

CHAPTER IV

EXPERIMENTAL

This chapter consists of experimental systems and procedures used in this work which is divided into three parts including catalyst preparation, catalyst characterization and reaction study in CO hydrogenation and FTS reaction.

The first part (section 4.1) is described catalyst preparation such as alumina supports with mixed γ - χ phase by solvothermal method, alumina supported Co catalyst using solvothermal synthesized-alumina support, alumina supported Fe catalysts and Cu-modified alumina supported Fe catalysts using commercial γ -Al₂O₃ support. The second part (section 4.2) is explained catalyst characterization by various techniques include of XRD, BET surface area, TEM, SEM, EDX, FT-IR, H₂ pulse chemisorption, CO pulse chemisorption, and TPR. Finally, the last part (section 4.3) is illustrated catalyst activity measurement in CO hydrogenation and FTS reaction.

4.1 Catalyst preparation

4.1.1 Chemicals

The chemicals used in this experiment are specified as follows:

1. Aluminum isopropoxide 98%+ (AIP, [(CH₃)₂CHO]₃Al)) available from Aldrich.
2. 1-butanol solution 99.5% (CH₃(CH₂)₃OH) available from Ajax Finechem.
3. Commercial γ -Al₂O₃ supports available from Johnson Matthey.
4. Cobalt (II) nitrate hexahydrate (Co(NO₃)₂ · 6H₂O) available from Aldrich.
5. Iron (III) nitrate nonahydrate (Fe(NO₃)₃ · 9H₂O) available from Alfa Aesar.
6. Copper (II) nitrate trihydrate (Cu(NO₃)₂ · 3H₂O) available from Acros Organics.

4.1.2 Preparation of nanocrystalline Al_2O_3

- Equipment

The equipment for the synthesis of alumina consisted of:

Autoclave reactor

- Made from stainless steel
- Volume of 1000 cm^3 and 10 cm inside diameter
- The thermocouple is attached to the reagent in the autoclave and maximum temperature of 350°C
- Pressure gauge in the range of 0-140 bar
- Test tube was used to contain the reagent and glycol

The autoclave reactor is shown in Figure 4.1

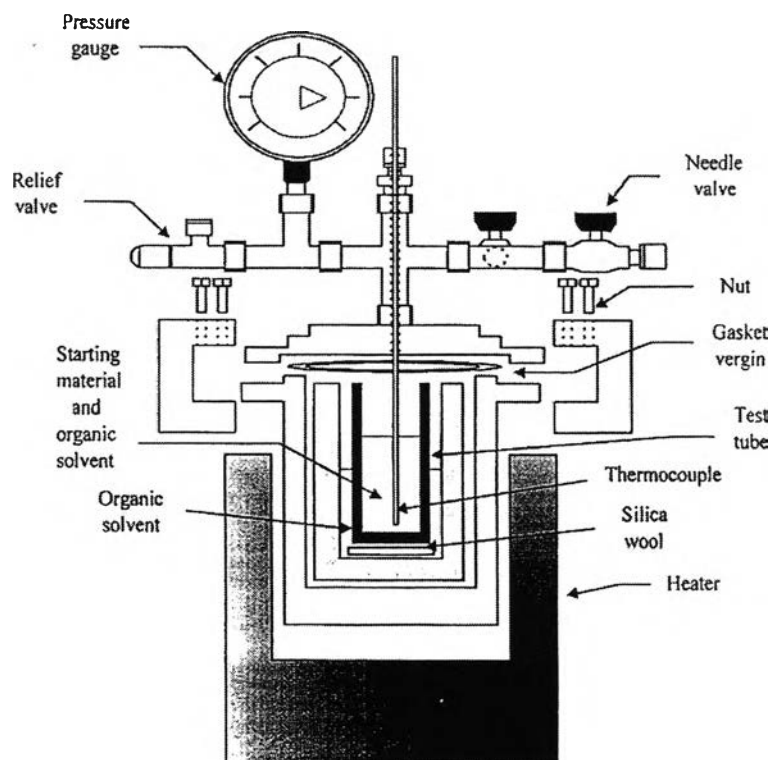


Figure 4.1 Autoclave reactor.

The diagram of the reaction equipment for synthesis of alumina is shown in Figure 4.2.

