

CHAPTER 4

EXPERIMENTAL METHODS

4.1 Introduction

In this work, besides the fabrication of the high pressure reactor, the other objectives are:

1. Preparation of catalysts
2. Experimentation for the reaction engineering at the design conditions.

4.2 Catalyst Preparation

Three types of catalyst have been prepared. One was prepared by Dr. W. Tanthapanichakoon in Professor T. Inui's laboratory at Kyoto University. The two others were prepared in the Chemical Engineering Department, Chulalongkorn University.

The catalyst that was prepared at Kyoto University comprises of rhodium, manganese and iron impregnated on silica gel. The prepared atomic ratio of Rh:Mn:Fe = 1:1:0.1.

The second catalyst, an IFP type, comprises of copper, cobalt, chromium and potassium at the atomic ratio of Cu:Co:Cr:K = 1:1:0.8:0.096.

The third catalyst is composed of cobalt, barium and silver impregnated on silica gel with the atomic ratio of Co:Ba:Ag = 1:0.05:0.1. It was prepared after a catalyst reported by H. Hachenberg of Hoechst Company, West Germany.

4.2.1 Rhodium Catalyst

4.2.1.1 Calculation of Catalyst Composition

The starting materials are $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with SiO_2 as carrier. At first the desired ratio of each component, including the rhodium content in the catalyst, must be determined. For example, if it is designed that rhodium content in the catalyst is 4.7 wt% and the atomic ratio of Rh:Mn:Fe is 1:1:0.1, then the required amounts of each component for 3 g. of the catalyst may be calculated as below.

Data

MW. of $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$	=	245.21
Atomic weight of Rh	=	102.91
MW. of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	=	197.92
Atomic weight of Mn	=	54.94
MW. of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	=	270.32
Atomic weight of Fe	=	55.85

Then the weight of rhodium in the catalyst equals 0.141 g. and the weights of manganese and iron, become 0.075 g. and 0.0077 g. respectively.

$$\begin{aligned} \text{The amount of silica gel required} &= 3 - (0.141 + 0.075 + 0.0077) \\ &= 2.7763 \quad \text{g.} \end{aligned}$$

Thus the amounts of starting materials are

$$\begin{aligned} \text{RhCl}_3 \cdot 2\text{H}_2\text{O} &= \frac{(0.141 \text{ g.})(245.21)}{102.91} = 0.336 \text{ g.} \\ \text{MnCl}_2 \cdot 4\text{H}_2\text{O} &= \frac{(0.075 \text{ g.})(197.92)}{54.94} = 0.270 \text{ g.} \\ \text{and FeCl}_3 \cdot 6\text{H}_2\text{O} &= \frac{(0.0077 \text{ g.})(270.32)}{55.85} = 0.037 \text{ g.} \end{aligned}$$



4.2.1.2 Preparation of Catalyst

Weigh 0.336 g. of $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$, 0.270 g. of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 0.037 g. of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Mix them together and dissolve with 7 ml. of ethanol. Pour the mixture gradually onto 2.7763 g. of SiO_2 and mix the solution and solid beds well. Place the slurry to dry, while mixing occasionally, in a dessicator at room temperature. Then leave the dried solid in the dessicator for 48 hours. The catalyst is calcinated by raising the temperature from room temperature, 20°C , to 430°C in 30 minutes and held constant at this temperature for 1/2 hour.

4.2.1.3 Reduction of Catalyst

Before carrying out experiments, the catalyst must be activated or reduced with H_2 in a reducing unit (Figure 4.1) as follows.

1. Purge the reducing unit with N_2 gas at 1 kg/cm^2 and room temperature for a few minutes.
2. Substitute the N_2 gas with H_2 gas at a gaseous flowrate equal to 5 l/hr at $P = 1.5 \text{ kg/cm}^2$.
3. Switch on the electric heater and raise the temperature from room temperature to 400°C within 30 minutes, and hold at this temperature for 30 minutes, then switch off the heater.
4. Stop the H_2 flow.
5. Purge with N_2 gas until the temperature in the boat drop to room temperature.
6. Stop the N_2 flow and close off the system for outside air, leaving it overnight.
7. Collect the catalyst in the following morning and keep it in an air-sealed vial.

