

## CHAPTER IV

### EXPERIMENTAL

The experimental systems and procedures used in this work are divided into three parts:

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

The details of the experiments are described as the following.

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

The reaction conditions are chosen as follows:

Catalysts	:	Co-Mg-O/TiO <sub>2</sub> , Co-Mg-O/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (8%wtCo, 1%wtMg)
Reactant liquid	:	1-Propanol and 2-Propanol
Flow rate of reactant	:	100 ml/min
Feed composition	:	Alcohol 8 vol% Oxygen 5 vol% Nitrogen balance
Reaction temperature	:	300°C and 500°C
Space velocity	:	60.000 mlg <sup>-1</sup> h <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** Chemicals used in this experiment.

Chemical	Grade	Supplier
Cobaltous acetate tetrahydrate ( $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ )	Analytical	Fluka, Switzerland
Magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ )	Analytical	Fluka, Switzerland
Titanium dioxide ( $\text{TiO}_2$ ) JRC-TIO4	Japan reference catalyst	Department of Material Science, Shimane University
Alumina ( $\text{Al}_2\text{O}_3$ ) JRC-ALO2	Japan reference catalyst	Catalysts and Chemicals Ind. Co., Ltd.

### 4.1.2 Preparation of catalyst

To study the effect of sequence of cobalt and magnesium loading, then three types of Co-Mg-O/ $\text{TiO}_2$  catalyst (8%wtCo, 1%wtMg) were prepared. In the first type of preparation, an appropriate amount of  $\text{TiO}_2$  powder was added to an aqueous solution of cobaltous acetate tetrahydrate ( $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) at  $70^\circ\text{C}$ . The suspension was evaporated at  $80^\circ\text{C}$ , then dried in the oven at  $110^\circ\text{C}$  in air over night. The resulting solid was calcined in air at  $550^\circ\text{C}$  for 6 hours. Magnesium was introduced into the calcined solid by impregnation from a magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ ) solution, evaporated at  $80^\circ\text{C}$  and dried at  $110^\circ\text{C}$  in air overnight. After drying the catalyst was calcined in air at  $550^\circ\text{C}$  for 6 hours. This catalyst was denoted as 8Co1MgTi catalyst.

In the second type of sample, magnesium was firstly introduced in the way given above on to pure titania surface and then cobalt was deposited on Mg-doped  $\text{TiO}_2$  support by the incipient wetness impregnation method. The catalyst was dried at

110°C in air overnight and calcined in air for 6 hours at 550°C. This catalyst was denoted as 1Mg8CoTi catalyst.

The third one was prepared by co-impregnation of cobalt and magnesium. An appropriate  $\text{TiO}_2$  was added to an aqueous solution containing both  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2$ . The conditions of drying and calcination liked the previous samples. This catalyst was denoted as co-8Co1MgTi.

Three types of Co-Mg-O/ $\text{Al}_2\text{O}_3$  catalysts were prepared using similar method to the three types of Co-Mg-O/ $\text{TiO}_2$  catalysts. The symbols of the three types of Co-Mg-O/ $\text{Al}_2\text{O}_3$  catalysts liked the three types of Co-Mg-O/ $\text{TiO}_2$  catalysts too i.e. 8Co1MgAl, 1Mg8CoAl, co-8Co1MgAl.

## **4.2 The characterization of catalyst**

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

The actual composition contents of all catalysts were determined by atomic absorption spectroscopy (AAS) at the Department of science service Ministry of science technology and environment. The calculation of the sample preparation is shown in Appendix A.

### **4.2.2 BET Surface area measurement**

#### **a) Apparatus**

The apparatus consisted of two gases feed lines for helium and nitrogen. The flow rate of gas was adjusted by means of fine-metering valve. The sample cell was made from pyrex glass. The operation conditions of the gas chromatograph (GOW-MAC) is shown in Table 4.2

**Table 4.2** Operation conditions of gas chromatograph (GOW-MAC)

Model	GOW-MAC
Detector	TCD
Helium flow rate	30 ml/min
Detector temperature	80°C
Detector current	80 mA

**b) Procedure**

The mixture of helium and nitrogen gas flowed through the system at the nitrogen relative pressure of 0.3. The sample was placed in the sample cell, which was then heated up to 150°C and held at this temperature for 2 hrs. The sample was cooled down to room temperature and ready to measure the surface area. There were three steps to measure the surface area.

1. Adsorption step

The sample cell was dipped into the liquid nitrogen. Nitrogen was adsorbed on the surface of the sample until an equilibrium was reached.

2. Desorption step

The nitrogen-adsorbed sample was dipped into the water at room temperature. The adsorbed nitrogen was desorbed from the surface of the sample. This step was completed when the recorder line return back to the base line.

