

CHAPTER III EXPERIMENTAL

In this chapter, catalyst preparation, reactor set-up for lab-scale and bench-scale, reaction activity and characterization methods will be explained. The Au/CeO₂ catalyst was prepared by deposition-precipitation (DP) method while commercial catalysts were received from Süd-chemie (Japan). The reactor set-up in lab-scale was referred to LTS unit connected with a Gas Chromatograph (GC), while the reactor set-up for bench-scale was related to a fuel processor unit. The characterization methods, X-ray powder diffraction (XRD), Transmission electron microscopy (TEM), Temperature-reduction programmed (TPR), and BET surface area measurement, were used to study the nature of the prepared catalysts.

3.1 Catalyst Preparation

3.1.1 High Temperature Shift Catalyst

The aim of HTS experiment is to determine the value of CO exit before passing through LTS unit and to fulfill the CO reducing unit. The experiment was first done in lab-scale with a commercial catalyst, Shiftmax 120. For bench-scale reaction, Shiftmax 120 was also used in HTS reaction in order to study the effect of LTS using the prepared catalyst.

3.1.1.1 Commercial Catalyst

The HTS catalyst (Shiftmax 120) combines high activity with extremely good physical robustness. In addition, this catalyst is very effective in preventing Fischer-Tropsch by product formation when operating at low steam conditions. The detail of Shiftmax 120 is shown below in Table 3.1.

Table 3.1 The chemical composition and physical details of Shiftmax 120 and Shiftmax 230

<u>Shiftmax 120</u>		<u>Shiftmax 230</u>	
Nominal Content	wt. %	Nominal Content	wt. %
Fe ₂ O ₃	80	CuO	58
Cr ₂ O ₃	8.5	ZnO	31
CuO	2	Al ₂ O ₃	11
Shape	Tablets	Shape	Tablets
Size [mm]	6*6	Size [mm]	4.8*3.2

3.1.2 Low Temperature Shift Catalyst

The varieties of gold loading on ceria catalysts were investigated in LTS reaction both lab-scale and bench-scale experiments. The LTS commercial catalyst, Shiftmax 230, was used as a benchmark with the same condition.

3.1.2.1 *Commercial Catalyst*

The LTS catalysts (Shiftmax 230) is next-generation products that offer unparalleled activity for water-gas shift, resulting in higher CO conversion for longer life, enhanced resistance to poisons, and excellent physical strength.

3.1.2.2 *Au/CeO₂ catalyst*

Au/CeO₂ catalyst was prepared by DP method. A solution of HAuCl₄ · 3H₂O (Alfa) was used as a gold precursor. Two types of ceria support from Aldrich were used to investigate in this work as shown in Table 3.3. Cerium (IV) oxide powder was denoted as low surface area ceria (CeO₂ – LS) and Cerium (IV) oxide nanopowder was denoted as high surface area ceria (CeO₂ – HS).

Table 3.2 Properties of Cerium (IV) Oxide; powder and nanopowder from Aldrich

Properties	Cerium(IV) oxide powder	Cerium(IV) oxide nanopowder
Assay	99.9%	Not specific
Form	Powder	Nanopowder
Particle Size	< 5 μm	10-20 nm
Surface Area	Not specific (7.8 m^2/g)*	80-100 m^2/g (70.34 m^2/g)*

* – Surface area from BET measurement

The gold catalysts were prepared by DP of gold hydroxide on ceria powder. In brief, the ceria support was suspended in deionized water under continuous stirring. The temperature was held constant at 60°C. Then, an aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Alfa) was mixed into a suspension of the ceria. Na_2CO_3 (0.5 M), as a precipitating agent, was added dropwise to maintain at pH 8. The resulting precipitate was aged for 1 hour with stirring (at 60°C). The excess ions were washed from the solution before filtering step. After washing with DI water on filter paper, the vacuum filtration is normally done. Besides this technique, centrifuge technique that using separation and dilution technique to reduce amount of excess ions from the solution is alternative. In this work, centrifuge technique was used with conductivity measurement instrument to ensure that was no excess ion in the solution. Centrifuge technique following by rinsed with warm DI water was used to separate any left ion out from the solution. After centrifugation, the water layer was separated from the precipitates. The precipitates were rinsed with DI water repeatedly until the conductivity of the solution was same as DI water. Then, the precipitate was dried overnight in an oven and calcined in air at 400° C for 4 hours.