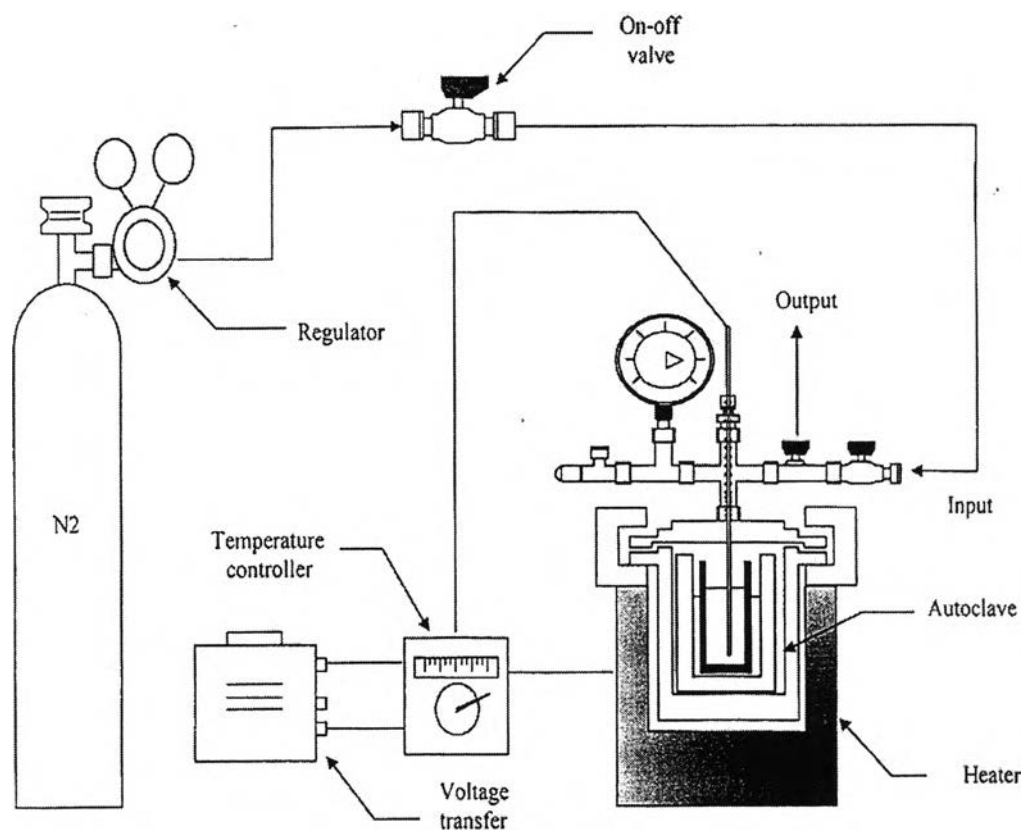


Figure 4.2 Diagram of the reaction equipment for the synthesis of alumina.

- Preparation method

The desired amount of aluminum isopropoxide (10, 15, 25, or 35 g) was suspended in 100 ml of 1-butanol in a beaker, which was then placed in a 300 ml autoclave. In the gap between the beaker and the autoclave wall, 30 ml of 1-butanol was added. After the atmosphere inside the autoclave was purged completely with nitrogen, the mixture was heated to 300°C at a heating rate of 2.5°C/min and was kept at that temperature for 2 h. After cooling to room temperature, the resulting powders were collected after repeated washing with acetone and were then air-dried. The calcination of the products was carried out in a box furnace by heating up to 600°C at a rate of 10°C/min and held at that temperature for 1 h.

- Catalyst nomenclature

In this study, alumina is referred to as Al-x where x is the amount (g) of AIP used in the preparation of alumina powders. For example, Al-10 refers to Al_2O_3 prepared with 10 g AIP.

4.1.3 Preparation of Al_2O_3 -supported Co catalysts using solvothermal-synthesized alumina support

- Preparation method

The Al_2O_3 -supported cobalt catalysts with different Co loadings (5, 10, 15, and 20 wt%) cobalt were prepared by incipient wetness impregnation of solvothermal synthesized-alumina support with a desired amount of an aqueous solution of cobalt (II) nitrate hexahydrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] (Aldrich). After impregnation, the catalysts were dried at 110°C for 24 h and calcined in air at 300°C for 2 h using a ramp rate of $1^\circ\text{C}/\text{min}$.