3. Calibration step

1 ml of nitrogen gas at atmospheric pressure was injected at the calibration port and the area was measure. The area was the calibration peak.

4. The BET surface area calculation is in Appendix C

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

The phase structures of samples 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  $20\text{-}80^\circ$ . 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 1:100 and then pressed into a thin wafer. Infrared spectra were recorded between  $400$  and  $2000\text{ cm}^{-1}$  on a microcomputer.

### **4.2.5 Temperature-Programmed Oxidation**

#### **a) Materials**

1 %vol oxygen in helium gas mixture was used as oxidizing agent. Ultra high purity helium was used for purging the system.

#### **b) Apparatus**

Temperature programmed oxidation of the catalyst was carried out in a quartz tube (8 mm O.D.) located in a tube furnace. The furnace temperature was controlled by a microprocessor base temperature controller (PC 600, Shinko). A gas mixture of 1 vol % oxygen in helium was used as an oxidizing gas. The oxidation process began by heating the catalyst with a flow rate of  $5^\circ\text{C}/\text{min}$  until the temperature reached  $800^\circ\text{C}$ . During the oxidation, the amount of  $\text{CO}_2$  in the effluent gas was first analyzed when the catalyst temperature reached  $50^\circ\text{C}$ , then at an interval of about 5 min, using a gas chromatograph (SHIMADZU 8 AIT) equipped with a gas sampling valve (1.5 ml sampling loop) and a thermal conductivity detector.

**Table 4.3** Operating condition of gas chromatograph (GC-8AIT, SHIMADZU)

Model	GC-8 AIT (SHIMADZU)
Detector	TCD
Packed column	Porapack QS (200x0.32 cm)
Helium flow rate	60 ml/min
Column temperature	90°C
Detector/injector temperature	110°C
Detector current	90 mA

**c) Procedure**

1. The catalyst was packed in the middle of the quartz microreactor before placing the reactor in the furnace. The catalyst section was placed in the constant temperature zone of the furnace.

2. The 1 %vol oxygen in helium gas was flowed through the system at a flow rate of 30 ml/min.

3. The Temperature-Programmed Oxidation of catalyst was started. The temperature was raised to 800°C at heating rate of 5°C/min. When the temperature was 50°C, the effluent stream was sampled every 5 min by the on-line gas sampler.

4. The amount of oxygen consumed and carbondioxide produced was measured.

5. After the catalyst temperature reached 800°C, the 1 %vol oxygen in helium gas was changed to ultra high purity helium and the reactor was cooled down.

6. The amount of coke (wt%) was calculated (Appendix G).

#### 4.2.6 Electron spinning resonance (ESR) analysis

Electron Spinning Resonance (ESR) analysis was chosen to study the presence of specie which has unpaired electron. The samples were investigated at room temperature by electron spinning resonance spectrometer model JES-RE2X, JEOL at the Scientific and Technology Research Equipment Center, Chulalongkorn University (STREC).

