CHAPTER IV

EXPERIMENTAL SYSTEMS

This chapter describes the experimental systems and the experimental procedures in this research. A description of catalyst preparation method is given in section 4.1. The experimental system of non-oxidative methane coupling reaction is explained in section 4.2. Details of experimental procedures, including the materials and apparatus are as follows.

The Scope of This Study

The catalysts used in non-oxidative methane coupling in this study were prepared by two methods ; ion exchange and wet impregnation.

The catalysts prepared by ion exchange method are as follows.

- (10 wt. %) Co/NaY
- (5-15 wt. %) Co/HY
- (10-20 wt. %) Ru/HY
- (10-20 wt. %) Pt/HY

A catalyst prepared by wet impregnation method is.

- (10 wt. %) Co/NaY

The reaction conditions of non-oxidative methane coupling are as follows :

Catalytic Reduction Temperature : 450 °C
Reaction Temperature : 200- 400 °C
Operation Pressure : 1 atm
Time of non-oxidative methane coupling : 60-180 min.
GHSV of CH_4 : 4960-6200 h^{-1}
GHSV of H_2 : 4960 h^{-1}
GHSV of Ar : 4960 h^{-1}

4.1 Preparation of Catalysts

4.1.1 Materials

Chemicals used in this experiment are normally Analytical Grade, but only some critical chemicals have to be specified as follows:

1. Sodium Aluminate [$NaAlO_2$] manufactured by Wako Pure Chemical Industries CO.,Ltd., Japan.

2. Sodium Silicate Solution [$Na_2Si_3O_7$] manufactured by Merck Ltd., Germany.

3. Cobalt Nitrate [$Co(NO_3)_2.6H_2O$] manufactured by Merck Ltd., Germany.

4. Ruthenium Chloride [$RuCl_3$] manufactured by Nacalai Tesque, Inc. Kyoto, Japan.

5. Hydrogen Hexachloroplatinate hexahydrate [$H_2PtCl_6.6H_2O$] manufactured by Nacalai Tesque, Inc. Kyoto, Japan.

6. Sodium Hydroxide [NaOH] manufactured by Merck Ltd., Germany.

4.1.2 Apparatus : Unit for calcination

The unit consists of an eletrical furnace, an automatic temperature controller, and a variable voltage transformer, this unit is used for calcining the wet impregnated and ion exchanged catalysts at high temperature.

4.1.3 Preparation of Transition metals

The transition metals; complexes solution was prepared by dissolving about 1 gram of Co ,Ru and Pt in de-ionized water to the total volume of 25 ml.

4.1.4 Preparation of Support Catalysts

4.1.4.1 Preparation of NaY-type zeolite

The synthesis of zeolite Y was described in patent literature [17]. The preparation procedure of zeolite Y is shown in figure 4.1, while reagents used are shown in Table 4.1.

Table 4.1 Reagents used for the preparation of zeolite Y [Jiratthitikan (1997)].

Reagents	Quantity
First step:	
<u>Solution S_1</u>	
$NaAlO_2$	32.81 g
Distilled water	158 ml
<u>Solution S_2</u>	
$Na_2Si_3O_7$	218.6 g
NaOH	95.91 g
Distilled water	534 ml

(continue)

Reagents	Quantity
Second step:	
Solution S_3	
$Na_2Si_3O_7$	216.72 g
NaOH	4.47 g
Distilled water	63.5 ml

a) Preparation of uniform slurry

Sodium aluminate and sodium siligate solution were used as sources of Al and Si , respectively; while Na source was substantially obtained from sodium hydroxide. The uniform slurry was prepared by the two main steps.

1. S_1 was slowly added into S_2 while vigorous stirring. The mixture was continuously stirred for 2 hrs. Then the mixture was heated to 60°C and maintained at that temperature for 1 hr, thereby to form a gel. The gel mixture was separated from the supernatant solution by a centrifuge. Then it was washed by water and separated by repeated cycles of centrifugation and decantation until the pH of supernatant solution was about 13.5.