- Catalyst nomenclature

Alumina-supported cobalt catalysts are referred to as mCo/Al-x where m is the percentage of cobalt loading and x is the amount (g) of AIP used in the preparation of alumina powders. For example, 15Co/Al-10 refers to 15 wt% Co/ Al_2O_3 catalyst prepared with 10 g AIP.

4.1.4 Preparation of Al_2O_3 -supported Fe catalysts and Cu-modified Al_2O_3 supported Fe catalysts using commercial $\gamma\text{-Al}_2\text{O}_3$ support

- Preparation method

The Al_2O_3 -supported iron catalyst was prepared by the sequential impregnation method. First, a solution of iron (III) nitrate nonahydrate was impregnated into the commercial $\gamma\text{-Al}_2\text{O}_3$ support (specific surface area of $100 \text{ m}^2/\text{g}$

and average particle size of ca. 0.1 μm) to give a final catalyst composition of 20 wt% iron. The impregnated catalyst was then dried at 110°C for 24 h followed by calcination in air at 350°C for 3 h. Second, 1 wt% Cu was impregnated into the sample using a solution of copper (II) nitrate trihydrate. The catalyst was dried at 110°C for 24 h and then calcined again in air at 460°C for 3 h.

Cu-modified alumina having 10 wt% of Cu was prepared from the commercial $\gamma\text{-Al}_2\text{O}_3$ support used above by the incipient wetness impregnation with a solution of copper (II) nitrate trihydrate. Samples were dried at 110°C for 24 h and then calcined in air on ramping the temperature at 10°C/min up to 300°C and holding for 1 h. The temperature was thereafter increased by 10°C/min up to 500°C and held for 6 h. Iron (III) nitrate nonahydrate and copper (II) nitrate trihydrate were used to impregnate the Cu-modified alumina support using the same procedure as given in the previous section to produce the Cu-modified alumina supported Fe catalysts following the compositions and conditions given in Table 4.1.

- Catalyst nomenclature

The catalyst nomenclature, the compositions, and the preparation conditions of the various Al_2O_3 supported Fe catalysts are given in Table 4.1. The Fe catalysts prepared basically had 3 metal components in addition to the Al_2O_3 support. The base catalyst is 1%Cu promoted 20% Fe/ Al_2O_3 . All the other catalysts were prepared on 10% Cu modified Al_2O_3 supports. The catalysts were either dried (D) or dried and calcined (C) after each metal loading step. The nomenclature used for these catalysts consists of 5 components. For examples, the base catalyst is referred to as “1-0-*CC”, where the first number “1” referred to 1% Cu promoted on 20% Fe/ Al_2O_3 and the second number “0” referred to 0% Cu added to the Al_2O_3 support. The symbol and the letters “*CC” indicate the pretreatment used in each metal loading step. The asterisk (*) means that there was no pretreatment for the first stage since no Cu was added to the Al_2O_3 support in this sample but the catalysts were dried and calcined after Fe and Cu loadings. The catalyst designated “1-10-DDC” indicates that it was 1% Cu promoted 20% Fe catalyst on 10% Cu modified- Al_2O_3 support. The Cu modified Al_2O_3 support was dried only (designated by the first D) but not calcined prior to Fe

impregnation. The 20% Fe on 10% Cu-modified Al_2O_3 was then dried again (designated by the second D) but not calcined prior to the addition of 1% Cu. After the final impregnation step, the catalyst was then dried and calcined (designated by the third C).

Table 4.1 Catalyst nomenclatures and the preparation conditions.

Catalyst	Metal loading (wt%)			Pretreatment after each metal impregnation		
	Cu	Fe	Cu on Al_2O_3	1 st (10% Cu on Al_2O_3)	2 nd (20% Fe)	3 rd (1% Cu)
1-0-*CC ^a	1	20	0	none	C	C ^b
1-10-CCC	1	20	10	C	C	C
1-10-CDC	1	20	10	C	D ^c	C
1-10-DDC	1	20	10	D	D	C
1-10-DDD	1	20	10	D	D	D
0-10-CC*	0	20	10	C	C	none
0-10-CD*	0	20	10	C	D	none
0-10-DC*	0	20	10	D	C	none

^a 1%Cu-promoted 20%Fe/ Al_2O_3 is the reference catalyst.

^b C = dried in air at 110°C for 24 h followed by calcination in air at desired temperature and holding time for each metal.

^c D = dried in air at 110°C for 24 h.

