

CHAPTER IV

EXPERIMENT

The experimental systems and the experimental procedure used in this work are divided into three parts: (i) The catalyst preparation; (ii) The catalyst characterization; (iii) The catalytic test by oxidation of phthalic anhydride, maleic anhydride. The details of the experiments are described as following:

The reaction conditions are chosen as follows:

catalyst	: V-Mg-O/TiO ₂
	: 6-16 wt%V*
	: 2-8 wt%Mg
Reactant	: benzene
	: toluene
	: ethyl benzene
	: phthalic anhydride
	: maleic anhydride
	: air (used as O ₂ source)
Flow rate of reactant	: 100 ml/min
Reaction temperature	: 200-550 °C
Gas hourly space velocity	: 60,000 ml/hr.g of catalyst

*The wt% of V calculated as V₂O₅

The wt% of Mg calculated as Mg

4.1 Preparation of catalyst

4.1.1 Materials

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

Table 4.1 The chemical used in this research

Chemical	Grade	Supplier
Titanium oxide [TiO ₂]	JRC-TIO1	Dept. of Material Science, Shimane University
Ammonium metavanadate [NH ₄ VO ₃]	Analytical	Carlo Erba, Italy
Magnesium nitrate [Mg(NO ₃) ₂]	Analytical	Fluka, Switzerland

4.1.2 Preparation of V-Mg-O/TiO₂ Catalyst

V-Mg-O/TiO₂ catalyst was prepared by wet impregnation method. First step of preparation, TiO₂ powder was added to an aqueous solution of ammonium metavanadate (NH₄VO₃) at 70°C. The suspension was dried at 80°C and calcined in air at 550°C for 6 hours. The sample obtained was V₂O₅/TiO₂. Then Mg was introduced into the obtained V₂O₅/TiO₂ by impregnation from magnesium nitrate [Mg(NO₃)₂] solution. The suspension was dried and calcined in the same above condition. The catalyst was denoted as xVyMgTi where x was wt% of V calculated as V₂O₅ and y is wt% of Mg. For example, 10V2MgTi, the vanadium oxide and magnesium content were 10 (as V₂O₅) and 2wt% (as Mg), respectively. Further details of the preparation method are shown in Appendix A.

4.2 Catalyst characterization

4.2.1 Determination of composition content of catalyst

The actual composition contents of the catalyst were determined by atomic absorption spectroscopy (AAS) at the center service of science.

4.2.2 Surface Area Measurement

The BET surface area of the sample was determined by nitrogen absorption in an automatic apparatus ASAP 2000 constructed by Micromeritics U.S.A. The data obtained were recorded by a microcomputer.

4.2.3 X-ray Diffraction Experiments

The crystal structure of the catalyst was identified by X-ray diffraction (XRD) analysis carried out on a Siemens D500 diffractometer with $\text{CuK}\alpha$ radiation in the 2θ range of $10\text{-}80^\circ$.

4.2.4 Fourier Transform Infrared Spectroscopy

The sample was mixed with KBr with ratio of sample:KBr equal to 1:100. Then the mixture was ground into a fine powder and pressed into a thin wafer. Infrared spectra were recorded between 2000 and 400 cm^{-1} with FT-IR spectroscopy, Nicolet Impact 400, Nicolet Instrument Corporation, U.S.A. The spectra were used to study the functional group of surface vanadium oxide species of V-Mg-O/TiO₂ catalyst.

4.3 Catalytic Reaction

4.3.1 Apparatus

The maleic anhydride and the phthalic anhydride system consists of a reactor, a saturator, an automatic temperature controller, an electrical furnace and a gas controlling system. Maleic anhydride and phthalic anhydride reactant is solid phase so they must be vaporised before passing to the microreactor. Maleic anhydride was heated at 100°C. Phthalic anhydride was heated at 150°C. The inlet and outlet lines were heated by heating tape. Flow diagram of the oxidation reaction system is shown in figure 4.1.

