CHAPTER IV

EXPERIMENTAL

The experiment system and produces used in this work are described in this chapter; they are divided into tree part: the catalyst preparation, the catalyst test by oxidative dehydrogenation reaction and the catalyst characterization. The details of the experimental are descried below

The scope of this study

The reaction conditions for oxidative dehydrogenation are as follows:

Catalyst : $ZnGa_2O_4$ (molar ratio of 0.25 0.33, 0.5 and 1.0)
$ZnAl_2O_4$ (molar ratio of 0.33, 0.5 and 1.0)
Reactance gas : 20 % propane in helium
Air (oxygen source)
Helium (99.99 %)
Reaction temperature : 400-600 ºC
Operation pressure : 1 atm
Flow rate of reactance : 100 ml/min
$C3:O_2$: He ratio : 4:8:88
Gas hourly space velocity : 60,000 ml h^{-1} g^{-1}

4.1 Catalyst preparation

4.1.1 Chemical

1. Zinc acetate [$(CH_3COO)_2Zn$] available from Aldrich, 99.9%.
2. Gallium acetylacetonate [$Ga(acac)_3$, $(CH_3COCH{=}C(O\text{-})CH)_3Ga$] available from Aldrich, 99.99%.

3. Aluminium Isoproproxide [API, $((CH_3)_2CHO)_3Al$] available form Aldrich, 98%+.
4. 1,4-Butanediol [$HO(CH_2)_4OH$] available from Aldrich, 99%.

Table 4.1 Reagent used for the synthesis of zinc gallate

Reagent	Weight/Volume
Gallium acetylacetonate	5.00 g
Zinc acetate (calculation of catalyst preparation, Appendix A)	
For Zn/Ga = 0.25	0.6806 g
Zn/Ga = 0.33	0.8330 g
Zn/Ga = 0.5	1.2496 g
Zn/Ga = 1.0	2.4991 g
Organic solvent (1,4-butanediol, 1-butanol toluene)	
In the synthesis mixtures	100 cm^3
In the gab	30 cm^3

Table 4.2 Reagent used for the synthesis of zinc aluminate

Reagent	Weight/Volume
Aluminium isopropoxide (API)	5.00 g
Zinc acetate (calculation of catalyst preparation, Appendix A)	
For Zn/Al = 0.33	1.4670 g
Zn/al = 0.5	2.2404 g
Zn/Al = 1.0	4.4012 g
Organic solvent (1,4-butanediol, 1-butanol toluene)	
In the synthesis mixtures	100 cm^3
In the gab	30 cm^3

4.1.2 Instrument and apparatus

The schematic diagram of the reaction apparatus for the synthesis of zinc gallate and zinc aluminate is show in figure 4.1.

Autoclave reactor: the auto clave reactor is made from stainless steel with 1000 cm^3 volume and 10 cm in side diameter. This consists of a pressure gauge within the range of 0 to 140 bar and relief valve, which use to con troll pressure in autoclave. This autoclave can be operated at high temperature and pressure. The reaction was carried out under autogeneous pressure, which gradually as the temperature was raised.

Automatic temperature controller: the consists of a magnetic switch connect to a variable voltage transformer and RCK temperature controller connected to a thermocouple with 0.5 mm diameter attached to the synthesis mixtures in autoclave. A dial setting establishes a set point at any temperature with in the rang 0 to 400 ºC.

Electric furnace (heater): this supplied the required heat to the autoclave for the reaction. Autoclave can be operated from room temperature up to 300 ºC at voltage of 200 volts.

Gas controlling system: nitrogen are equipped with a pressure regulator (0-150 bar), and needle valves were used to release gas from autoclave.

4.1.3 Procedure

This synthesis of zinc gallium ($ZnGa_2O_4$) and zinc aluminate($ZnAl_2O_3$) by using organic solvent (solvothermal method)

The synthesis zinc gallate and gallium acetylacetonate. For zinc gallate, gallium acetylacetoate 5.0 g and appropriate amount of zinc acetate (Zn/Ga molar ratio of 0.33, 0.5 and 1.0) were dissolved in the100 cm^3 of organic solvent in test tube, which was them set in an autoclave. In gab between the test tube wall, 30 cm^3 of organic solvent was add (Figure 4.1).