4.2.2 Hoechst's Catalyst

4.2.2.1 Catalyst Preparation and Reduction

The patented Hoechst's catalyst is composed of cobalt as major component and modified by gold and/or silver and/or rhenium (Hachenberg et al. 1979). The two modifying elements are not only very expensive but also hard to obtain in Thailand. In this experiment, it was decided to use silver and barium as modifiers for the cobalt catalyst. The desired atomic ratio of Co:Ba:Ag equalled 1:0.05:0.01. The starting materials for the catalysts were cobaltous acetate $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, barium acetate $[\text{Ba}(\text{CH}_3\text{COO})_2]$, and silver acetate $[\text{Ag}(\text{CH}_3\text{COO})]$. Silica was used as carrier. The preparation procedure was as follows.

Weigh 5.75 g. of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 0.3 g. of $\text{Ba}(\text{CH}_3\text{COO})_2$ and 0.4 gm. of $\text{Ag}(\text{CH}_3\text{COO})$, Dissolve them in 6 ml. of 7 vol% aqueous CH_3COOH . Add 10 gm. of silica gel into the solution, mix the slurry thoroughly, Add another ml. of 7 vol% aqueous CH_3COOH and mix the slurry thoroughly again while drying it at 60°C on a hot plate. The calcination temperature is 400°C , and the reduction temperature is 300°C . This catalyst should be reduced in situ prior to its use with hydrogen gas and not reduced in the reduction unit as in the case of the other two catalysts.

4.2.3 IFP-type Catalyst

4.2.3.1 Catalyst Preparation

The IFP-type catalyst that was prepared for investigation comprises of Cr, Cu, Co and K with the atomic ratio of $\text{Co}:\text{Cu}:\text{Cr}:\text{K} = 1:1:0.8:0.09$. The starting materials are

CrO_3 , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and KOH. The catalyst was prepared as follows.

Add 4 grams of chromium trioxide (CrO_3), 12.075 g. of copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and 14.55 g. of cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) into 12 ml. of water. Stir and grind the slurry for 20 minutes to obtain a homogeneous paste. Then add 0.265 g. of KOH and mix it into the paste. Dry it in the oven at 150°C for 1 hr. and then raise the oven temperature to 200°C and hold for 2 hrs. After that let it cool in dessicator. The following day calcine the catalyst at 400°C for 2 hrs. by heating it from 32°C to 400°C within 1.5 hrs. and keeping the temperature at 400°C for 2 hrs. Then leave it overnight at that temperature in the electric furnace. The catalyst powder is pelletized as tablets of 5 mm. diameter and 3 mm. height.

4.2.3.2 Catalyst Reduction

The catalyst tablets were placed in a ceramic boat and the boat was inserted into the central part of the reduction unit (Fig.4.2). The reduction procedure was the same as in 4.2.1.3 which the reduction temperature was 450°C . The final catalyst was bright black.

4.3 Experimental Conditions

All the above three catalysts were tested for synthesis of alcohols under various conditions. The experimental conditions are summarized in Table 4.1

