CHAPTER IV

EXPERIMENT

The experiments, which used in this research, are categorized into three parts: i) the preparation of V-Mg-O catalyst, ii) the characterization methods, iii) the catalyst test by oxidative dehydrogenation of propane to propene. The details of the experiments are described below.

The scope of this study

The reaction conditions for the oxidative dehydrogenation are chosen as follows:

Catalysts	: 28* V-Mg-O (reference catalyst)
	(0-3 wt%) Li / 28 V-Mg-O
	(0-3 wt%) Na / 28 V-Mg-O
	(0-3 wt%) K / 28 V-Mg-O
Reactant gas	: 20% C_3H_8 in N_2
	air (used as O_2 source)
	99.99% argon
O_2: HC ratio	: 2 : 1
Flow rate of reactant	: 100 ml/ min
Reaction temperature	: 300-600 °C
Gas hourly space velocity	: 60000 ml hr^{-1} g^{-1}

* The wt.% of V are calculated as V_2O_5

4.1 Preparation of catalysts

4.1.1 Chemicals

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

Table 4.1 The chemicals used in this research.

Chemical	Grade	Manufacturer
Magnesium oxide [MgO]	analytical	Carlo Ebra, Italy
Ammonium metavanadate [NH_4VO_3]	analytical	Carlo Ebra, Italy
Lithium nitrate [$LiNO_3$]	analytical	J.T. Baker Inc., U.S.A.
Sodium nitrate [$NaNO_3$]	analytical	Carlo Ebra, Italy
Potassium nitrate [KNO_3]	analytical	Eagle Manufacturing, U.S.A.
30 wt.% of ammonium hydroxide solution [NH_4OH]	analytical	Carlo Ebra, Italy

4.1.2 Preparation of 28 V-Mg-O catalyst and 28 V-Mg-O mixed alkali metal catalyst

28 V-Mg-O catalyst (28% V as V_2O_5) was prepared by the conventional wet impregnation method which has been previously described [Chaar et al. 1987)]. Briefly, an appropriate amount of MgO powder was added to an aqueous solution containing 0.5 wt.% ammonium metavanadate and 1 wt.% ammonium hydroxide at 70 °C. With stirring, the suspension was evaporated to dryness. The resulting solid was calcined in air at 550 °C for 6 hours. Finally, yellow fine powder is obtained as 28 V-Mg-O catalyst.

28 V-Mg-O mixed alkali metal catalyst was prepared by the same method as of 28 V-Mg-O catalyst except for adding the appropriate amount of $LiNO_3$, $NaNO_3$, or KNO_3 into the vanadate solution with MgO powder at the same time.

4.2 The characterization of catalyst

4.2.1 Determination of composition content of catalyst

Each catalyst prepared in this study was dissolved in 1 ml. of conc. nitric acid (HNO_3). The dissolved catalyst was diluted by water into 100 ml.. After that the actual composition content of the catalyst solution was determined by atomic absorption spectroscopy (AAS) at the Scientific and Technological Research Equipment Center, Chulalongkorn university. The calculation of the sample preparation is shown in Appendix A.

4.2.2 Surface area measurement

The BET surface area was determined by nitrogen adsorption in an automatic apparatus ASAP 2000 constructed by Microceritics, U.S.A. The data obtained were recorded by a microcomputer.

4.2.3 X-ray Diffraction (XRD)

The sample is placed into XRD plate before placing on the measured position of XRD, using SIEMENS D5000 diffractrometer. Experiment was performed by using CuKα radiation in the 2θ range of 4-80°. The XRD spectrum will identify the crystal structure of sample.

4.2.4 Fourier Transform Infrared Spectrometer (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 2000 and 400 cm^{-1} on a microcomputer.

4.2.5 Thermogravimetric analysis (TGA)

The decomposition pattern of the catalyst during heating up was analyzed by Shimadzu TGA model 50. The catalyst was loaded in a platinum pan located in a

furnace. The purging gas was N_2 with flow rate 30 ml./ min. The furnace temperature was programmed to raise from room temperature to 600°C at a constant rate of 10°C/ min. The data were displayed and recorded using a microcomputer.

4.2.6 Temperature programmed decomposition (TPD)

The experiment was performed by packing catalyst sample in a quartz tube.The quartz tube was then placed inside a furnace. Catalytic activity was tested between 300 - 600°C. 99.99% He gas was used as purging gas. The effluent gas was analyzed using a gas chromatograph Shimadzu GC-8AIT equipped with a 1 ml. gas sampling loop, a TCD detector and a Porapak QS column. The operating condition of GC was shown as follows.

GC model	: GC-8AIT (Shimadzu)
Detector	: TCD
Packed column	: Porapak QS
Column temperature	: 90°C
Detector / injector temperature	: 110°C
Detector current	: 90 mA.
He flow rate	: 60 ml./min.

The peak area was used to evaluated the amount of evolving species during the decomposition of the catalysts.

4.2.7 CO_2 adsorption

The basicity measurement of the catalysts was assessed by using the CO_2 adsorption. In each experiment, 0.2 g. of catalyst sample was placed in a stainless steel tube. The pretreatment gas, Ar or air, was introduced into the reactor at a flowrate of 30 ml./min. The reactor was then heated from room temperature to 500°C with a constant heating rate of 10°C/min. After holding at 500°C for 1 hour, the

reactor was cooled down to room temperature with 30 ml./min. of He gas. At room temperature, 100 μl. of CO_2 gas was injected, using a micro syringe, above the catalyst bed. The injection was repeated until the sample did not adsorb CO_2 anymore. The amount of CO_2 adsorbed on the catalyst during each injection was measured by thermal conductivity detector (GOWMAC). The operating conditions listed below.:

GC model	: GOWMAC
Detector	: TCD
Detector temperature	: 80°C
Detector current	: 80 mA.
He flow rate	: 30 ml./min.