4.2 Catalyst characterization

Various characterization techniques were used in this study in order to clarify the catalyst structure and morphology, surface composition of various alumina supports and alumina-supported Co and Fe catalysts.

4.2.1 Nanocrystalline Al₂O₃ by solvothermal method

- X-ray diffraction (XRD)

X-ray diffraction patterns of the samples were collected using a SIEMENS D-5000 X-ray diffractometer with Cu K_α radiation ($\lambda = 1.54439 \text{ \AA}$). The spectra were scanned at a rate of 0.04°/step from $2\theta = 15^\circ$ to 80° . The crystallite size is estimated from line broadening according to the Scherrer equation and α -Al₂O₃ was used as standard.

- N₂ physisorption (BET surface area)

BET apparatus for the single point method

The reaction apparatus of BET surface area measurement consisted of two feed lines for helium and nitrogen. The flow rate of the gas is adjusted by means of fine-metering valve on the gas chromatograph. The sample cell is 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. 0.3 to 0.5 g) will be placed in the sample cell, which will be then heated up to 160 °C and held at this temperature for 2 h. After the catalyst sample is cooled down to room temperature, nitrogen uptakes will be measured as follows:

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

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

Step (3) Calibration step: 1 ml of nitrogen gas at atmospheric pressure will be injected through the calibration port of the gas chromatograph and the area will be measured. The area below curve will be considered as a calibration peak.

Calculation of BET surface area of the catalyst samples are given in Appendix B.

- Transmission Electron Microscope (TEM)

Transmission electron microscopy (TEM) was performed to study the morphology of the alumina supports using a JEOL JEM1220 operated at 100 kv.

- Fourier transform Infrared (FT-IR)

The functional group on the alumina supports surface was determined by FT-IR using Nicolet model Impact 400. Each sample was mixed with KBr with ratio of sample: KBr equal to 1:100 and then pressed into a thin wafer. Infrared spectra were recorded between 1400 and 3900 cm^{-1} on a microcomputer.

4.2.2 Al₂O₃-supported Co catalysts

- X-ray diffraction (XRD)

X-ray diffraction patterns of the samples were collected using a SIEMENS D-5000 X-ray diffractometer with Cu K_α radiation ($\lambda = 1.54439 \text{ \AA}$). The spectra were scanned at a rate of 0.04°/step from $2\theta = 15^\circ$ to 80° . The crystallite size is estimated from line broadening according to the Scherrer equation and α -Al₂O₃ was used as standard.

- Nitrogen physisorption (BET surface area)

BET apparatus for the single point method

The reaction apparatus of BET surface area measurement consisted of two feed lines for helium and nitrogen. The flow rate of the gas is adjusted by means of fine-metering valve on the gas chromatograph. The sample cell is 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. 0.3 to 0.5 g) will be placed in the sample cell, which will be then heated up to 160 °C and held at this temperature for 2 h. After the catalyst sample is cooled down to room temperature, nitrogen uptakes will be measured as follows:

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

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

Step (3) Calibration step: 1 ml of nitrogen gas at atmospheric pressure will be injected through the calibration port of the gas chromatograph and the area will be measured. The area below curve will be considered as a calibration peak.

Calculation of BET surface area of the catalyst samples are given in Appendix B.

- Electron microscopy

SEM and EDX were performed to study the morphology and elemental distribution of the catalyst particles using a JEOL JSM-35CF scanning electron microscope in the back scattering electron (BSE) mode at 20 kV. EDX was performed using Link Isis 300 software.

- Hydrogen pulse chemisorption

H₂ pulse chemisorption was carried out to determine the number of active surface cobalt and overall cobalt dispersion on the reduced catalyst samples at 100°C according to the method based on the static method described by Reuel and Bartholomew (Reuel and Bartholomew, 1984) using a Micromeritics Pulse Chemisorb 2750 system. Prior to H₂ chemisorption, the catalyst samples were reduced at 350°C in flowing H₂ for 3 h.

- Temperature programmed reduction (TPR)

Temperature-programmed reduction (TPR) was performed to study the reduction behaviors of the catalysts using an in-house system. Approximately 0.1 g of the catalyst was placed in the middle of stainless steel reactor. A temperature ramp from 35 to 600°C at a ramp rate 5°C/min and the reduction gas 5% H₂ in Ar were used. A thermal conductivity detector (TCD) was used to determine the amount of hydrogen consumed. A cold trap was placed before the detector to remove water produced during the reduction.