3.2 Reactor Set-up

3.2.1 Reactor Set-Up for Lab Scale

The apparatus used in this experiment and their alignment are schematically shown in Figure 3.1. It can be roughly divided into **three** main sections: gas blending section, catalytic reactor section and analytical instrument section.

3.2.1.1 Gas Blending Section

Three types of gas; CO, H₂, and He, were supplied through flow controller (AALBORG model GFC1715). All gases were joined and mixed each other at a mixing chamber. Helium gas could alternatively switch to gas bubbling section. Water vapor was carried by helium from gas bubbling bulb. The temperature of gas bubbling bulb was controlled in order to meet the desired final volume of water vapor in the total volume flow rate. Heating tape was rounded along the tube to prevent condensing of water vapor until entering of the reactor.

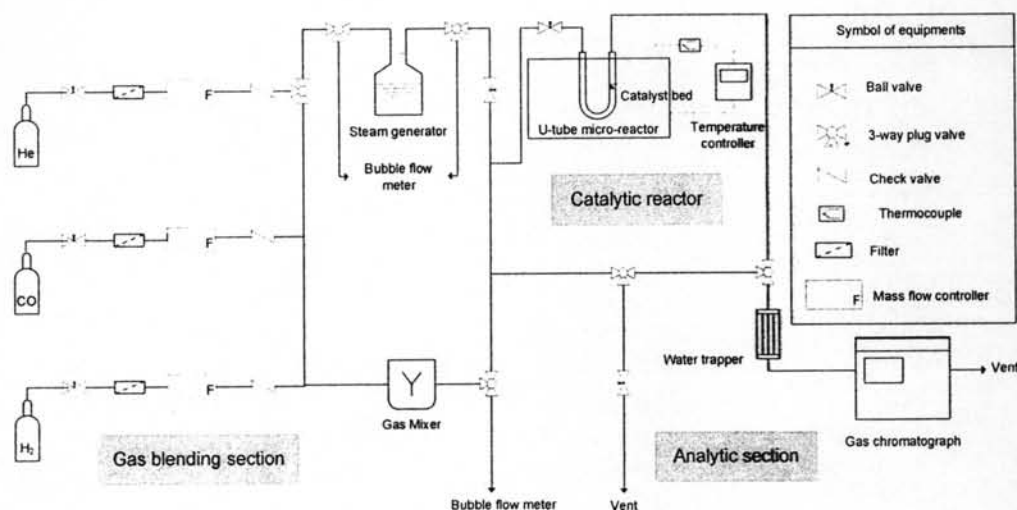


Figure 3.1 Schematic flow diagram of the lab-scale experimental setup.

3.2.1.2 Catalytic Reactor

A Pyrex glass U-tube reactor having an inside diameter of 6 mm was used as a catalytic reactor. It was placed in a furnace where the temperature of the catalyst bed was monitored and controlled by a PID temperature controller (Shinko FCR-13A-S/M model) equipped with a type K thermocouple. Catalyst was packed inside a tube reactor. Each side was covered by a layer of quartz wool.

3.2.1.3 Analytical Instrument

Gas chromatograph (GC, Agilent Technologies 6890N model) equipped with a thermal conductivity detector (TCD) was used to analyze the effluent gas. The effluent gas stream from the reactor was dehumidified with ice bath before auto-sampling into a GC. The carbosphere, 80/100 mesh, and 10 ft · 1/8 inch stainless steel packed column was used to separate all components. The conditions of GC are listed as follows:

Injector temperature: 120° C,

Oven temperature: 100° C

Carrier gas: He (99.999% UHP grade)

TCD condition:

Temperature: 175° C,

Reference gas: He (99.999% UHP grade)

The result was recorded by Agilent chemstation software. The observed peak is identified by comparison time of the standard gas. For quantitative analysis, the peak area is converted to the concentration of each component based on the calibration curves obtained from known composition gases.