2. 181 g. of obtained gel from the above step was added into S_3. Subsequently, the resultant mixture was stirred to obtain a uniform slurry.

b) Crystallization

1. The uniform slurry was charged into a closed glass vessel and placed at room temperature for 16 hrs for aging.

2. The glass vessel charged with slurry was heated at 95°C in an oven and maintained at this temperature for 72 hrs.

3. The prepared zeolite Y was left to cool down to ambient temperature and then it was washed by distilled water until the pH of slurry becames 7 by repeating cycles of centrifugation and decantation.

4. The obtained crystals were dried overnight at 110°C.

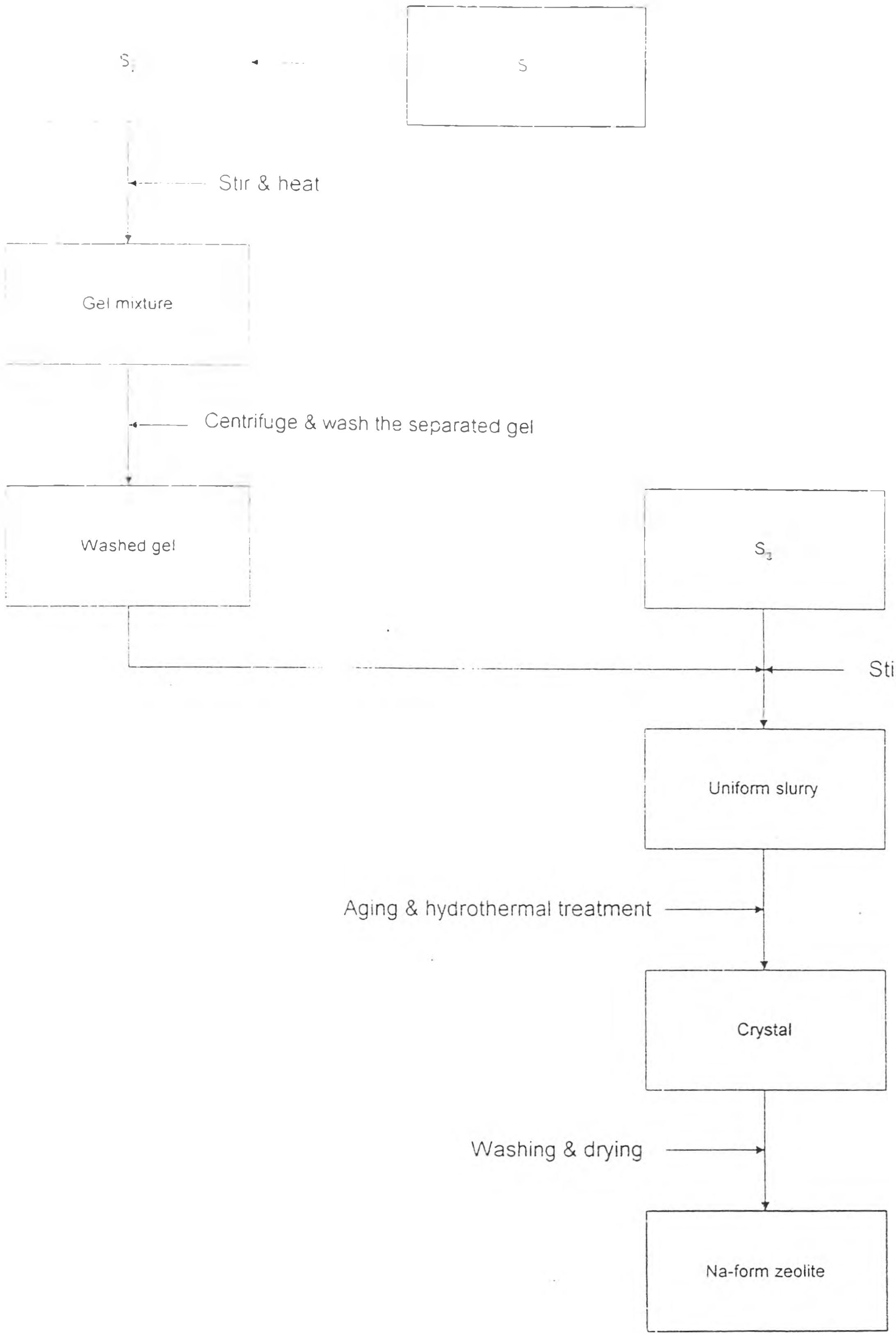


Figure 4.1 The preparation procedure of NaY-zeolite catalyst.

