



CHAPTER IV

EXPERIMENTAL

This chapter consists of experimental systems and procedures used in this work which is divided into three parts consisting of catalyst preparation (4.1), catalyst characterization (4.2) and reaction study in CO hydrogenation (4.3).

The samples were prepared and analyzed by means of X-ray diffraction (XRD), transmission electron spectroscopy (TEM), and temperature-programmed reduction (TPR). The reaction study was performed in order to measure activity and product selectivity toward CO hydrogenation at 220°C and 1 atm.

4.1 Catalyst preparation

4.1.1 Chemicals

The details of chemicals used in this experiment are shown in Table 4.1

Table 4.1 Chemicals used in the preparation of catalysts.

Chemical	Supplier	CAS. Number	Product Number
Cobalt (II) nitrate exahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)	Aldrich	10026-22-9	239267
Toluene ($\text{C}_6\text{H}_5\text{CH}_3$)	Fisher Scientific	-	-
Silicon dioxide (SiO_2), nano powder	Aldrich	7631-86-9	637246
Silicon dioxide (SiO_2), micron powder	Strem chemical	1343-98-2	142518
Zirconium dioxide (ZrO_2), nano powder	Flame spray pyrolysis	-	030324
Zirconium dioxide (ZrO_2), micron powder	Aldrich	1314-23-4	230693

4.1.2 Preparation of micron- and nano-SiO₂-ZrO₂ supports

The mixed oxide supports consisting of various ratios by weight [0-100 wt%] of ZrO₂ in SiO₂ were prepared by the solution mixing. The desired amounts containing 1 g of mixture of SiO₂-ZrO₂ were mixed and stirred continuously in toluene (20 ml) with a magnetic stirrer for 30 min. The solvent was removed and the mixture was dried at 110 °C for 12 h and, then calcined in air at 350 °C for 2 h.

4.1.3 Preparation of the supported Co samples

A 20 wt% of cobalt dispersed on the mixed SiO₂-ZrO₂ supports was prepared by the incipient wetness impregnation. A desired amount of cobalt nitrate [Co(NO₃)₂•6H₂O] (Aldrich) was dissolved in deionized water and then impregnated onto the support obtained from 4.1.2. The sample was dried at 110°C for 12 h and calcined in air at 500°C for 4 h.

4.1.4 Sample nomenclature

The nomenclature used for the samples in this study is following:

Si-a-Zr-b (M or N) refers to the mixed SiO₂-ZrO₂ support where:

a is the weight percents of SiO₂

b is the weight percent of ZrO₂

M refers to the micronscale

N refers to the nanoscale

Co/Si-a-Zr-b refers to the mixed SiO₂-ZrO₂-supported cobalt catalyst

4.2. Catalyst characterization

Various characterization techniques were used in this studied in order to clarify the catalyst structure and morphology, surface composition of various mixed SiO₂-ZrO₂-supported cobalt catalyst

4.2.1 N₂ physisorption

BET apparatus for the single point method

The reaction apparatus of BET surface area measurement consisted of two feed lines for helium and nitrogen using a Micromeritics Chemisorb 2750. The flow rate of the gas was adjusted by means of fine-metering valve on the gas chromatograph. The sample cell made from pyrex glass. The mixture gases of helium and nitrogen flowed through the system at the nitrogen relative of 0.3. The catalyst sample (ca. 0.2 to 0.5 g) was placed in the sample cell, which was then heated up to 200 °C and held at this temperature for 1 h. After the catalyst sample was cooled down to room temperature, nitrogen uptakes were measure as follows.

Step (1) Adsorption step: The sample that set in the sample cell was dipped into liquid nitrogen. Nitrogen gas that flowed through the system was adsorbed on the surface of the sample until equilibrium was reached.

Step (2) Desorption step: The sample cell with nitrogen gas-adsorption catalyst sample dipped into the water at room temperature. The adsorbed nitrogen gas was desorbed from the surface of the sample. This step was completed when the indicator line was in the position of base line.

Step (3) Calibration step: 1 ml of nitrogen gas at atmospheric pressure was injected through the calibration port of the gas chromatograph and the area was measured. The area was the calibration peak.

4.2.2 X-ray diffraction (XRD)

XRD were performed to determine the bulk phase of catalysts by SIEMENS D 5000 X-ray diffractometer connected with a computer with Diffract ZT version 3.3 program for fully control of the XRD analyzer. The experiments were carried out by using CuK α ($\lambda = 1.54439 \text{ \AA}$) radiation with Ni filter in the 2θ range of 20-80 degrees resolution 0.04°. The crystallite size was estimated from line broadening according to the Scherrer equation and $\alpha\text{-Al}_2\text{O}_3$ was used as standard.