In autoclave was purged with nitrogen, heated to a desired temperature (300 ºC) at rate 2.5 ºC/min and held at this temperature for 2 hour. Autogeneous pressures during the reaction gradually increased as temperature was rised and depend on the kind of organic solvent. After autoclave was cooled, the resulting products were washed with methanol. Centrifugation and dried in air. The calcinations of the thus-obtained product carried out in a box furnace [carblite]. The product was heat at rate 10 ºC/min to temperature 400 ºC and held at that temperature for 1 hour.

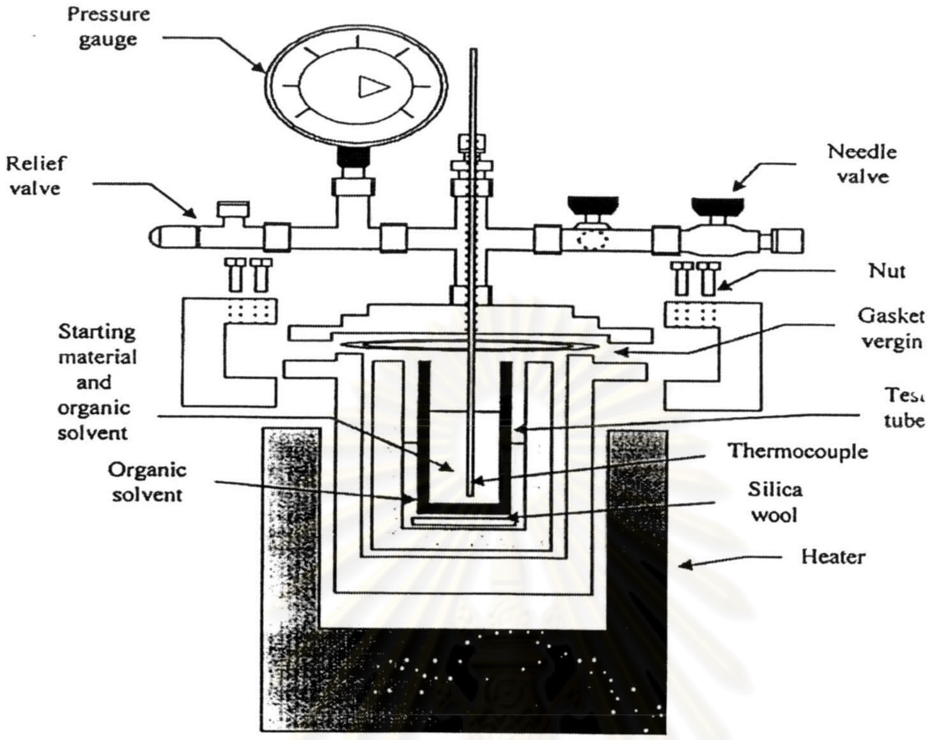


Figure 4.1 Autoclave reactor

4.2 Oxidative dehydrogenation reaction

4.2.1 Material

The mixed of 20% propane in helium, oil free air and helium was used as feed stream for oxidative dehydrogenation reaction of this study.

4.2.2 Apparatus

Flow diagram of propane oxidative dehydrogenation system is show in figure 4.1. The system consists of a reactor, an automatic temperature controller, an electric furnace, and gas controlling system.

Reactor: The micro reactor is made from a quartz tube and can be operated from room temperature up to 1000 °C under atmospheric pressure. The samplings are provided below the catalyst bed. Catalyst was placed in quartz tube between quartz wood layers.

Automatic temperature controller: Automatic controller consists of a solid state relay, a variable voltage transformer, a temperature controller (Chino LT230, SSR) and a thermocouple. The temperature was measured at the bottom of the bed of catalyst in the reactor. The temperature control set point is adjustable with in the range of 0-800 ºC.