4.1.4.2 Preparation of the Proton-Type Y (HY)

a) Ammonium Ion-Exchange of NaY-Type Zeolite

1. 2 g portion of the NaY-type zeolite was added by 80 ml of 1 N NH_4NO_3 aqueous solution, after that the mixture was heated at 80°C for 1 hr.

2. The powder was washed twice by distilled water to remove nitrate ions by using a centrifugation separator.

3. The above steps (1) and (2) were repeated for 5 times.

4. The sample was dried overnight in an oven at 110°C. The Na-form crystal was thus changed to "NH_4-form catalyst".

b) HY-Type zeolite

The NH_4 Y-type zeolite was converted to HY-type zeolite by removing NH_3 species from the catalyst surface. NH_3 can be removed by thermal treatment of the NH_4-type zeolite. This was done by heating a sample in an air stream at 500°C for 2 hrs, by heating them from room temperature to 500°C in 60 minutes. After the catalyst was cooled down, it was stored in a glass bottle in a desicater for further used.

4.1.5 Preparation of Metal Catalysts

The bimetallic catalysts used in this research were prepared by two methods; wet impregnation and ion exchange. Both procedures would be described below.

4.1.5.1 Wet impregnation

1. Volume of transition metal , impregnating solution for 1 g of catalyst support could be specified by calculating the amount of the stock solution to yield the required metal loading.

2. 1 g of catalyst support was immersed in 20 ml of distilled water and stirred slowly. The impregnating solution obtained from (1) was slowly dropped to the slurry by using a dropper. Then, the mixture was heated to 70°C in order to slowly evaporated the slurry to be a dry powder, finally.

4.1.5.2 Ion exchange

1. The zeolite support was first stirred carefully with deionized water (200 $cm^3/g_{zeolite}$) at 70°C for 1 hr.

2. The transition metal solution, that was calculated the amount of the stock solution to yield the required metal loading, was added dropwise to the zeolite slurry under stirring at 70°C.

3. After stirring at 70°C for 24 hrs., the samples were centrifuged and thoroughly washed by distilled water.

4.1.5.3 Calcination

All of the metal catalysts obtain from both methods were dried at 110°C over night. Subsequently they were calcined in a stream of O_2 (99.95%,40 ml/min) with a temperature ramp of 0.5°C/min from room temperature to 300°C and hold at this temperature for 2 hrs. The calcined catalyst were finally cooled to room temperature.

4.1.5.4 Pelletization

All catalyst were pelletized by using a stainless steel die with has about 1 cm diameter opening inside the die. The pelletization was performed at the pressure of about 200 psi, by applying a manual press, for 5 minutes for the approximate 0.25 g. catalyst sample per one pellet. The pellets obtained then were cut by a clean cutter into small granular pieces and were sieved to acquire grain sized to 20-40 mesh for used in the reaction experiment.

4.2 Reaction of Non-Oxidation Methane Coupling

4.2.1 Material

High purity methane (99.99 %) supplied by Thai Industrial Gas Limited was used as feed stream for the non-oxidative methane coupling in this study. The hydrogen was used for reducing the catalysts. The ultra-high purity argon was used for purging the system.

4.2.2 Apparatus

Flow diagram of the non-oxidative methane coupling system is shown in figure 4.2. The system consists of a reactor, an automatic temperature controller, an electrical furnace and gas controlling system. The details of each instrument are described below.

