

CHAPTER IV

EXPERIMENT

The experimental system and the experimental procedures used in this work are described in this chapter. They are divided into three parts: the catalyst preparation, the catalyst characterization and the catalyst testing by propane ODH reaction. In each part, details of procedure, including the materials and apparatus are described as the following.

The Scope of This Study

The reaction conditions for the ODH are chosen as follows:

Catalysts : MgO
V₂O₅
(0-28)V-Mg-O
(0-3wt%)Na/28V-Mg-O
(0-3wt%)K/28V-Mg-O

Reactant Gas : 20% C₃H₈ in N₂
air

99.99% argon

O₂:HC ratio : 1:1, 2:1

flow rate of reactant : 100 ml/min

Reaction Temperature : 300-600°C

gas hourly space velocity : 60000 ml hr⁻¹ g⁻¹

4.1. Preparation of Catalysts

4.1.1 Materials

The chemicals used in this experiment are the following:

- (1) Magnesium Oxide [MgO], manufactured by Carlo Ebra, Italy.
- (2) Vanadium Oxide [V₂O₅], Analar Grade, manufactured by Fluka Chemie AG, Switzerland.
- (3) Ammonium Metavanadate [NH₄VO₃], Analar Grade, manufactured by Carlo Ebra, Italy.
- (4) Sodium Nitrate [NaNO₃], manufactured by E. Merck, Germany.
- (5) Potassium Nitrate [KNO₃], Analar Grade, manufactured by the Eagle Manufacturing, U.S.A.

4.1.2 Apparatus

a) Impregnation Unit

This unit consists of a flask, a magnetic stirrer and heater, and a thermometer. They were used for preparing aqueous solution and impregnating the solution onto the support.

b) Calcination Unit

This unit, which consists of an electrical furnace, an automatic temperature controller, and a variable voltage transformer, was used for calcining the impregnated catalysts at high temperature.

4.1.3 Preparation of V-Mg-O Catalyst

a) Preparation of mixed oxide catalysts of V-Mg-O

An appropriate amount of MgO powder was added to an aqueous solution containing 0.5 wt% ammonium metavanadate (NH_4VO_3) and 1 wt% ammonium hydroxide (NH_4OH) at 70°C . With stirring, the suspension was evaporated to dryness. The resulting solid was calcined in air at 550°C for 6 hours (standard condition). This solid was slightly crushed to break up the crumbs and used as catalyst.

In this work, the effect of calcination temperature and period of time for calcination has also been investigated. The calcination temperature and time were varied between $400\text{--}550^\circ\text{C}$, and 4-6 hours in this work.

b) Preparation of modified V-Mg-O catalysts

28V-Mg-O mixed alkali metal catalyst was prepared by the same method of V-Mg-O catalyst except for adding the appropriate amount of NaNO_3 or KNO_3 into the aqueous solution of NH_4VO_3 and NH_4OH with MgO powder at the same time.

4.2. Catalyst Characterization

4.2.1 Determination of Metal Content

Percentage of each metal loaded onto the catalysts and the actual composition of V-Mg-O catalysts which were prepared in this work was determined by atomic absorption spectroscopy. The prepared catalyst was dissolved in 0.1 M nitric acid (HNO_3) before sending to be analyzed by the Scientific and Technological Research Equipment Center, Chulalongkorn University. Sample calculation was shown in Appendix A.

4.2.2 Surface Area Measurement

The BET surface areas of samples were determined by nitrogen adsorption in an automatic apparatus ASAP 2000 constructed by Micromeritics, U.S.A.

4.2.3 X-ray Diffraction Experiments

In this study, all samples were sent to analyze their lattice structures using X-ray diffraction with Cu K α radiation which were performed by Department of Geology, Faculty of Science, Chulalongkorn University.

4.2.4 Infrared Spectroscopy

The sample was mixed with KBr with ratio of sample:KBr equal to 1:200. Afterwards it was grinded 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 catalysts.

