CHAPTER IV
EXPERIMENTAL

This chapter is categorized into three parts:

1. The preparation of catalysts
2. The characterization methods
3. The catalytic activity measurements

The details of the experiments are described below.

The scope of this study.

The reaction conditions for the oxidation are chosen as follows :

Catalyst	:	Co-Mg-O (0-12 wt%Co)
Reactant gas	:	100% C_3H_8
		7% C_3H_6 in N_2
		5% CO in N_2
Reactant liquid	:	C_3H_7OH
Organic : oxygen ratio		
Propane : O_2	:	1 : 5
1-Propanol : O_2	:	1 : 5
Propene : O_2	:	1 : 2
CO : O_2	:	1 : 1
Flow rate of reactant	:	100 ml/min
Reaction temperature	:	100-500°C
Gas hourly space velocity	:	60 000 ml/ hr.g

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 research.

Chemical	Grade	Manufactuer
Cobaltous acetate tetrahydrate ($Co(CH_3COO)_2.4H_2O$)	Analytical	Fluka, Switzerlan
Magnesium oxide (MgO)	Analytical	Carlo Ebra, Italy

4.1.2 Catalyst preparation

Co-Mg-O catalysts (0-12 wt%Co) were prepared by the conventional wet impregnation method. Calculating the amount Co to yield the required metal loading, then adding de-ionized water to the total volume 50 ml. The aqueous solution was stirred from room temperature to 70°C. An approximate amount of MgO powder was added to the aqueous solution and heated from 70°C to 80°C. With heating and stirring, the suspension was evaporated, then dried in the oven at 110°C in air over night. The resulting solid was calcined in air at 600°C for 6 hours.

Co-Mg-O samples consist of 4 %weight cobalt in Co-Mg-O catalyst (4Co-Mg-O), 8 %weight cobalt in Co-Mg-O catalyst (8Co-Mg-O), and 12 %weight cobalt in Co-Mg-O catalyst (12Co-Mg-O) were used in this research.

4.2 The characterization of catalyst

4.2.1 Determination of composition content of catalyst

Percentage of metal cobalt loading was measured by atomic absorption spectroscopy (AAS). The calculation of the sample preparation is shown in Appendix A.

4.2.2 Surface area measurement

The specific surface areas were determined by using the BET adsorption isothermal of nitrogen at −196°C using an automatic apparatus ASAP 2000 constructed by Microceritics, U.S.A.

4.2.3 X-ray Diffraction (XRD)

The phase structures were determined by X-ray diffraction, Siemens D 5000 X-ray diffractometer using CuKα filtered radiation in the 2θ range of 4-80°. 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 Nocolet 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 400 and 2000 cm^{-1} on a microcomputer.

4.2.5 Temperature-programmed reduction (TPR)

TPR profiles were measured by the continuous flow technique with a thermal conductivity detector. A gas mixture of 5 vol.% hydrogen in argon (flow rate 50 ml/min) was passed over the oxidic sample (0.2 grams catalyst) in a stainless steel reactor tube. The temperature was increased from room temperature to 700°C with linear temperature program (10°C/min). Any reaction products generated during TPR can be trapped by a dry ice trap located between the reactor and the thermal conductivity detector (TCD).

4.2.6 Electron Spin Resonance (ESR) Spectroscopy

Electron spin resonance of the catalyst was measured by Electron Spin Resonance Spectrometer model JES-RE2X, Joel, Japan at Scientific And Technological Research Equipment Center, Chulalongkorn University.