4.2.3 Temperature programmed reduction (TPR)

TPR was used to determine the reducibility of catalysts:

1. The catalyst sample 0.2 g used in the sample cell.
2. Prior to operation, the catalysts were heated up to 200 °C in flowing nitrogen and held at this temperature for 1 h.
3. After the catalyst sample was cooled down to room temperature, carrier gas (10 % H₂ in Ar) were ramping from 35°C to 800°C.
4. During reduction, a cold trap will be placed to before the detector to remove water produced.

4.2.4 Electron microscopy

Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX) was used to determine the morphology and elemental distribution of the catalyst particles. Model of SEM: JEOL mode JSM-5800LV and EDX will be performed using Link Isis Series 300 program at the Scientific and Technological Research Equipment Center, Chulalongkorn University (STREC).

4.2.5 Transmission Electron Microscopy (TEM)

The dispersion of cobalt oxide supports was determined using JEOL JEM- 1220 transmission electron spectroscopy operated at 100 kV with 50 k magnification. The sample was dispersed in ethanol prior to the TEM measurement.

4.2.6 Hydrogen Chemisorption

Static H₂ chemisorption at 100 °C on the reduce catalysts was used to determine the number of reduce surface cobalt metal atoms and overall cobalt dispersion. The total hydrogen chemisorption was calculated from the number of injection of a known volume. H₂ chemisorption was carried out following the procedure discribed by CO- pulse chemisorption technique using a Micrometricics Chemisorb 2750 (pulse chemisorption system). Prior to chemisorption, the catalysts were reduced at 350 °C for 3 hours after ramping up at a rate of 1 °C/min.

4.3. Reaction study in CO hydrogenation

4.3.1 Material

The reactant gas used for the reaction study was the carbon monoxide in hydrogen feed stream as supplied by Thai Industrial Gas Limited (TIG). The gas mixture contained 9.73 vol % CO in H₂ (22 cc/min). The total flow rate was 30 ml/min with the H₂/CO ratio of 10/1. Ultra high purity hydrogen (50 cc/min) and high purity argon (8 cc/min) manufactured by Thai Industrial Gas Limited (TIG) were used for reduction and balance flow rate.

4.3.2 Apparatus

Flow diagram of CO hydrogenation system is show in Figure 4.1. The system consists of a reactor, an automatic temperature controller, an electrical furnace and a gas controlling system.

4.3.2.1 Reactor

The reactor was made from a stainless steel tube (O.D. 3/8 "). Two sampling points were provided about and below the catalyst bed. Catalyst was placed between two quartz wool layers.

4.3.2.2 Automation Temperature Controller

This unit consisted of a magnetic switch connected to a variable voltage transformer and a solid state relay temperature controller model no.SS2425DZ connected to a thermocouple. Reactor temperature was measured at the bottom of the catalyst bed in the reactor. The temperature control set point is adjustable within the rang of 0-800 °C at the maximum voltage output of 220 volt.

4.3.2.3 Electrical Furnace

The furnace supplied heat to the reactor for CO hydrogenation. The reactor could be operated from temperature up to 800 °C at the maximum voltage of 220 volt.

4.3.2.4 Gas Controlling System

Reactant for the system was each equipped with a pressure regulator and an on-off valve and the gas flow rates were adjusted by using metering valves.