4.2.2.1 Reactor

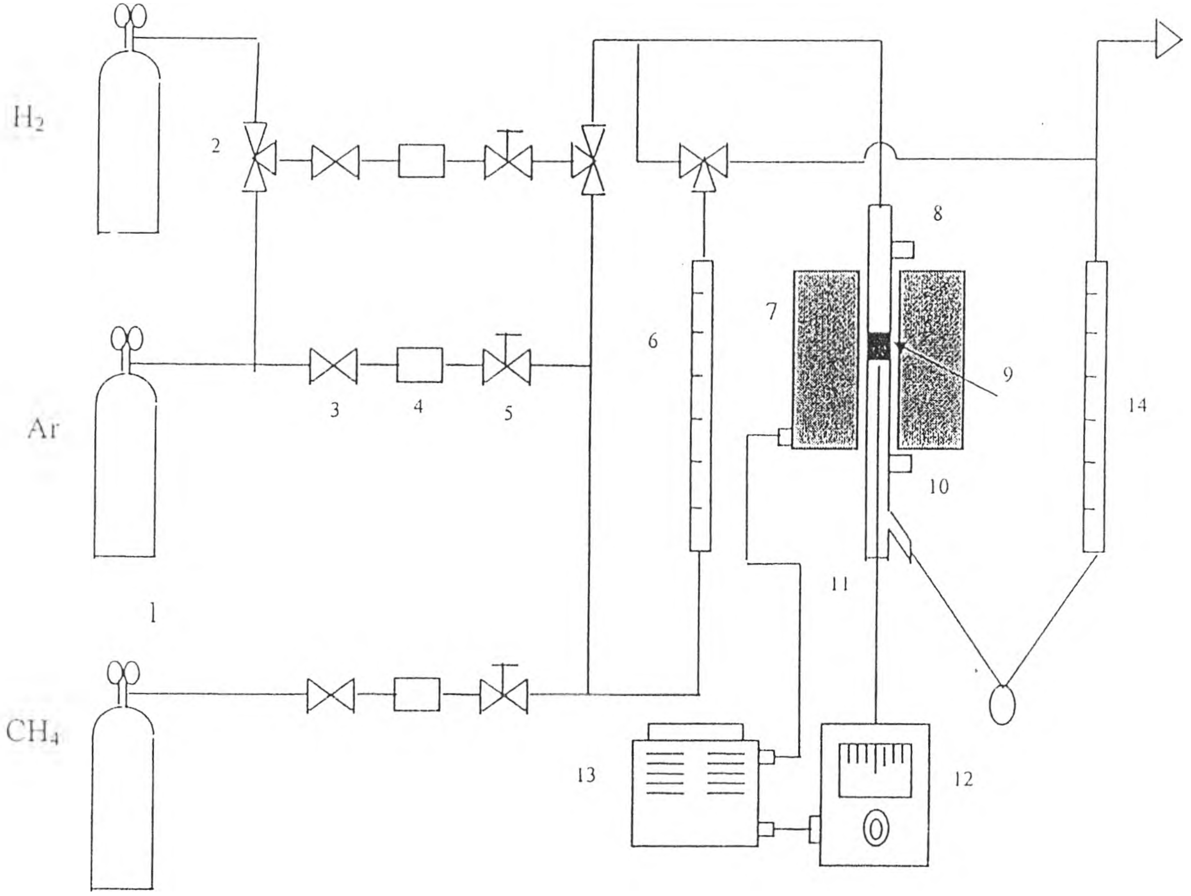
The non-oxidative methane coupling reactor is made from a 7 mm inner diameter quartz tube. It can be operated from room temperature up to 1000°C under atmospheric pressure. Catalyst is packed between quartz wool layer.

4.2.2.2 Automatic temperature controller

An automatic temperature 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 a reactor. The temperature control setpoint is adjustable within the range of 0-800°C

4.2.2.3 Electrical furnace

An electric furnace with power of 2000 watts supplies heat to the reactor. Therefore the reactor can be operated from room temperature up to 800°C at the maximum voltage of 220 volts.



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 port
11. Thermometer
12. Temperature indicator
13. Variable voltage transformer
14. Bubble flow meter

Figure 4.2 Flow diagram of the non-oxidative methane coupling system

4.2.2.4 Gas controlling system

The gas controlling system consists of :

1. A cylinder of ultra high purity methane, equipped with a pressure regulator, an on-off valve and a fine-metering valve in used for adjusting the flow rates of this gas.

2. The cylinders of 99.995 % purity argon and hydrogen, equipped with pressure regulators, on-off valves and fine-metering valves, are used for adjusting the flow rates of these gases.

