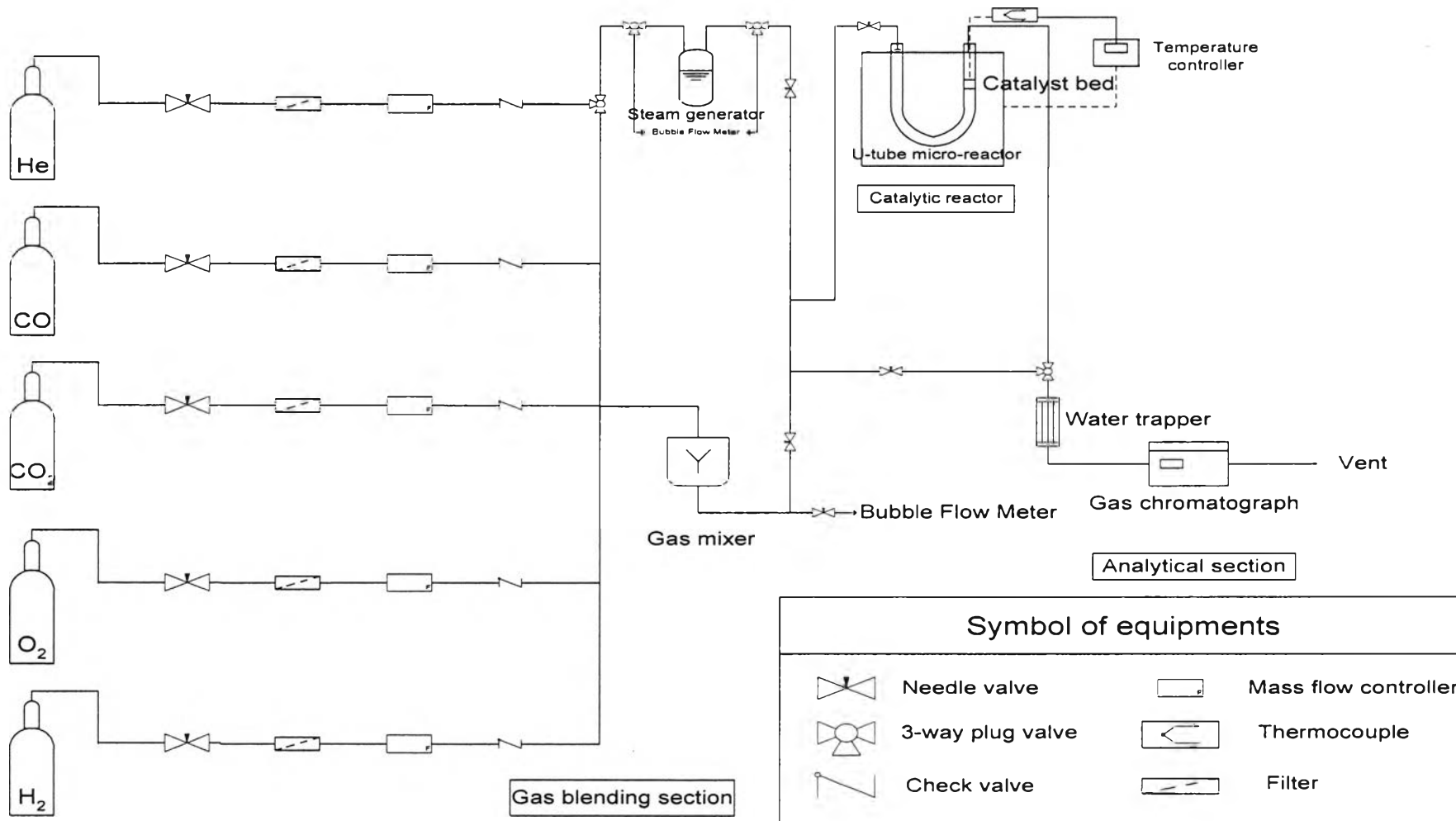


Figure 3.2 Schematic flow diagram of the experimental setup.