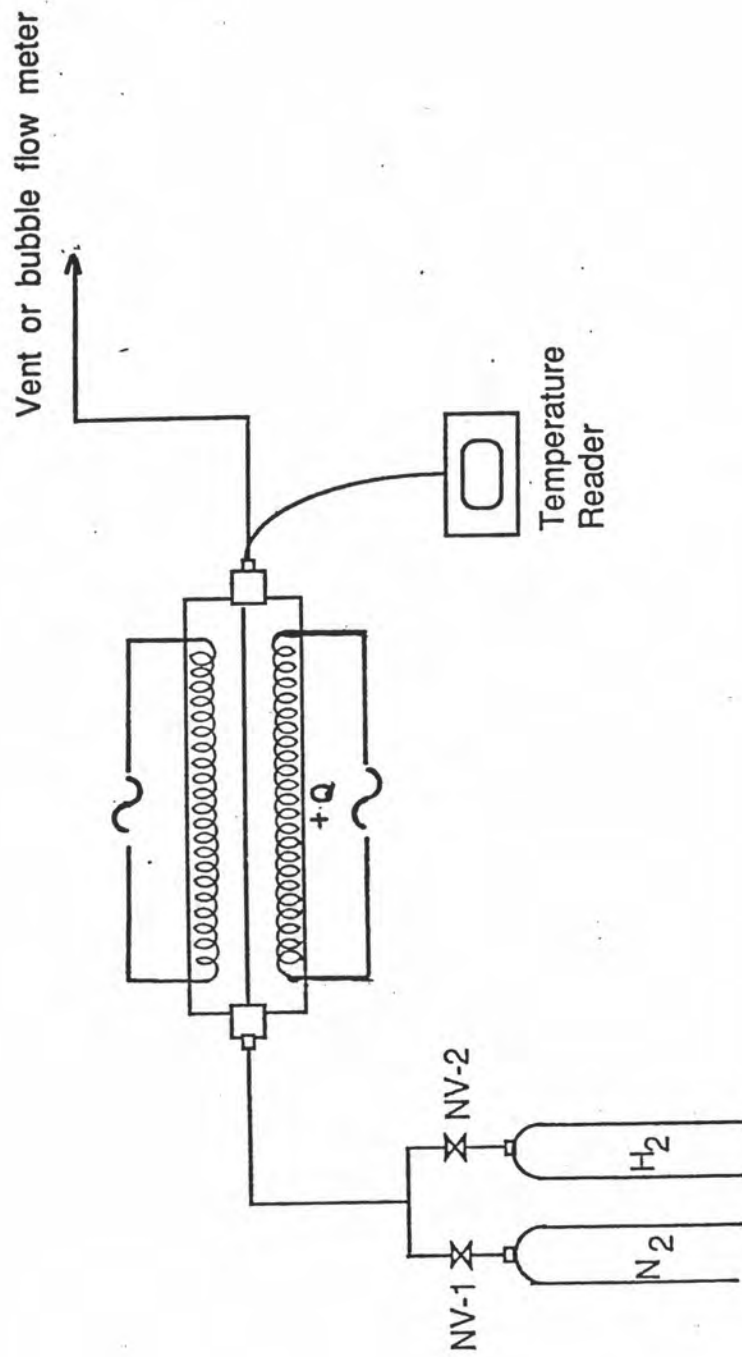


Fig. 4.1 Diagram of The Catalyst Reduction Unit.

