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 propane, 1-propanol, propene and carbon monoxide. The details of the experiments are described as the following:

The Scope of This Study

The reaction conditions are chosen as follow:

Catalyst : 5 wt%V_2O_5/TiO_2
: 5[*]wt%V1wt%Mg/TiO_2
: (3-10)wt%V2wt%Mg/TiO_2
Reactant : propane
: 7% propene in N_2
: 1-propanol
: 5%CO in N_2
: air (used as O_2 source)
Flow rate of reactant : 100 ml/min
Reaction temperature : 300-500°C
Gas hourly space velocity : 60,000 ml/hr.g

[*] The wt% of V calculated as V_2O_5

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 chemicals used in this research

Chemical	Grade	Manufacturer
Titanium oxide [TiO_2]	analytical	BDH Laboratory Supplies
Ammonium metavanadate [NH_4VO_3]	analytical	Carlo Ebra, Italy
Magnesium nitrate [$Mg(NO_3)_2$]	analytical	Fluka, Switzerland

4.1.2 Preparation of Catalyst

- Preparation of 5wt%V_2O_5/TiO_2 catalyst

An appropriate amount of TiO_2 powder was added to an aqueous solution of ammonium metavanadate (NH_4VO_3) at 70°C. The suspension was dried at 80°C and the resulting solid was then calcined in air at 550°C for 6 hours. Finally, yellow fine powder was used as **5VTi** catalyst.

- Preparation of V-Mg-O/TiO_2 catalyst

The first step of the preparation of V-Mg-O/TiO_2 catalyst was the same as the 5 wt%V_2O_5/TiO_2 catalyst. Vanadium was first deposited on TiO_2 support and Mg was then introduced into the calcined V_2O_5/TiO_2 by impregnation from a $Mg(NO_3)_2$ solution, evaporating and calcination in air at 550°C for 6 hours. These catalysts were denoted as xVyMgTi where x was wt% of V calculated as V_2O_5 and y is wt% of Mg. For **5V1MgTi** and **5V2MgTi**, the percentages of Mg were 1 and 2 which gave V/Mg atomic ratio equal to 1/1 and 2/3, respectively. In the case of **3V2MgTi** and

10V2MgTi, the vanadium oxide content was varied to 3 wt% and 10 wt%, respectively and the Mg content of both catalysts was fixed to 2 wt%.

In addition, two catalysts were prepared to investigate the effect of sequence of magnesium loading, the first one was prepared by the same method of 5V1MgTi catalyst but magnesium was first impregnated to pure TiO_2 and then vanadia was deposited on Mg-doped TiO_2 support. The vanadium oxide content (calculated as V_2O_5) and the Mg content were 5 wt% and 1 wt%, respectively. This catalyst was denoted as **1Mg5VTi** catalsyt.

The last one was prepared by co-impregnation of vanadium and magnesium. An appropriate TiO_2 was added to an aqueous solution containing both NH_4VO_3 and $Mg(NO_3)_2$. The suspension was evaporated to dryness and then the resulting solid was calcined in the same above condition. The vanadium and Mg content were the same as 5V1MgTi and 1Mg5VTi. This catalyst is denoted in the text as **co-5V1MgTi** catalyst.

4.2 The catalyst characterization

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 center service of science. The sample calculation is shown in Appendix A.

4.2.2 Surface area measurement

The BET surface area 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 Fourier Transform Infrared Spectrometer (FT-IR)

Each sample was mixed with KBr with ration of sample : KBr equal to 1:100 and then 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 species of catalyst.

4.2.4 X-ray diffraction (XRD)

The crystal structure of sample was characterized by X-ray diffraction using SIEMENS D5000 diffractrometer with CuKα radiation in the 2θ range of 4-80°.

4.3 Catalytic reaction

4.3.1 Apparatus

The propane, propene and CO oxidation system consists of a reactor, an automatic temperature controller, an electrical furnace and a gas controlling system. For liquid reactant, 1-propanol, a saturator and an automatic temperature controller are installed for evaporating 1-propanol into air before entering the reactor. Flow diagram of the oxidation reaction system is shown in figure 4.1.

The microreactor is made from a quartz tube. Sampling points are provided above and below the catalyst bed. Catalyst is placed between quartz glass wool layer.

An automatic controller consists of magnetic contactor, a variable voltage transformer, RKC series RE-96 temperature controller and Eurotherm digital temperature indicator model Telex 87114. 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.

