

## CHAPTER IV

### EXPERIMENTAL

The experiments are categorized into three parts:

1. The preparation of catalysts
2. The characterization methods
3. The catalytic activity measurements

The details of the experiments are described below.

#### **The scope of this study.**

The reaction conditions for the oxidation are chosen as follows:

Catalysts	:	Co/MgO, Co/SiO <sub>2</sub> , Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (8%wtCo)
Reactant liquid	:	CH <sub>3</sub> OH, C <sub>2</sub> H <sub>5</sub> OH, 1-C <sub>3</sub> H <sub>7</sub> OH, 2-C <sub>3</sub> H <sub>7</sub> OH and 1-C <sub>4</sub> H <sub>9</sub> OH
Flow rate of reactant	:	100 ml/min
Reaction temperature	:	200-500°C
Gas hourly space velocity	:	20,000 hr <sup>-1</sup>

## 4.1 Preparation of catalysts

### 4.1.1 Chemicals

The details of chemicals used in this experiment are shown in table 4.1.

**Table 4.1** the chemicals used in this research.

Chemical	Grade	Manufacture
Cobaltous acetate tetrahydrate ( $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ )	Analytical	Fluka, Switzerland
Magnesium oxide (MgO)	Analytical	Carlo Erba, Italy
Silica gel ( $\text{SiO}_2$ )	Analytical	Merck, Germany
Alumina pellet ( $\text{Al}_2\text{O}_3$ )	Analytical	Sumitomo Aluminum Smelting Co.,Ltd ., Japan

### 4.1.2 Catalyst preparation

Co/MgO catalyst (8%wtCo) was prepared by the conventional wet impregnation method. Calculating the amount Co to yield the required metal loading, then adding de-ionized water to the total volume 50 ml. The aqueous solution was stirred from room temperature to 70°C, added required amount of support to an aqueous solution and heated from 70°C to 80°C. The suspension was evaporated until achieving a thick paste and dried in the oven at 110°C in air over night. The solid was then calcined in air at 600°C for 6 hours.

In case of Co/SiO<sub>2</sub> and Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (8%wtCo), they were prepared by impregnating SiO<sub>2</sub> or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (mesh 40-60) with an aqueous solution of cobalt acetate. The amount of the aqueous solution was adjusted to be 1.2 ml and 1 ml per gram of SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> respectively, left 6 hours at room temperature. The solids were dried at 110°C, then calcined in air at 600°C for 6 hours.

## **4.2 The characterization of catalyst**

### **4.2.1 Determination of composition content of catalyst**

Percentage of metal cobalt loading was measured by atomic absorption spectroscopy (AAS). The calculation of the sample preparation is shown in Appendix A.

### **4.2.2 Surface area measurement**

The specific surface areas were determined from the BET absorption isotherm of nitrogen at  $-196^{\circ}\text{C}$  measured by an automatic apparatus ASAP 2000 constructed by Micromeritics, U.S.A.

### **4.2.3 X-ray diffraction (XRD)**

The phase structures were determined by X-ray diffraction, Siemens D 5000 X-ray diffractometer using  $\text{CuK}\alpha$  radiation with Ni filter in the  $2\theta$  range of  $4-80^{\circ}$ . The sample is placed into XRD plate before placing on the measured position of XRD diffractometer.

### **4.2.4 Fourier transform Infrared (FT-IR)**

The functional group on the catalyst surface was determined by FT-IR using Nicolet model Impact 400. Each sample was mixed with KBr with ratio of sample: KBr equal to 1:200 before being formed into a thin wafer. Infrared spectra were recorded between  $400$  and  $2000\text{ cm}^{-1}$  on a microcomputer.

### 4.3 The catalytic activity measurements

#### 4.3.1 Equipment

Flow diagram of the reaction system is shown in figure 4.1. The system consists of a saturator, a reactor, an automatic temperature controller, an electrical furnace and a gas controlling system. Liquid phase reactants were passed through the saturator in order to evaporate them into gas phase before passing to the microreactor.