4.3.2.5 Gas Chromatograph

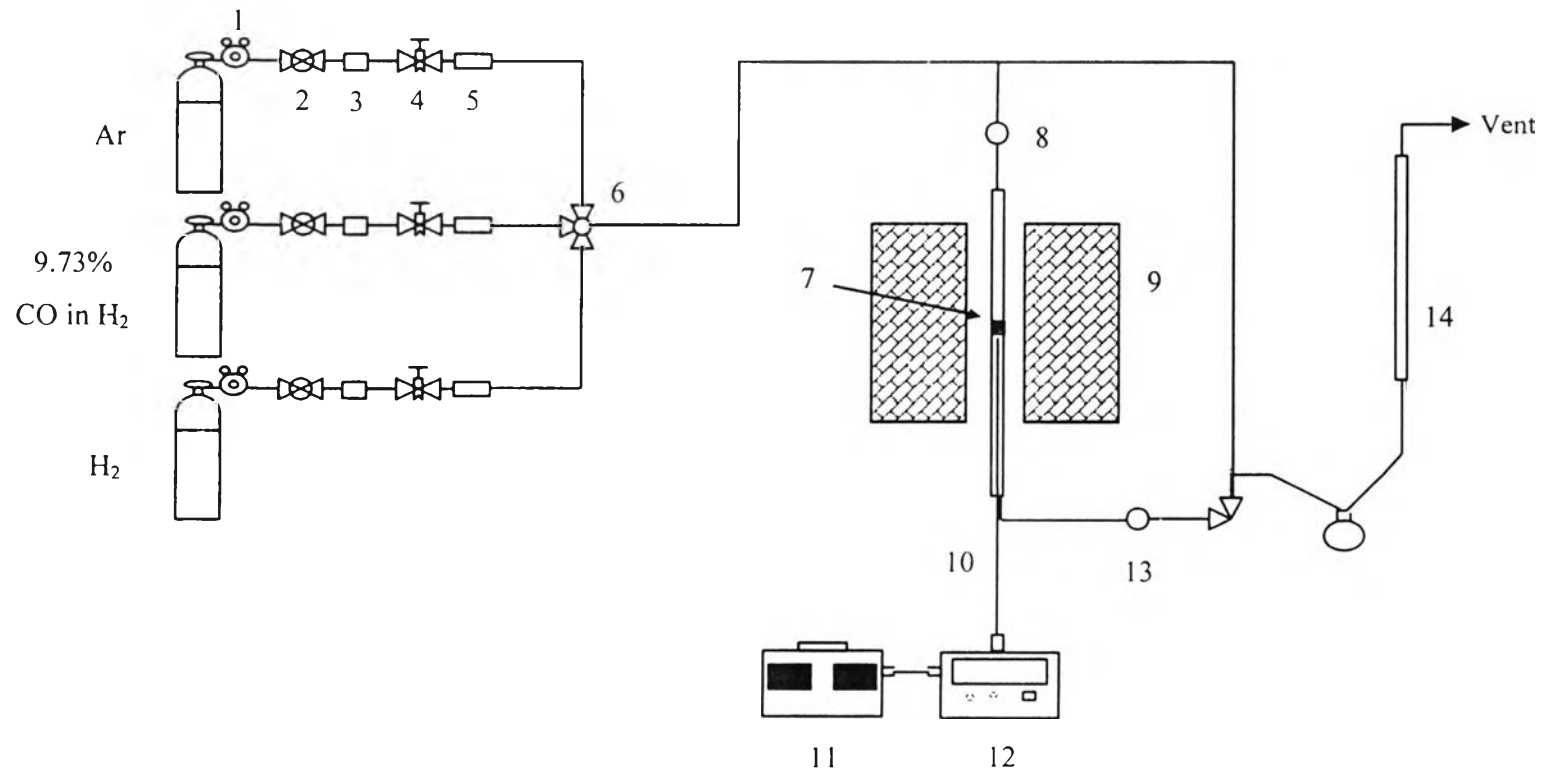
The composition of hydrocarbons in the product stream was analyzed by a Shimadzu GC-14B (VZ10) gas chromatograph equipped with a flame ionization detector. A Shimadzu GC-8A (molecular sieve 5A) gas chromatograph equipped with a thermal conductivity detector was used to analyze CO and H₂ in the feed and product streams. The operating conditions for each instrument are shown in the Table 4.2.

Table 4.2 Operating condition for gas chromatograph

Gas Chromatograph	SHIMADZU GC-8A	SHIMADZU GC-14B
Detector	TCD	FID
Column	Molecular sieve 5A	VZ 10
- Column material	SUS	-
- Length	2 m	-
- Outer diameter	4 mm	-
- Inner diameter	3 mm	-
- Mesh range	60/80	60/80
- Maximum temperature	350 °C	80°C
Carrier gas	He (99.999%)	N ₂ (99.999%)
Carrier gas flow	20 cc/min	-
Column gas	He (99.999%)	Air , H ₂
Column gas flow	20 cc/min	-
Column temperature		
- initial (°C)	60	70
- final (°C)	60	70
Injector temperature (°C)	100	100
Detector temperature (°C)	100	150
Current (mA)	80	-
Analysed gas	Ar, CO, H ₂	Hydrocarbon C ₁ -C ₄

4.3.3 Procedured

1. Using 0.2 g of catalyst packed in the middle of the stainless steel microreactor, which is located in the electrical furnace.
2. A flow rate of Ar = 8 cc/min, 9% CO in H₂ = 22 cc/min and H₂ = 50 cc/min in a fixed-bed flow reactor. A relatively high H₂/CO ratio was used to minimize deactivation due to carbon deposition during reaction.
3. The catalyst sample will be re-reduced *in situ* in flowing H₂ at 350°C for 10 h prior to CO hydrogenation.
4. CO hydrogenation will be carried out at 220°C and 1 atm total pressure in flowing 9% CO in H₂.
5. The effluent was analyzed using gas chromatography technique [Thermal conductivity detector (TCD) will be used for separation of carbon monoxide (CO) and methane (CH₄) and flame ionization detector (FID) will be used for separation of light hydrocarbon such as methane (CH₄), ethane (C₂H₆), propane (C₃H₈), etc.] In all cases, steady-state was reached within 5 h.



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| 1. Pressure Regulator | 2. On-Off Valve | 3. Gas Filter | 4. Metering Valve |
| 5. Back Pressure | 6. 3-way Valve | 7. Catalyst Bed | 8. Sampling point |
| 9. Furnace | 10. Thermocouple | 11. Variable Voltage Transformer | 12. Temperature Controller |
| 13. Heating Line | 14. Bubble Flow Meter | | |

Figure 4.1 Flow diagram of CO hydrogenation system

RESEARCH METHODOLOGY