3.3 Reaction Condition

3.3.1 High Temperature Shift Reaction

For lab-scale experiment, Shiftmax 120 catalyst was grounded and sieved (0.148-0.224 mm). 90 mg of catalyst was plainly loaded in a U-tube reactor between two plugs of quartz wool. The catalyst was pretreated in helium gas at 110° C for one hour prior to the reaction. The total flow rate was 75 ml/min, 60 ml/min of

10% CO in Helium and 15 ml/min of Helium (to get 8% of CO) at the temperature range of 300-450° C.

3.3.2 Low Temperature Shift Reaction

In the same manner, Shiftmax 230 catalyst was grounded and sieved (0.148-0.224 mm). The catalyst was loaded in a U-tube reactor between the two plugs of quartz wool. It was pretreated in helium gas at 110° C for one hour prior to the reaction. An appropriate amount of 10% CO in helium was also mixed with helium to get a final composition of 4% CO in dry reactant feed. The LTS reaction was performed in the temperature range of 100-325° C.

The prepared Au/CeO₂ catalyst was grounded and sieved (0.148-0.224 mm). All of the steps were the same as the commercial catalysts did. The total flow rate was adjusted to get the desired gas space hour velocities, 30, 60 and 90 ml/min, respectively with the final concentration of 4% CO. The reaction activity was studied in the temperature range of 100-350° C.

3.4 Reaction Activity

3.4.1 Effect of Space Velocity

Effect of space velocity of reactant flow (dry gas) on the LT-WGS reaction was studied with the certain amount of catalyst. The velocity of reactant flow was varied from 30, 60 and 90 ml/min in order to get an exact space velocity of 4,000, 8,000 and 12,000 ml·h⁻¹·g⁻¹ respectively.

3.4.2 Effect of Gold Loading

Effect of gold loading on ceria oxide support on the LT-WGS reaction was studied. In this work, 1, 2 and 5 wt.% of gold over ceria oxide catalyst was prepared by DP method. The activity of LT-WGS was studied as a function of temperature.

3.4.3 Effect of H₂-Pretreatment

To study the effect of H₂-pretreatment, the prepared catalyst was reduced with a mixture 5% H₂ in N₂ at temperature of 200° C for 2 hours prior to the reaction. The activity of LT-WGS was studied as a function of temperature.

3.4.4 Effect of Type of CeO₂

As mentioned in the section 3.1, CeO₂-HS and CeO₂-LS were used as commercial support in this work to identify the dependence of the support on the WGS activity. The same amount of gold loading was loaded on each ceria support and was performed at the same condition.

3.4.5 Effect of Water/CO Ratio

Water in form of steam is one of the reactant of WGS reaction. The varied water/CO ratio was studied in this work. The ratios of 1/1 and 3/1 of water/CO ratio were studied in LTS reaction. The effect of water absence was also studied. The total percent volume including water is

- For 0/1 ratio (absence of water): 4%CO balanced with helium
- For 1/1 ratio: 4% H₂O, 4%CO balanced with helium
- For 3/1 ratio: 12% H₂O, 4%CO balanced with helium

3.4.6 Effect of H₂ Mixing in the Feed

The presence of H₂ in the LTS reactant was set to simulate as in the real hydrogen production system as a product from reforming and HTS unit. Normally, the percent of H₂ mixing is 60-70%. In this work, 60% of H₂ was added into reactant feed before passing through the reactor.

3.4.7 Deactivation

The stability of prepared catalyst was also investigated. The optimized gold-ceria catalyst was tested with normal condition; 4%CO and 4%H₂O balanced with helium to investigate the stability of prepared catalyst. The reaction temperature was 250 °C as same as the bench scale reaction temperature. The studied reaction duration was 500 minutes and the data were taken every 10 minutes.

3.4.8 Bench-Scale Experiment

Bench-scale experiment integrated H₂ production unit (steam reforming) and CO treatment units (water-gas shift and preferential oxidation) together. Each unit was continuously connected and built in the same structure. The initial reactant was pretreated natural gas. For LT-WGS unit, prepared gold-ceria catalyst and Shiftmax 230 were used. 4.5 g of catalyst was used with 20-60 mesh. The space velocity was set to ~ 4,000 ml g⁻¹ h⁻¹. The LT-WGS reaction was performed at 250 °C for ~500 minutes.