Electric furnace: Electric furnace supplies heat to the reactor for oxidative dehydrogenation. The reactor can be operating from room temperature up to 800 ºC at maximum voltage of 220 volts.

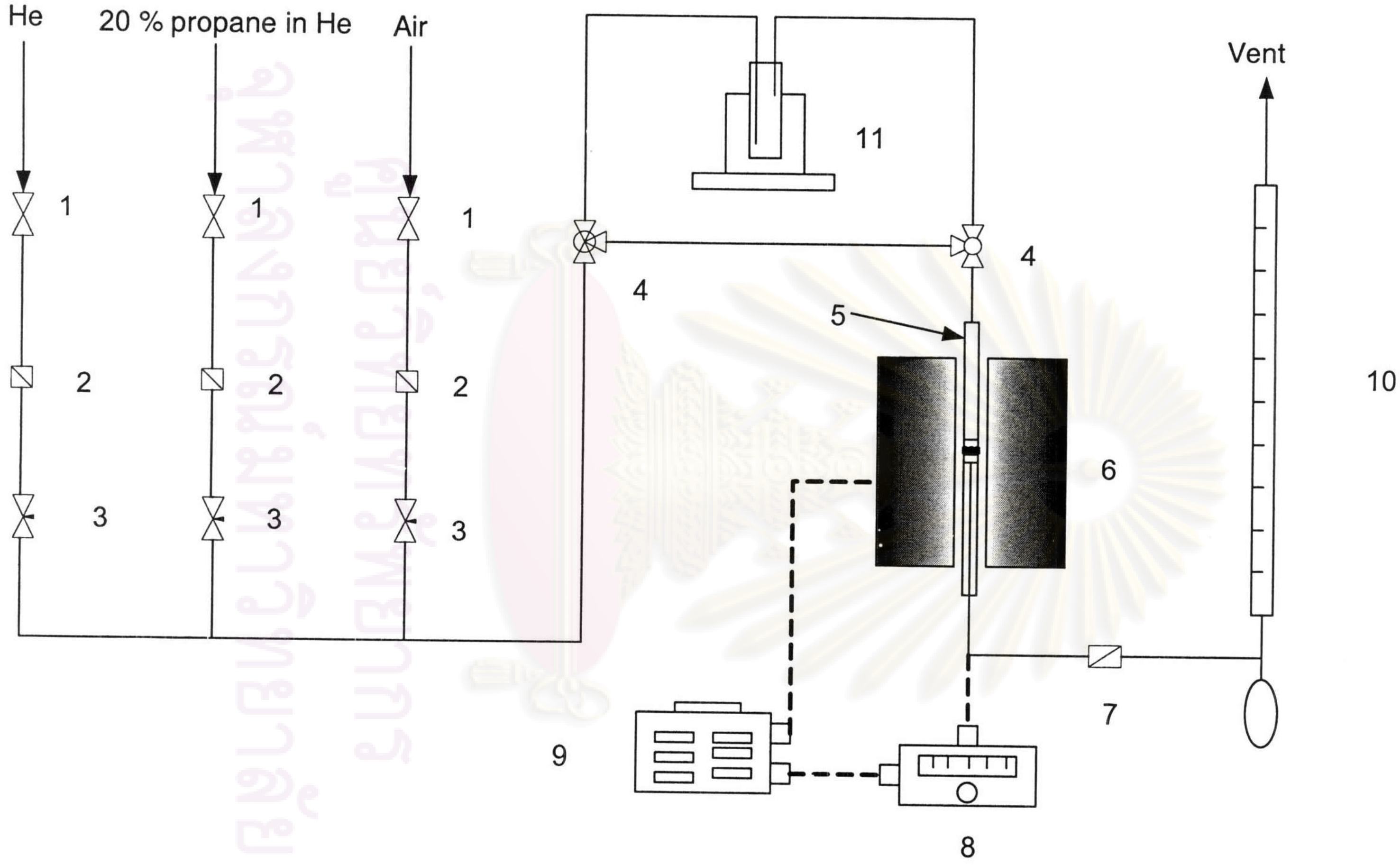
Gas controlling system: The gas controlling system consists of a cylinder of 20 % propane in helium, high purity helium and air, equipped with regulator (0-50 psi), an on-off valve and fine-metering valve used for adjusting the floe rate of propane.