4.2.5 Thermogravimetric Analysis Experiments (TGA Experiment)

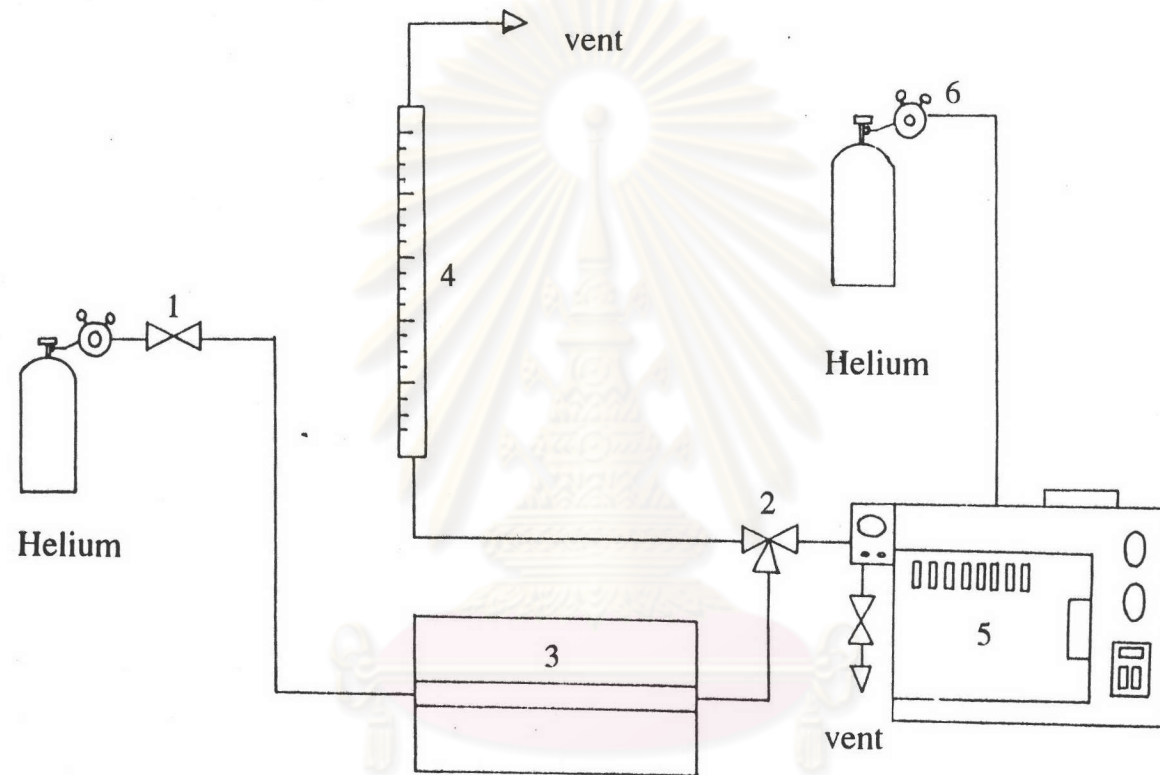
Shimadzu TGA model 50 (Japan) was used in this research. The catalyst was placed into a Pt pan before placing in the furnace. Air or Ar were used as purging gas. The furnace temperature was then raised from room temperature up to 700 $^{\circ}\text{C}$ at a constant rate of 10 $^{\circ}\text{C}/\text{min}$. The data were displayed and recorded using a microcomputer. The data were used to study the decomposition pattern of the catalyst during heating up.

4.2.6 Thermal Analysis

This analysis was carried out to analyse species evolved during the decomposition of the catalysts. The analysis was performed by packing catalyst sample in a quartz tube. Then, placed the quartz tube into a furnace and increased the sample temperature from room temperature to 600 °C at a heating rate of 10 °C/min. The system was purged with 99.99% He. The effluent gas was analysed using a gas chromatograph Shimadzu GC-8AIT (Japan) equipped with a 1 ml gas sampling loop. The operating conditions of the GC and flow diagram of this apparatus are shown in Table 4.1 and Figure 4.1 respectively.