3.5 Catalyst Characterization

All catalysts were characterized by X-ray diffraction (XRD), Temperature-programmed reduction (TPR), Transmission Electron Microscopy (TEM), and BET surface area measurement. The details are described as follows:

3.5.1 X-Ray Diffraction

X-ray diffraction (XRD) profiles of the prepared catalysts can be obtained by using a Rigaku RINT 2000 diffractometer equipped with a Ni filtered Cu K α radiation source ($\lambda = 1.542 \text{ \AA}$) of 40 kV and 30 mA. A catalyst sample was pressed into a hollow of glass holder and held in place by a glass window. Then, it was scanned in the range of 2θ from 20° to 60° in the continuous mode with scan speed 5 degrees/minute and scan step 0.02 degree. The XRD results gave peak parameters, including the full line width at half the maximum intensity (B), d-value and intensity. The mean crystallite size was calculated from the XRD data from X-ray line broadening, using the full line width at half maximum of intensity and the 2θ values and plugging them into the Scherrer's equation:

$$t = \frac{0.9\lambda}{B \cos \theta_b} \quad (13)$$

where t is crystallite size (\AA)

λ is the X-ray wavelength (1.542 \AA for Cu anode source)

B is the line broadening

θ_B is the Bragg angle

This equation works well for particle sizes of less than 1,000 Å. The broadening of diffraction lines measured at half the maximum intensity (B) is corrected by using Warren's method, which is

$$B^2 = B_M^2 - B_S^2. \quad (14)$$

where B_M is the breadth of the diffraction line and
 B_S is the breadth of the line from a standard.

3.5.2 Transmission Electron Microscopy

The catalyst morphology distribution analysis was performed with a vacuum generator TECHNAI 20 FEI COMPANY transmission electron microscope. TEM was conducted with a JEOL 3011 UHR microscope operating at 200 kV. To achieve the appropriate electron transparency, the catalyst was crushed to a fine powder, the catalyst powder was dispersed on a copper or nickel grid coated with a carbon film and elemental maps were obtained on 128*128 data matrix. Particle size distribution was determined from several Z-contrast images from different areas of the samples.

3.5.3 Temperature-Programmed Reduction (TPR)

Temperature programmed reduction by hydrogen (H₂-TPR) was conducted in a Thermoquest 1100 instrument equipped with a thermal conductivity detector to detect H₂ consumption. Prior to TPR analysis, the prepared catalysts, 0.1 g in fine powder form were pretreated under a flow of N₂ (20 ml/min) with a heating rate of 10 °C/min from 50 °C to 250 °C. For TPR analysis, the catalysts were heated at a heating rate of 10 °C/min from 50 °C to 700 °C in a 4.95% H₂/N₂ (20 ml/min). The curves in H₂-TPR profiles correspond to H₂ consumption.

3.5.4 BET Surface Area

The BET surface area was measured by multipoint BET N₂ adsorption/desorption cycles in an Autosorb 1 instrument. Sample was heated in oven to expel humidity prior to the analysis. The powder sample, ~0.4 g, and glass tube were cleaned again with N₂ at 150 °C.

3.6 Catalytic Activity Measurement

Both lab-scale and bench-scale were analyzed with gas chromatograph (GC, Agilent Technologies 6890N model) equipped with a thermal conductivity detector (TCD). The auto-sampling (on-line) method was used for lab-scale while the injection method was used for bench-scale. For quantitative analysis, the peak area is converted to the concentration of each component based on the calibration curves obtained from known composition gases.

The WGS activity measurements were carried out in a fixed bed reactor at atmospheric pressure in the range of 150-350 °C. The CO and CO₂ conversions were determined according to Equation 15.

$$X_{\text{CO}} = \frac{[\text{CO}]_{\text{IN}} - [\text{CO}]_{\text{OUT}}}{[\text{CO}]_{\text{IN}}} \times 100 \quad (15)$$

where:

- X = CO conversion (%)
- [CO]_{IN} = inlet concentration of CO
- [CO]_{OUT} = outlet concentration of CO