Table 4.2 Operating condition of the thermal conductivity detector for TPR.

Model	GOW-MAC
Detector type	TCD
Carrier gas	5 %H ₂ in Ar
Carrier gas flow rate (ml/min)	30
Detector temperature (°C)	80
Detector current (mA)	80

4.2.3 Al₂O₃-supported Fe catalysts

- X-ray diffraction (XRD)

X-ray diffraction patterns of the catalysts were collected with a Scintag 2000 x-ray diffractometer, using monochromatized Cu K_α radiation (40 kV, 40 mA) and a Ge detector using a step scan mode. The spectra were scanned at a scan rate of 0.04° (2θ) per second from 2θ = 10° to 80°.

- Nitrogen physisorption (BET surface area)

The BET surface area, pore volume, and average pore size were measured by N₂ physisorption at liquid N₂ temperature (-196°C) using a Micromeritics ASAP 2020 automated instruments. The samples were degassed under vacuum at 100°C holding for 1 h then increasing the temperature by 10°C/min up to 300°C and holding for 2 h prior to each measurement.

- Electron microscopy

SEM and EDX were performed to study the morphology and elemental distribution of the catalyst particles using a JEOL JSM-35CF scanning electron microscope in the back scattering electron (BSE) mode at 20 kV. EDX was performed using Link Isis 300 software.

- Carbon monoxide pulse chemisorption

CO pulse chemisorption was performed on the reduced catalyst samples at 50°C using a Micromeritics Pulse Chemisorb 2750 system. Prior to CO chemisorption, the catalyst samples were pretreated in flowing (50 ml/min) H₂ at 460°C for 16 h with a ramping rate of 10°C/min. Afterwards, the sample was purged with helium and finally cooled down. Carbon monoxide was pulsed at 50°C over the reduced catalyst until the TCD signal was constant.

- Temperature programmed reduction (TPR)

Temperature-programmed reduction (TPR) was performed to study the reduction behaviors of the catalysts using a Micromeritics Pulse Chemisorb 2750 system. Approximately 0.1 g of the catalyst was placed in the quartz tube. A temperature ramp from 35 to 800°C at a ramp rate 5°C/min and the reduction gas 10% H₂ in Ar were used. A thermal conductivity detector (TCD) was used to determine the amount of hydrogen consumed. A cold trap was placed before the detector to remove water produced during the reduction.

4.3 Reaction study

4.3.1 CO hydrogenation

4.3.1.1 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. The total flow rate was 120 ml/min with the H₂/CO ratio of 10/1. Ultra high purity hydrogen and high purity argon manufactured by Thai Industrial Gas Limited (TIG) were used for reduction and balanced flow rate.

4.3.1.2 Apparatus

The diagram of the flow CO hydrogenation system is shown in Figure 4.3. The system consists of a reactor, an automatic temperature controller, an electrical furnace and a gas controlling system.

4.3.1.3 Procedures

CO hydrogenation was carried out in a fixed-bed quartz reactor under differential reaction conditions (<10% conversion) at 220°C, 1 atm total pressure, and H₂/CO = 10/1. The total flow rate of H₂/CO/Ar was 80/8/32 cc/min. Typically, 0.1 g of the catalyst sample was reduced *in situ* in flowing H₂ (50 cc/min) at 350°C for 3 h prior to CO hydrogenation. After the startup, samples were taken in 1-h interval and analyzed by gas chromatography. Steady state was reached within 6 h in all cases.

4.3.2 FTS reaction

4.3.2.1 Material

The reactant gases used for the reaction study was carbon monoxide and hydrogen as supplied by National Specialty Gases. The total flow rate was 60 ml/min with the H₂/CO ratio of 2/1. Ultra high purity hydrogen and high purity helium manufactured by National Specialty Gases were used for reduction and balanced flow rate.

4.3.2.2 Apparatus

The system consists of a reactor, an automatic temperature controller, an electrical furnace and a gas controlling system.