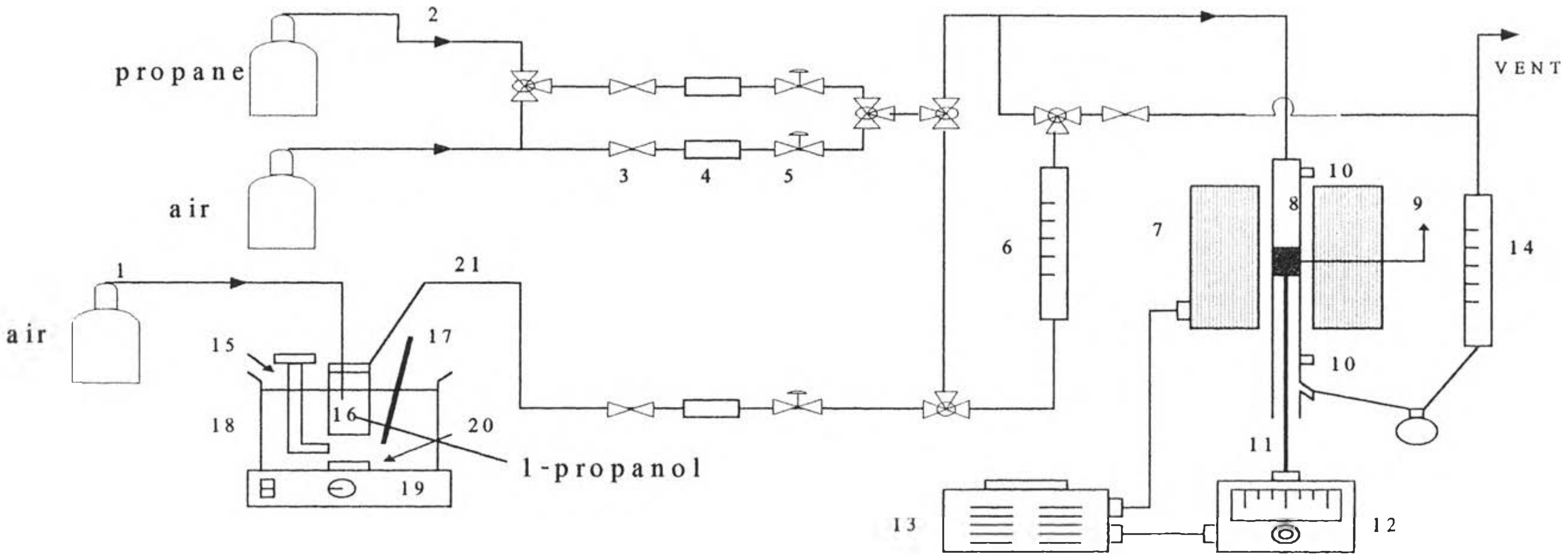
Electrical furnace supplies heat to the reactor for propane, propene, 1-propanol and CO oxidation. The reactor can be operated from room temperature up to 800°C at maximum voltage of 220 volt.

The gas supplying system consists of cylinder of:

1) A cylinder of propane, 7% propene in nitrogen, 5%CO in nitrogen and air, each equipped with a pressure regulator (1-120 psig), on-off valves and fine-metering valves used for adjusting the flow rated of these gases.

2) A cylinder 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 passes through the liquid 1-propanol saturator.

The compositions of hydrocarbons in the feed and product streams were analyzed by flame ionization detector gas chromatograph Shimadzu 14B and 14A. The amount of CO_2 formed in the reaction was measured using a gas chromatograph Shimadzu GC-8A equipped with thermal conductivity detector. The operating conditions of GC are described in appendix C.



1. Pressure regulator
2. Three-way valve
3. On-off valve
4. Gas filter
5. Needle valve
6. Flow meter
7. Furnace
8. Reactor
9. Catalyst bed
10. Sampling point
11. Thermocouple
12. Temperature controller
13. Variable voltage transformer
14. Bubble flow meter
15. Heater
16. Saturator
17. Thermocouple
18. Solvent bath
19. Stirring controller
20. Magnetic bar
21. Heating line

Figure 4.1 Flow diagram of the oxidation reaction system.

4.3.2 Procedure

1. 0.1 g of catalyst was packed in the middle of the quartz tube and then the reactor was placed in the electrical furnace.

2. Flow rates of reactants were adjusted to the required values and fed into the reactor. The feed compositions were:

- 4 vol% propane, 20 vol% O_2 and balance N_2
- 4.2 vol% propene, 8.4 vol% O_2 and balance N_2
- 4 vol% 1- propanol, 20 vol% O_2 and balance N_2
- 4 vol% CO, 4.2 vol% O_2 and balance N_2

3. The reaction temperature was between 300-500°C. The reactor was heated up with heating rate of 10°C/min. Effluent gas was analyzed by gas chromatograph equipped with FID and TCD detectors.

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

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

$$\%\ \text{selectivity to B} = \frac{\text{mole of A converted to B}}{\text{mole of A reacted}} \times 100\%$$

when A is reactant

B is reaction product