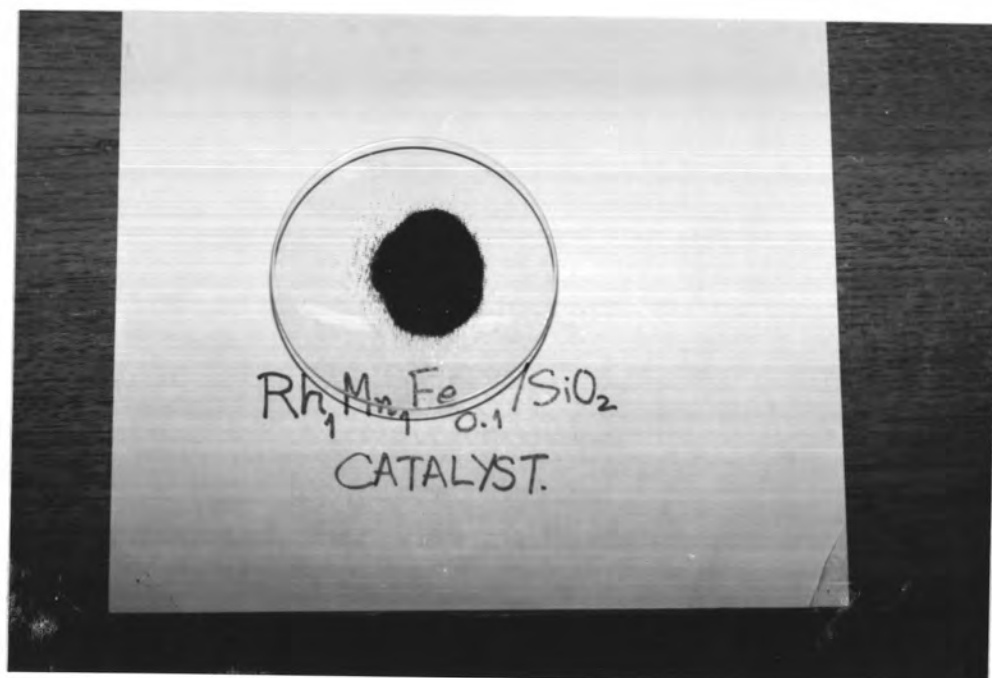


Fig. 4.2 Photograph of the $\text{Rh}_1\text{Mn}_1\text{Fe}_{0.1}/\text{SiO}_2$ catalyst



Fig. 4.3 Photograph of The $\text{Co}_1\text{Ba}_{0.05}\text{Ag}_{0.1}/\text{SiO}_2$ catalyst



Fig. 4.4 Photograph of the $\text{Co}_1\text{Cu}_1\text{Cr}_{0.8}\text{K}_{0.096}$ catalyst