4.2.3 Gas chromatograph

Flame ionization detector gas chromatograph (Chimadzu 14 B) was used to analyst the hydrocarbon composition in the feed and product stream. The operating conditions are illustrated in table 4.3.

Table 4.3 Operating condition for gas chromatograph.

Parameter	Condition
Detector	FID
Packed column	VZ-10
Nitrogen flow rate	60 ml/min
Injection temperature	110 ºC
Detector temperature	150 ºC
Column temperature	70 ºC



1. On-off Valve
2. Gas filter
3. Needle Valve
4. Three-way Valve
5. Quartz reactor
6. Furnace
7. Sampling port
8. Temperature Controller
9. Variable Voltage Transformer
10. Bubble Flow Meter

Figure 4.1 Flow diagram of measurement of propane oxidative dehydrogenation.

4.2.4 Oxidative dehydrogenation procedure

The experimental procedures are as follows:

1) 0.1 g of catalyst was packed in the middle of the quartz tube (micro reactor). Then the reactor was placed in the electric furnace.

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

3) For the catalyst pretreatment, the reactor was heated up with heating rate of 10 ºC/min to desired temperature and remained at this temperature for 1 hour. Purging gas used for pretreatment of catalyst was helium.

4) The reactor was heat up with an increasing rate of 10 ºC. The first gas analysis was performed at 400 ºC. The reaction temperatures were between 400-600 ºC. The feed gas was introduced into the reactor. Effluent gas was analyst by using FID gas chromatograph. The chromatogram data were change into mole of propane or propylene by calibration cave in appendix E.

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

$$\%\text{propane conversion} = \frac{moleC_3H_8.reacted}{moleC_3H_8in.feed} x100$$

$$\%\text{propylene selectivity} = \frac{moleC_3H_6.fromed}{moleC_3H_8in.reacted} x100$$

4.3 Catalyst characterization

4.3.1 X-ray diffraction pattern

X-ray diffraction (XRD) patterns of the catalysts were performed with SIMENS XRD D5000, accurtely measured by using Ni-filtered Cu K radiation in the 2 rang of 10-80 2θ angular region for zinc gallate and 20-80 2θ angular region for zinc aluminate, at Petrochemical Engineering Research Laboratory, Chulalongkorn University.

4.3.2 BET apparatus for the single point method

The reaction apparatus of BET surface area measurement consisted of two feed lines for helium and nitrogen. The flow rate of the gas was adjusted by means of fine-metering valve on the gas chromatograph. The sample cell made from Pyrex glass.

The mixture gases of helium and nitrogen flowed through the system at the nitrogen relative pressure of 0.3. The catalyst sample (ca. 0.3 to 0.5 g) was placed in the sample cell, which was then heated up to 160°C and held at this temperature for 2 h. After the catalyst sample was cooled down to room temperature, nitrogen uptakes were measured as follows.

Step (1) Adsorption step: The sample that set in the sample cell was dipped into liquid nitrogen. Nitrogen gas that flowed through the system was adsorbed on the surface of the sample unit equilibrium was reached.

Step (2) Desorption step: The sample cell with nitrogen gas-adsorbed catalyst sample was dipped into the water at room temperature. The adsorbed nitrogen gas was desorbed from the surface of the sample. This step was completed when the indicator line was in the position of the base line.

Step (3) Calibration step: 1 ml of nitrogen gas at atmospheric pressure was injected through the calibration port of the gas chromatograph and the area was measured. The area was the calibration peak. The calculation method is explained in Appendix C.