4.3 The catalytic activity measurements

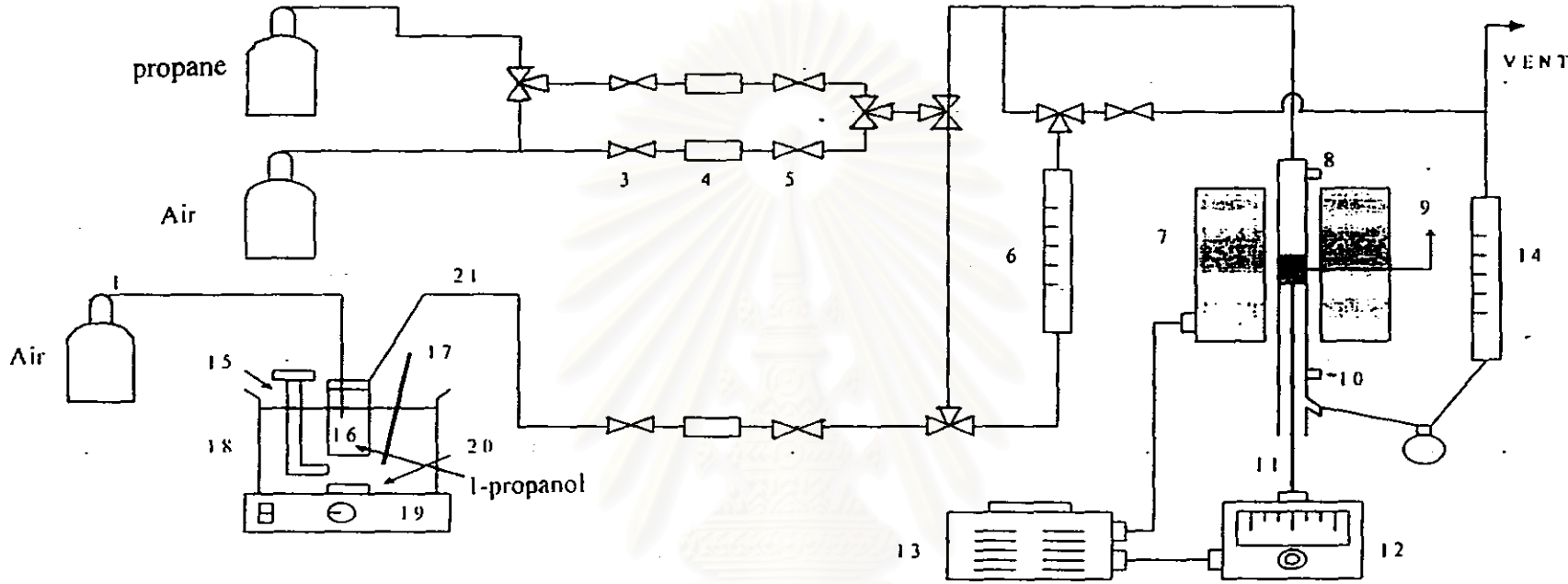
4.3.1 Equipment

Flow diagram of the propane, propene, 1-propanol and CO oxidation system shown in figure 4.1 consists of a reactor, an automatic temperature controller, an electrical furnace, and a gas controlling system. 1-Propanol reactant is liquid phase so it is passed through a saturator in order to evaporate 1-propanol into gas phase before passing to the microreactor.

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 set point is adjustable within the range of 0-800°C.

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



1. Pressure regulator
2. Three-way valve
3. On-off valve
4. Gas filter
5. Needle valve
6. Flow meter
7. Funace
8. Reactor
9. Catalyst bed
10. Sampling
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 propane, 1-propanol, propene, and CO oxidation system.

The gas supplying system consists of cylinders of pure propane , 7% propene in nitrogen, 5% CO in nitrogen, and air, each equipped with pressure regulators (0-120 psig), on-off valves and fine-meter valves used for adjusting the flow rate of these gases.

The composition of hydrocarbons in the feed and product streams was analyzed by flame ionization detector gas chromatograph Shimadzu GC14B.

The composition of oxygenate compounds in the feed and product stream were analyzed by flame ionization detector gas chromatograph Shimadzu GC14A

The composition of carbon monoxide was analyzed by a molecular sieve 5A column and carbon dioxide and water were analyzed by a Porapak-Q column which were connected with gas chromatograph Shimadzu 8ATP. The operating conditions are listed in the Table 4.2.

Table 4.2 Operating condition for gas chromatograph

Gas chromatograph	ShimadzuGC-8A	ShimadzuGC 14A	ShimadzuGC 14B
Detector	TCD	FID	FID
Column	MS-5A, Porapak-Q	Capillary	VZ10
Carrier gas	He (99.99%)	N_2(99.99%)	N_2(99.99%)
Carrier gas flow	25 ml/min	25 ml/min	25 ml/min
Column temperature			
- Initial	80	35	55
- Final	80	140	65
Detector temperature	130	150	150
Injector temperature	130	100	150
Analyzed gas	CO, CO_2, H_2O	1-Propanol, formaldehyde, propanal	Hydrocarbon, C_1-C_4

4.3.2 Oxidation procedure

The oxidation procedures are described in detail below.

1. 0.1 gram of catalyst was packed in the middle of the quartz microreactor located in an electrical furnace.

2. The total flow rate was 100 ml./min. Flow rate of propane, propene, propanol, CO, and air were adjusted to the required values.

- The gas mixtures for propane oxidation were 4 vol.% propane, 20 vol.% oxygen and balance with nitrogen.
- The gas mixtures for 1-propanol oxidation were 4 vol.% 1-propanol, 20 vol.% oxygen and balance with nitrogen.
- The gas mixtures for propene oxidation were 4 vol.% propene, 8 vol.% oxygen and balance with nitrogen.

- The gas mixtures for CO oxidation were 4 vol.% CO, 4 vol.% oxygen and balance with nitrogen.

3. The reaction temperature was between 100-500°C. The effluent gas was analyzed using the FID and TCD gas chromatograph. The chromatograph data were changed into mole of propane, propene, 1-propaol, methane, ethylene, propanal, formaldehyde, CO, and CO_2 by calibration curves shown in Appendix C.