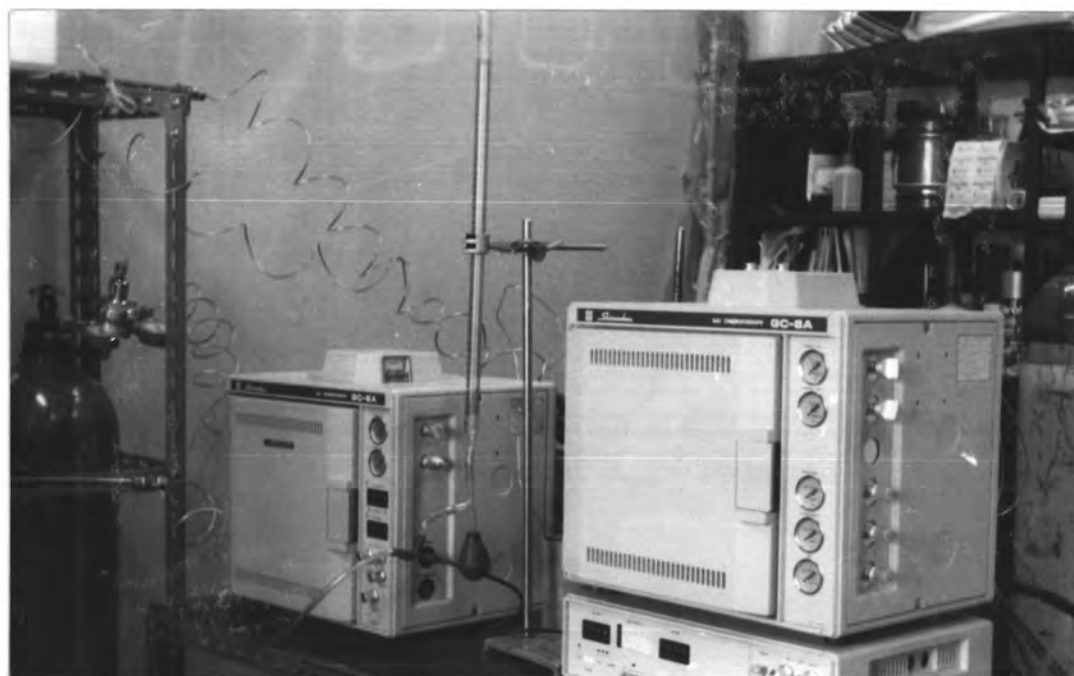


Fig. 4.5 Photograph of The two GC's: GC-8AIT, GC-8AIF

Type of Catalyst	CO:H ₂	Pressure(atg)	GHSV (hr ⁻¹)	Temperature(°C)
Rh ₁ Mn ₁ Fe _{0.1} /SiO ₂	1:2	40	2,000	250, 280, 310, 340
		60	2,000	250, 280, 310, 340
		80	1,000, 2000, 4000, 8,000	250, 280, 310, 340
Rh ₁ Mn ₁ Fe _{0.1} /SiO ₂	1.25:1	40	2,000	250, 280, 310, 340
		60	2,000	250, 280, 310, 340
		80	1,200, 2,000, 4,000, 8,000	250, 280, 310, 340
Cu ₁ Co ₁ Cr _{0.8} K _{0.056}	1.25:1	40	2,000	250, 280, 310, 340
		60	2,000	250, 280, 310, 340
		75	1,000, 2,000, 4,000	250, 280, 310, 340
Co ₁ Ba _{0.05} Ag _{0.01} /SiO ₂	1.25:1	40	2,000	250, 280, 310, 340
		60	2,000	250, 280, 310, 340
		80	1,000, 2,000, 4,000	250, 280, 310, 340

Table 4.1 Summary of the experimental conditions

4.4 The Experimental Procedure

Before starting each experimental run, it is necessary to switch on the two GC's and wait until they are ready for analyses. Then start the experiment by following the procedures below.

a. Open the valve of the N_2 gas cylinder and purge the reactor system in **Fig 3.1** with N_2 for 10 minutes at nearly atmospheric pressure.

b. Shut off the N_2 gas, open the valve of the premixed $CO+H_2$ gas cylinder and let the synthesis gas substitute the N_2 gas for 10 minutes. To ensure that all the N_2 gas has been completely substituted, take a gas sample from SP-2 and inject into the MS-5A column of the GC-8AIT. Check for any N_2 peak, if none is observed, go to **step C**. Otherwise continue to purge the system with synthesis gas until N_2 has been completely purged.

c. Increase the pressure of the system to the desired pressure by turning the PCV knob.

d. Adjust the gas flowrate to obtain the desired GHSV with the aid of NV-3, NV-4. Use a wet-test flowmeter to measure the flowrate.

e. Next set the reaction temperature by applying voltage to electric furnace. Two slidacs are used to adjust the voltage and hence the temperature. Raise the temperature from room temperature, say $32^\circ C$, to $230^\circ C$ within 30 minutes. Hold at this temperature for 30 minutes.

f. Raise the temperature to $250^\circ C$ within 10 minutes and hold at the new temperature for 50 minutes before taking three gas samples from SP-1, SP-2, and SP-1 respectively.

g. Inject one wet sample taken from SP-1 into the PORAPAK-T column of the GC-8AIF-T for analysis of hydrocarbons and alcohols. Inject the dry sample from SP-2 into the MS-5A column

of the GC-8AIT. Then inject the second wet sample from SP-1 into the PORAPAK-Q column of the GC-8AIT.

h. After the three gas samples have been analyzed, raise the temperature from 250°C to 280°C within 10 minutes.

i. Repeat the procedure explained in steps f. and g. Next increase the temperature to 310°C and 340°C , respectively.

j. When all samples at 250 , 280 , 310 , 340°C have been taken and their analyses completed turn off the slidacs and gradually cool down the reactor while decreasing the pressure in the reactor.

k. When the temperature drops down to 70°C , shut off the synthesis gas valve and substitute the synthesis gas with N_2 gas.

l. Purge the system with N_2 gas until there is no synthesis gas left in the system. Use the gas chromatography for confirmation.

m. Shut down the gas chromatographys according to the manuals.