4.3.2.3 Procedures

Steady-state FTS reaction rates and selectivities were measured in a stainless steel fixed-bed reactor under differential reaction conditions at 280°C and 1.8 atm total pressure. The H₂/CO ratio used was 2/1. Typically, 0.1 g of the catalyst sample was pretreated *in situ* in flowing H₂ (50 ml/min) at 460°C for 16 h prior to reaction. After pretreatment the reaction mixture containing 5 ml/min of CO, 10 ml/min of H₂, and 45 ml/min of He was then introduced into the reactor at 280°C. The system was pressurized to 1.8 atm. Product samples were taken at 1.5-h intervals and analyzed by gas chromatography. Steady-state was reached within 6 h in all cases.

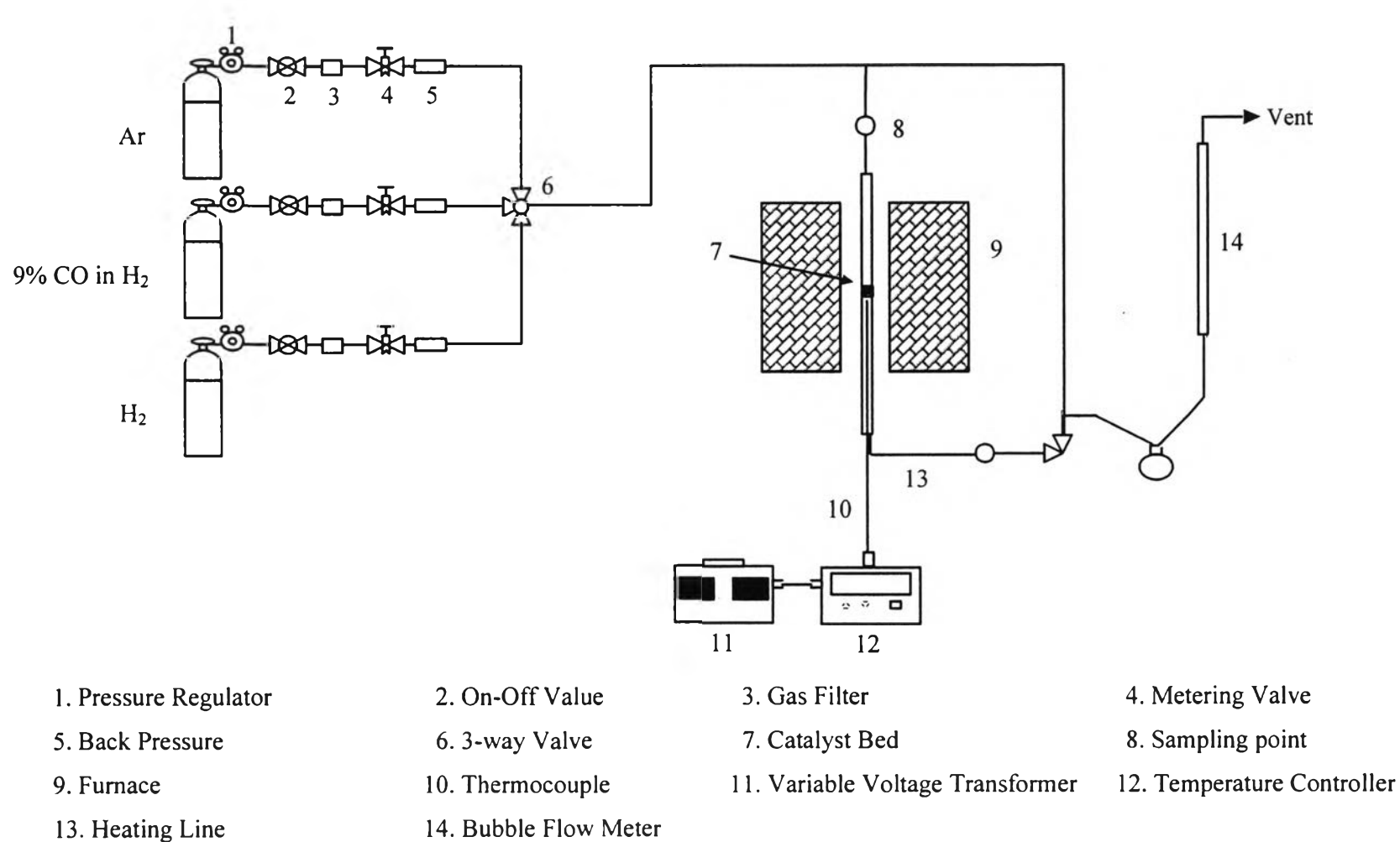


Figure 4.3 Flow diagram of CO hydrogenation system.