Table 4.1 Operating condition of gas chromatograph (GC-8AIT).

Parameter	Condition
Detector	TCD
Packed column	Porapak QS
Column temperature	90 °C
Detector/injector temperature	110 °C
He flow rate	60ml./min.
Detector current	90 mA.



- 1. On-off valve
- 2. Three-way valve
- 3. Furnace and reactor
- 4. Flow meter
- 5. Gas chromatograph
- 6. Pressure regulator

Figure 4.1 Flow diagram of Thermal Analysis

4.3 Oxidative Dehydrogenation Reaction

4.3.1 Materials

Mixture of 20% propane in nitrogen supplied by Thai Industrial Gases Limited (Thailand), oil free air and the ultra-high purity argon were used as feed stream for the ODH in this study.

4.3.2 Apparatus

Flow diagram of the propane oxidative dehydrogenation system is shown in Figure 4.2. The system consists of a reactor, an automatic temperature controller, an electrical furnace, and a gas controlling system.

a) Reactor

The oxidative dehydrogenation microreactor is made from quartz tube and can be operated from room temperature up to $1,000^{\circ}\text{C}$ under atmospheric pressure. Sampling points are provided above and below the catalyst bed. Catalyst was placed between quartz glass wool layer.

b) Automatic Temperature Controller

Automatic temperature controller consists of a magnetic switch, a variable voltage transformer, a temperature controller (PF-96, RKC), and a thermocouple. Temperature was measured at the bottom of the bed of catalyst in the reactor. The temperature control setpoint is adjustable within the range between $0-800^{\circ}\text{C}$.

c) Electrical Furnace

Electrical furnace supplies heat to the reactor for propane oxidative dehydrogenation. The reactor can be operated from room temperature up to 800°C at maximum voltage of 220 volt.

d) Gas Controlling System

The system consists of:

(1) A cylinder of 20% propane in nitrogen, equipped with a pressure regulator (0-50 psig), an on-off valve and a fine-metering valve used for adjusting the flow rate of propane.

(2) Cylinders of ultra high purity argon, and air, each equipped with a pressure regulators (0-120 psig), on-off valves and fine-metering valves used for adjusting the flow rates of these gases.

e) Gas Chromatograph

Flame ionization detector gas chromatograph was used to analyse the compositions of hydrocarbons in the feed and product streams. The operating conditions are illustrated in Table 4.2.

Table 4.2 Operating conditions of gas chromatograph (GOW-MAC).

Parameter	Condition
Detector	FID
Packed column	VZ-10
Nitrogen flow rate	25 ml./min.
Hydrogen flow rate	30 ml./min.
Air flow rate	250 ml./min.
Column temperature	45 °C
Injection temperature	75 °C
Detector temperature	100 °C

4.3.3 Procedure

(1) 0.1 gram of catalyst was packed in the middle of the quartz microreactor. Then, the reactor was placed in the furnace.

(2) Flow rates of propane, argon and air were adjusted to the required values. The feed was 4 vol% propane, 8 vol% oxygen, and the balance He. The flow rate was 100 ml/min.

(3) The reactor was heated up with an increasing rate of $10^{\circ}\text{C}/\text{min}$. The first gas analysis was performed at 300°C . The reaction temperature was between $300\text{-}600^{\circ}\text{C}$.