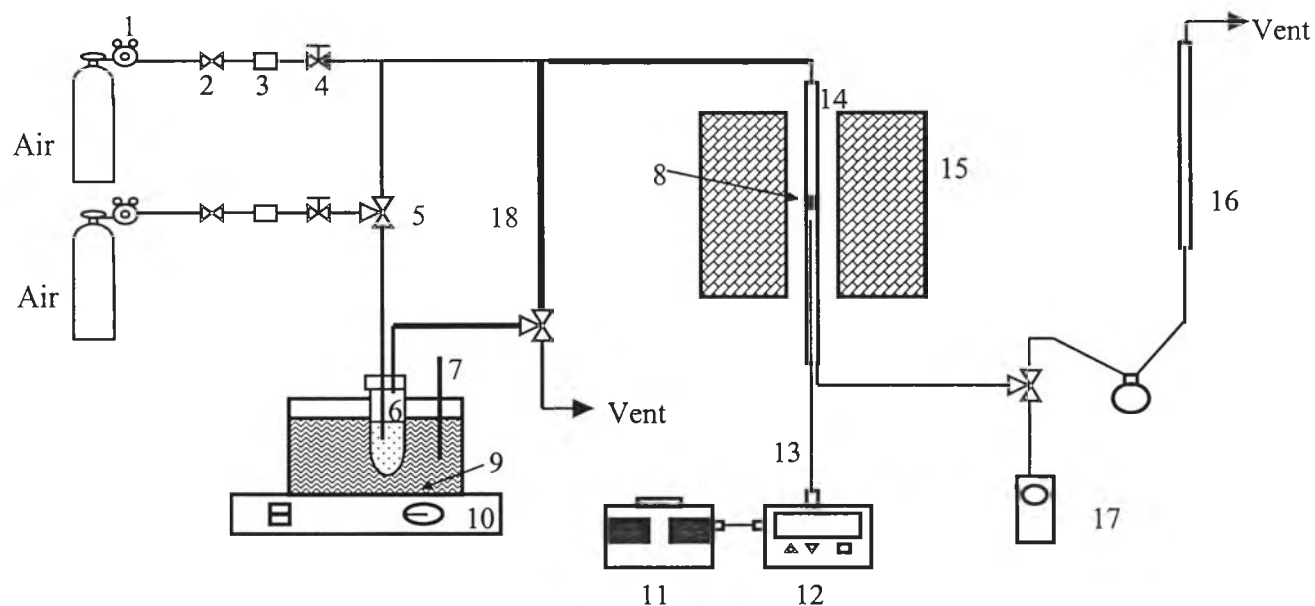
The microreactor is made from a stainless steel tube (O.D. 3/8"). Two sampling points are provided above and below the catalyst bed. The catalyst is placed between two quartz wool layers.

An automatic temperature controller consists of a magnetic contactor model Telex 87114. 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 maximum voltage of 220 volt.

The gas supplying system consists of two cylinders of air, equipped with a pressure regulator (0-120 psig), an on-off valve and a fine-metering valve used for adjusting the flow rate of air that one passes through the saturator, another directly flows to the microreactor.

The composition of oxygenated compound 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



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

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

sieve to separate oxygen and Co and a Porapak-Q column to separate CO₂ and water were operated in parallel. The operating conditions of GC are listed in the Table 4.2.

Table 4.2 Operating condition for gas chromatograph

Gas chromatograph	Shimadzu GC8A	Shimadzu GC9A
Detector	TCD	FID
Column	MS-5A, Porapak-Q	
Carrier gas	He (99.999%)	N ₂ (99.999%)
Carrier gas flow	25 ml/min	25 ml/min
Column temperature		
- Initial	100	100 (maleic anhydride) 150 (phthalic anhydride)
- Final	100	100 (maleic anhydride) 150 (phthalic anhydride)
Detector temperature	130	250
Injector temperature	130	250
Analyzed gas	CO, CO ₂ , H ₂ O	Oxygenates

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 maleic anhydride and phthalic anhydride, air was adjusted to the required values.
3. The reaction temperature was between 200-550°C. The effluent gases were 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 show in Appendix C.

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

$$\%A \text{ conversion} = \frac{\text{mole of A converted}}{\text{mole of A in feed}} \times 100$$

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

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

where A is reactant

B is product

C is carbon atom of hydrocarbon