4.3 Propane oxidative dehydrogenation

4.3.1 Equipment

The propane oxidative dehydrogenation system, as shown in figure 4.1, consists of a reactor, an automatic temperature controller, an electrical furnace, and a gas controlling system.

The microreactor is made from a quartz tube. Two sampling points are provided above and below the catalyst bed. Catalyst was placed between two quartz wool layers. The reactor is operable in the temperature range of room temperature to 1000°C.

The controller consists of a magnetic contactor, a variable voltage transformer, RKC series RE-96 temperature controller and Eurotherm digital temperature indicator model Telex 87114. It was operated in conjunction with a type K thermocouple installed in a thermowell. Temperature was measured at the bottom

of the catalyst bed in the reactor. The temperature control setpoint is adjustable within the range of 0-800°C .

Electrical furnace supplies heat to the reactor for propane oxidative dehydrogenation. The reactor, therefore, 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 20% propane in nitrogen, high purity argon and air, each equipped with pressure regulators (0-120 psig), on-off valves and fine-metering valves used for adjusting the flow rates of these gases.

The compositions of hydrocarbons in the feed and product stream were analyzed by flame ionization detector gas chomatograph Shimadzu 14 B. The operating conditions are described below.

GC model	: Shimadzu 14B
Detector	: FID
Packed column	: VZ-10
Nitrogen flow rate	: 60 ml./min.
Column temperature	: 55°C
Injection temperature	: 100°C
Detector temperature	: 150°C

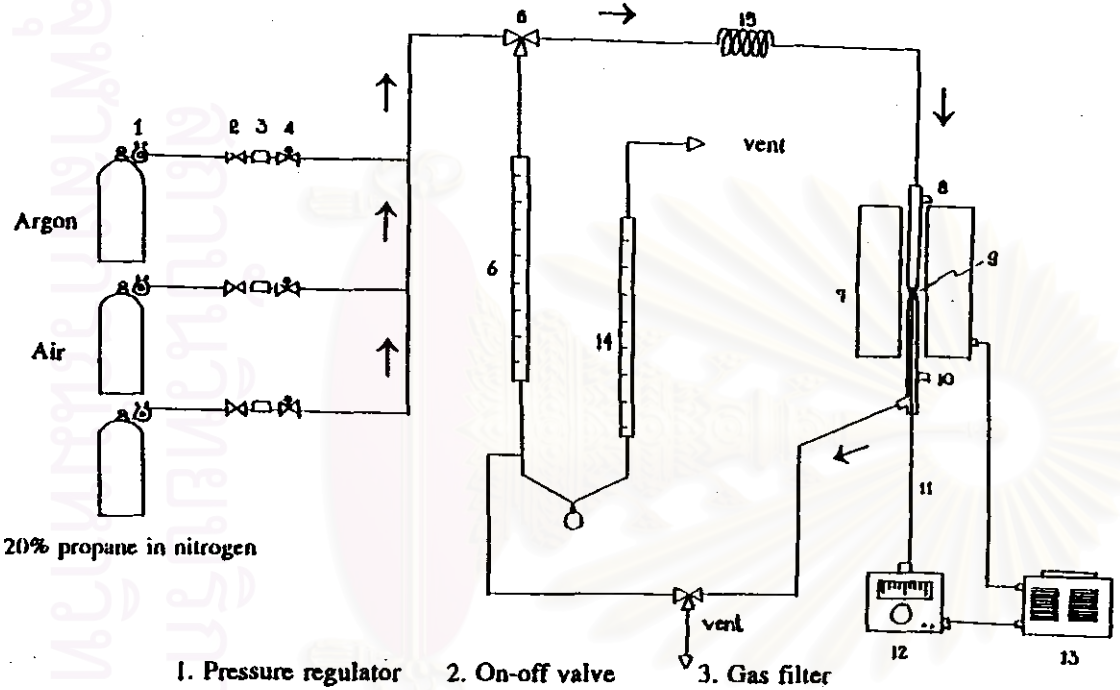

Figure 4.1 Flow diagram of the propane oxidative dehydrogenation system

4.3.2 Oxidative dehydrogenation procedure

The experimental procedures are as follows :

1) 0.1 g. of catalyst was packed in the quartz tube located in an electrical furnace.

2) Flow rates of propane, argon and air were adjusted to the required values. The gas mixture was 4 vol.% propane, 8 vol.% oxygen and balance Ar. The total flowrate was 100 ml. /min.

3) For catalyst pretreatment, the reactor was heated up with heating rate of 10 °C/ min. to 500°C and remained at this temperature for 1 hr. Purging gas used for pretreatment of catalyst was either Ar or air.

4) The reactor was then cooled down to the reaction temperature. The reaction temperature was between 300-600°C. The feed gas was introduced into the reactor. Effluent gas was analyzed using FID gas chromatograph. The chromatogram data were changed into mole of propane or propene by calibration curve in Appendix B

5) The result of catalytic test was calculated in the term of:

$$\% \text{ propane conversion} = \frac{\text{mole } C_3H_8 \text{ reacted}}{\text{mole } C_3H_8 \text{ in feed}} \times 100$$

$$\% \text{ propene selectivity} = \frac{\text{mole } C_3H_6 \text{ formed}}{\text{mole } C_3H_8 \text{ reacted}} \times 100$$