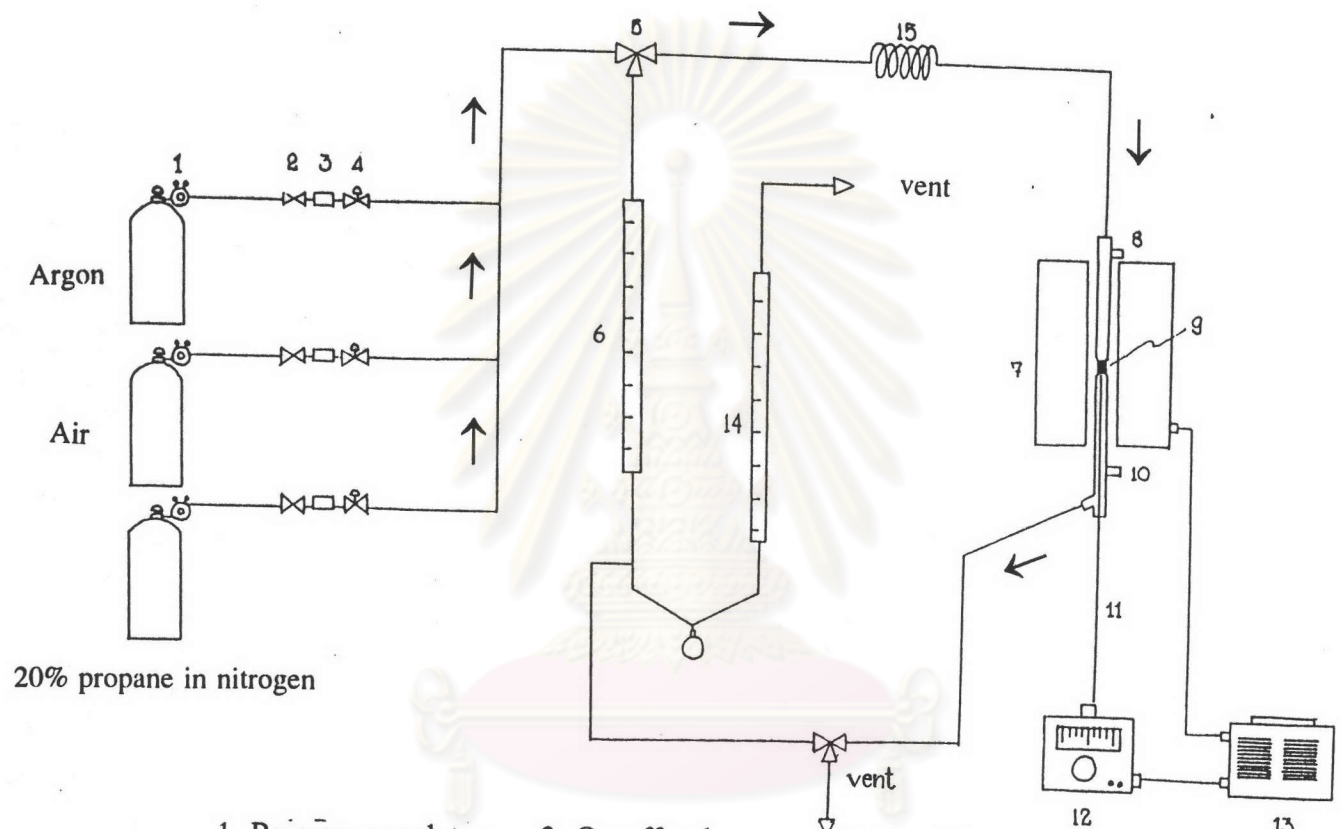
(4) The result of catalytic test was calculated in the term of:

% propane conversion = mole of propane reacted / mole of propane feed

% selectivity to A = mole of A formed / mole of propane reacted

when A is reaction product

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20% propane in nitrogen

- | | | |
|----------------------------------|-----------------------|----------------------------|
| 1. Pressure regulator | 2. On-off valve | 3. Gas filter |
| 4. Needle valve | 5. Three-way valve | 6. Flow meter |
| 7. Furnace | 8. Reactor | 9. Catalyst bed |
| 10. Sampling port | 11. Thermocouple | 12. Temperature controller |
| 13. Variable voltage transformer | 14. Bubble flow meter | 15. Coil mixer |

Figure 4.2 Flow diagram of the propane oxidative dehydrogenation system.