

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/Al ₂ O ₃
Reactant	:	C ₈ H ₄ O ₃ , C ₄ H ₂ O ₃
Flow rate of reactant	:	100 ml/min
Reaction temperature	:	200-550°C
Space velocity	:	60 000 ml g ⁻¹ h ⁻¹

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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 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 (TiO_2) JRC TIO4	Japan reference catalyst	Department of Material Science, Shimane University
Alumina (Al_2O_3) JRC ALO2 (γ -phase)	Japan reference catalyst	Catalysts and Chemicals Ind. Co., Ltd.

4.1.2 Preparation of catalyst

Co-Mg-O/ Al_2O_3 catalyst was prepared by co-impregnation of cobalt and magnesium. An appropriate amount of Al_2O_3 was added to an aqueous solution containing both $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2$ at 70°C . The suspension was evaporated at 80°C , then dried in the oven at 110°C in air over night. The resulting solid was calcined in air at 550°C for 6 hours.

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

4.2.2.1 Apparatus

The apparatus consisted of two gas feed lines for helium and nitrogen. The flow rate of gas was adjusted by means of a 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

4.2.2.2 Procedure

The mixture of helium and nitrogen gas flowed through the system at the nitrogen gauge 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 h. 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 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 is calculated using procedures described in Appendix C.

4.2.3 X-ray diffraction (XRD)

The phase structures of the samples were determined by X-ray diffraction, Siemens D 5000 X-ray diffractometer using $\text{CuK}\alpha$ radiation with Ni filter in the 2θ 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 cm^{-1} on a microcomputer.

4.3 The catalytic activity measurements

4.3.1 Equipment

The phthalic anhydride and maleic anhydride combustion system, as shown in Figure 4.1, consists of a reactor, a saturator, an automatic temperature controller, an electrical furnace and a gas controlling system.

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 contractor 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 phthalic anhydride and maleic anhydride combustion. 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 air zero, each equipped with pressure regulators (0-120 psig), on-off valves and fine-meter valves used for adjusting the flow rate.

The composition in the feed and product stream was analyzed by flame ionization detector gas Chromatograph Shimadzu GC9A.

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 CO₂ and water were operated in parallel. The operating conditions of the GC are listed in the Table 4.3.

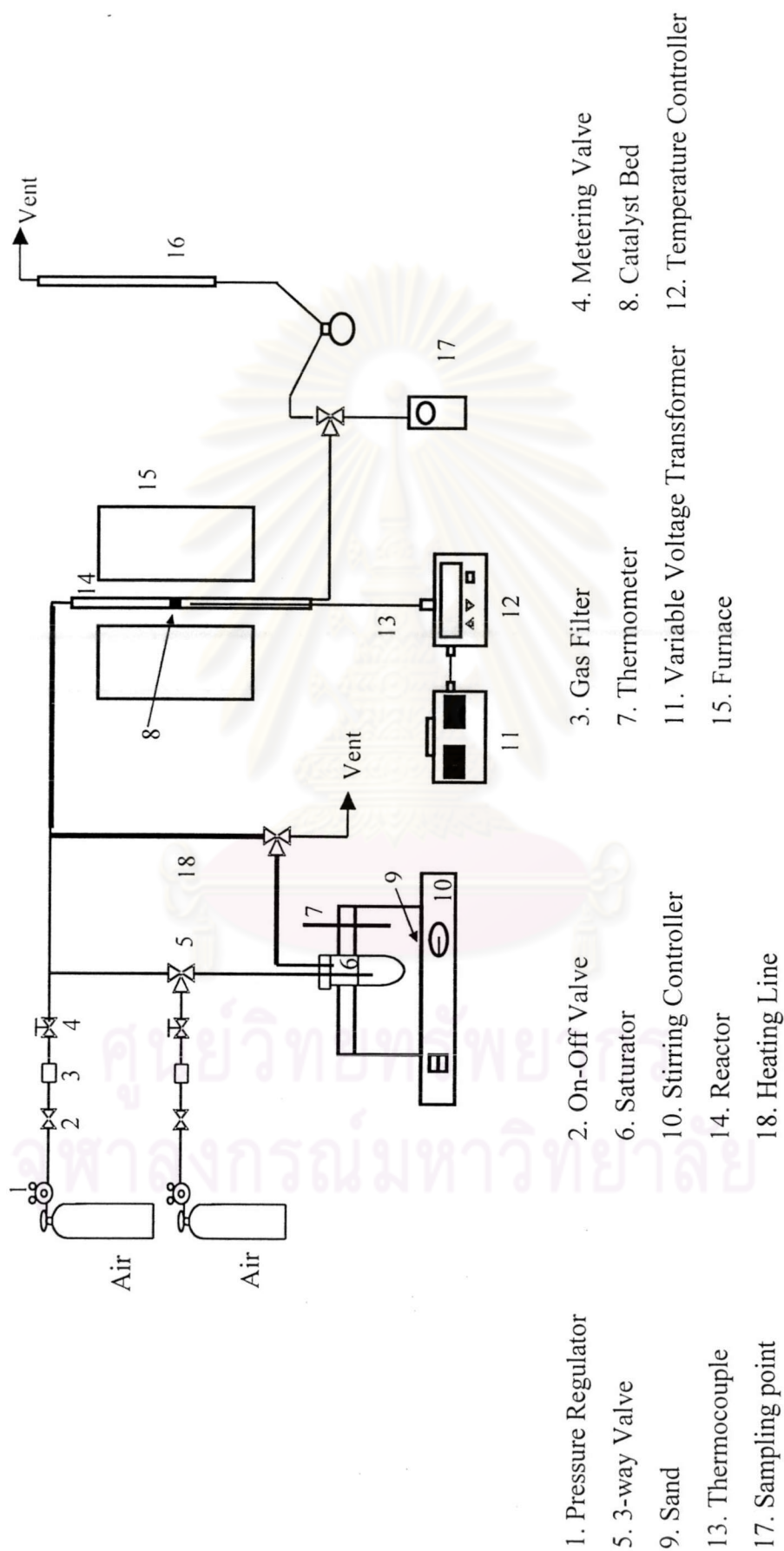


Figure 4.1 Flow diagram of phthalic anhydride and maleic anhydride combustion system

Table 4.3 Operating conditions for gas chromatographs

Gas chromatograph	GC8A	GC9A
Detector	TCD	FID
Column	MS-5A, Porapak-Q	Chromosorb WAW
Carrier gas	He (99.999%)	N ₂ (99.999%)
Carrier gas flow	25 ml/min	30 ml/min
Column temperature		
- Initial	100 °C	160°C for maleic anhydride 210°C for phthalic anhydride
- Final	100°C	160°C for maleic anhydride 210°C for phthalic anhydride
Detector temperature	130°C	250°C
Injector temperature	130°C	250°C
Analyzed gas	CO, CO ₂ , H ₂ O	maleic anhydride phthalic anhydride

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. The concentrations of maleic anhydride, phthalic anhydride in air were adjusted to the required values.
3. The reaction temperature was between 200-550°C. The effluent gas was analyzed by using the FID and TCD gas chromatograph. The chromatograph data were changed into mole of maleic anhydride, phthalic anhydride and CO₂ by calibration curves in Appendix D.

The operating conditions selected have been checked to confirm that there is no external and internal mass transfer resistance. The calculation is shown in Appendix B.



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