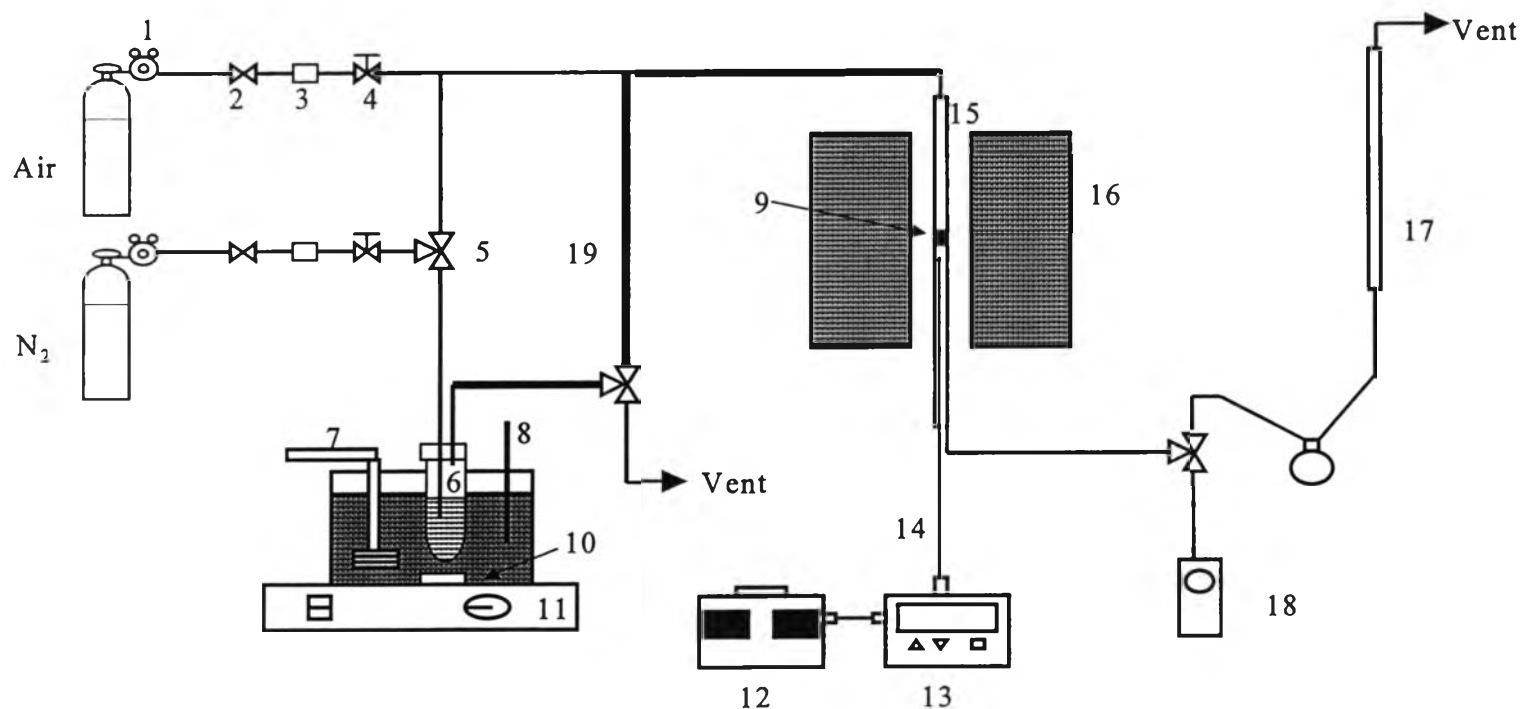
The reactor is made from a stainless steel tube. Two sampling points are provided above and below the catalyst bed. Catalyst was placed between two quartz wool layers.

The gas supplying system consists of cylinders of ultra high purity nitrogen and air, each equipped with pressure regulators (0-120 psig), on-off valves and fine-meter valves used for adjusting the flow rate of these gases.

The composition of hydrocarbons in the product stream was analyzed by a Shimadzu GC14B gas chromatograph equipped with flame ionization detector.

The composition of oxygenates compounds in the feed and product stream was measured by a Shimadzu GC14B gas chromatograph equipped with flame ionization detector.

A Shimadzu GC8A gas chromatograph equipped with a thermal conductivity detector was used to analyze permanent gases and water. Two columns, a 5A molecular sieve to separate oxygen and carbon monoxide and a Porapak-Q column to separate CO<sub>2</sub> and water were operated in parallel. The operating conditions are shown in the Table 4.2.



- |                            |                    |                         |                                  |
|----------------------------|--------------------|-------------------------|----------------------------------|
| 1. Pressure Regulator      | 2. On-Off Valve    | 3. Gas Filter           | 4. Metering valve                |
| 5. 3-way Valve             | 6. Saturator       | 7. Heater               | 8. Thermometer                   |
| 9. Catalyst Bed            | 10. Magnetic bar   | 11. Stirring controller | 12. Variable Voltage Transformer |
| 13. Temperature Controller | 14. Thermocouple   | 15. Reactor             | 16. Furnace                      |
| 17. Bubble Flow Meter      | 18. Sampling point | 19. Heating Line        |                                  |

**Figure 4.1** Flow diagram of methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol oxidation system

**Table 4.2** Operating condition for gas chromatograph

Gas chromatograph	Shimadzu GC8A	Shimadzu GC14A	Shimadzu GC14B
Detector	TCD	FID	FID
Column	MS-5A, Porapak-Q	Capillary	VZ10
Carrier gas	He (99.999%)	N <sub>2</sub> (99.999%)	N <sub>2</sub> (99.999%)
Carrier gas flow	25 ml/min	25 ml/min	25 ml/min
Column temperature			
- Initial	100	40	70
- Final	100	140	70
Detector temperature	130	150	150
Injector temperature	130	100	100
Analyzed gas	CO, CO <sub>2</sub> , H <sub>2</sub> O	Oxygenates	Hydrocarbon C <sub>1</sub> -C <sub>4</sub>

#### 4.3.2 Oxidation procedure

The oxidation procedures are described in the detail below.

- 0.1 gram of catalyst was packed in the middle of the stainless steel microreactor located in an electrical furnace.
- The total flow rate was 100 ml/min. Flow rate of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, nitrogen and air were adjusted to the required values.
  - The gas mixtures for methanol oxidation were 8 vol.% methanol, 5 vol.% oxygen and balance with nitrogen.
  - The gas mixtures for ethanol oxidation were 8 vol.% ethanol, 5 vol.% oxygen and balance with nitrogen.
  - The gas mixtures for 1-propanol oxidation were 8 vol.% 1-propanol, 5 vol.% oxygen and balance with nitrogen.
  - The gas mixtures for 2-propanol oxidation were 8 vol.% 2-propanol, 5 vol.% oxygen and balance with nitrogen.

- The gas mixtures for 1-butanol oxidation were 8 vol.% 1-butanol, 5 vol.% oxygen and balance with nitrogen.

3. The reaction temperature was between 200-500°C. The effluent gases were analyzed by using the FID and TCD gas chromatograph. The chromatograph data were converted into mole of methane, ethylene, propane, propylene, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, formaldehyde, acetaldehyde, propionaldehyde, and CO<sub>2</sub> by calibration curves in Appendix C.