### 4.3 The catalytic activity measurements

#### 4.3.1 Equipment

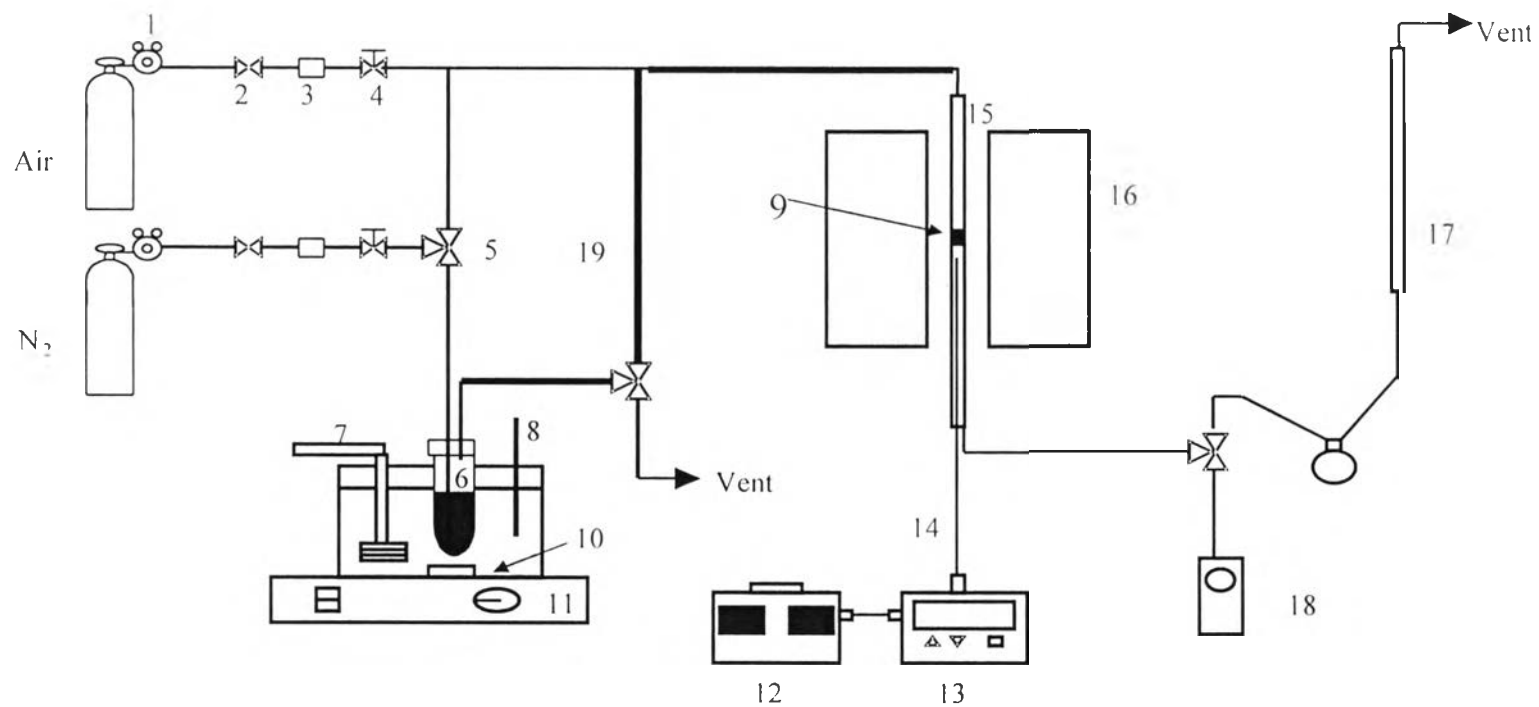
The 1-propanol and 2-propanol system consists of a reactor, a saturator, an automatic temperature controller, an electrical tube furnace and a gas controlling system. 1-propanol and 2-propanol reactant were fed via the saturator. Flow diagram of the oxidation reaction system is shown in figure 4.1.

The reactor is made from a stainless steel tube (O.D. 3/8"). Sampling points are provided above and below the catalyst bed. Catalyst is placed between two quartz wool layers.

An automatic temperature controller consists of a magnetic contactor model Telex 87114. Reactor temperature was measured at the bottom of the catalyst bed in the reactor. The temperature control set point is adjustable within the range of 0-800°C at the maximum voltage output of 220 volt.

The electrical furnace supplies heat to the reactor for 1-propanol and 2-propanol oxidation. The reactor can be operated from room temperature up to 800°C at the maximum voltage of 220 volt

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.



- |                            |                   |                        |                                  |
|----------------------------|-------------------|------------------------|----------------------------------|
| 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 1-propanol and 2-propanol oxidation system



The composition of oxygenated compounds in the feed and product stream was analyzed by flame ionization detector gas Chromatograph Shimadzu GC14A.

The composition of hydrocarbons in the product stream was measured by flame ionization detector gas Chromatograph Shimadzu GC14B.

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 CO and a Porapak-Q column to separate CO<sub>2</sub> and water were operated in parallel. The operating conditions of GC are listed in the Table 4.4.

**Table 4.4** Operating condition for gas chromatographs

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.

1. 0.1 gram of catalyst was packed in the middle of the stainless steel microreactor located in an electrical furnace.

2. The total flow rate was 100 ml/min. Flow rate of 1-propanol and 2-propanol, nitrogen and air were adjusted to the required values.

- 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.

3. The reaction temperatures were 500°C and 300°C for 48 hrs. The effluent gases were analyzed by using the FID and TCD gas chromatograph. The chromatograph data were changed into mole of methane, ethylene, propane, propylene, methanol, ethanol, 1-propanol, 2-propanol, formaldehyde, acetaldehyde, propionaldehyde, and CO<sub>2</sub> by calibration curves in reported Appendix D.

4. The result of catalytic test was calculated in the term of

$$\%A \text{ conversion} = \frac{\text{mole of A converted}}{\text{mole of A in feed}}$$

$$\% \text{selectivity to B} = \frac{\text{mole of B formed}}{\text{mole of A converted}} \times \frac{\text{no. of C atom of B}}{\text{no. of C atom of A}} \times 100$$

$$\% \text{yield to B} = \frac{\%A \text{ conversion} \times \% \text{selectivity to B}}{100\%}$$

where A is reactant

B is product