4.2.2.5 Gas Chromatograph

Flame ionization detector-type gas chromatographs, Shimudzu GC-14B was used to analyze the quantity of hydrocarbon in feed and effluent gases. Operating conditions used are shown in table 4.2

Table 4.2 Operating conditions for gas chromatograph

Detector	FID
Column	VZ-10 ϕ 3x3 m.
Carrier gas	N_2 (99.99 %)
Flow rate of carrier gas	60 ml/min
Detector temperature	150 °C
Injection temperature	80 °C
Analyzed gas	gaseous hydrocarbon
Column temperature -Initial -heating rate -Final	 40 °C 5 °C/min 65 °C

4.2.3 Experimentation

1. 0.2 g of catalyst was packed in the middle of the quartz tube reactor. The reactor was then firmly placed into the furnace.

2. The hydrogen gas was introduced into the reactor at a flow rate of 40 ml/min in order to perform reduction treatment.

3. The reactor was heated up at a constant heating rate of 2°C/min. until the temperature reached 450°C. The reactor was hold at this temperature for 3 hrs and then was cooled down to room temperature under 40 ml/min ultra high purity argon gas.

4. When the reduction process was completed, the reactor was heated up again to a required temperature.

5. The argon gas was switched to ultra high purity methane gas for 20 min at a desired flow rate for chemisorption.

6. After methane chemisorption step the catalyst bed was flushed with 40 ml/min argon gas for 1 hr.

7. For the second step, the catalyst was treated with hydrogen or argon, for 60 min. The reaction products were analyzed by the gas chromatograph

4.3 Catalysts Characterization

4.3.1 X-ray Diffraction patterns

X-ray powder diffraction (XRD) was used to obtain information about the catalyst structure, composition, and state of polycrystalline materials. Before testing, the sample powder was mounted in a sample holder with appropriate smooth surface. After that, the sample holder was place in x-ray diffractometer. The beam of monochromatic x-radiation was directed at the sample. The reflection or diffraction of the x-ray was observed at various angles with respect to the primary beam. The diffraction pattern of the prepared catalyst was compared with the standard diffraction pattern for confirmation.

XRD used in this study is SIEMENS XRD D5000 diffractometer, accurately measured in the 4-40° 2θ angular region, at Petrochemical Engineering Research Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

4.3.2 Determination of composition content of catalyst

Percentage of metals was analyzed by atomic absorption spectroscopy(AAS) at the department of science service, Ministry of Science, Technology and Environment.

4.3.3 FT-IR pyridine adsorption

Infrared spectroscopy and temperature programmed desorption of pyridine was used to investigate the acidic properties of Y-type zeolites. The flow diagram of on-situ FT-IR apparatus is depicted in figure 4.3. All gas lines, valves and fitting in this apparatus are made of Pyrex glass except for IR gas cell and sample dish holder which are made of quartz glass in order to avoid the adsorption of any gas species which may remain on the inner surface of glass tube while the system was evacuated. A Nicolet model impact 400 FT-IR equipped with deuterated triglycine sulfate (DTGS) detector and connected to a personal computer with Omnic version 1.2a on Windows software (to fully control the functions of the IR analyzer) were applied to this study. The analyzer was place on a movable table for conveniently adjustment.

About 0.06 g. of catalyst powder was pressed into self-supporting dish form with about 1 cm. diameter by using a stainless steel press apparatus. The sample dish was placed into a quartz in situ IR gas cell. The cell was attached with two KBr windows at both ends. Prior to adsorption, the sample was evacuated to about 10^{-4} torr for 1 hr. Pyridine was introduced into the IR cell by self vaporizing in vacuum condition and was circulated through the system by electromagnetic pump. After 1 hr of adsorption, the excess and weakly adsorped pyridine was removed by evacuating at room temperature for 1 hr to ca. 10^{-4} torr. Presumably only the chemisorbed pyridine remained on the surface. Desorption was then carried out by evacuation at progressively higher temperature, every 50°C, and IR spectra were recorded at the various stages of desorption. Each spectrum was completed by 500 scans at a resolution of 4 cm^{-1}. Background spectrum, i.e., prior to adsorption, were substracted from all spectra so that the effects of adsorption and thermal treatments could be more clearly seen.

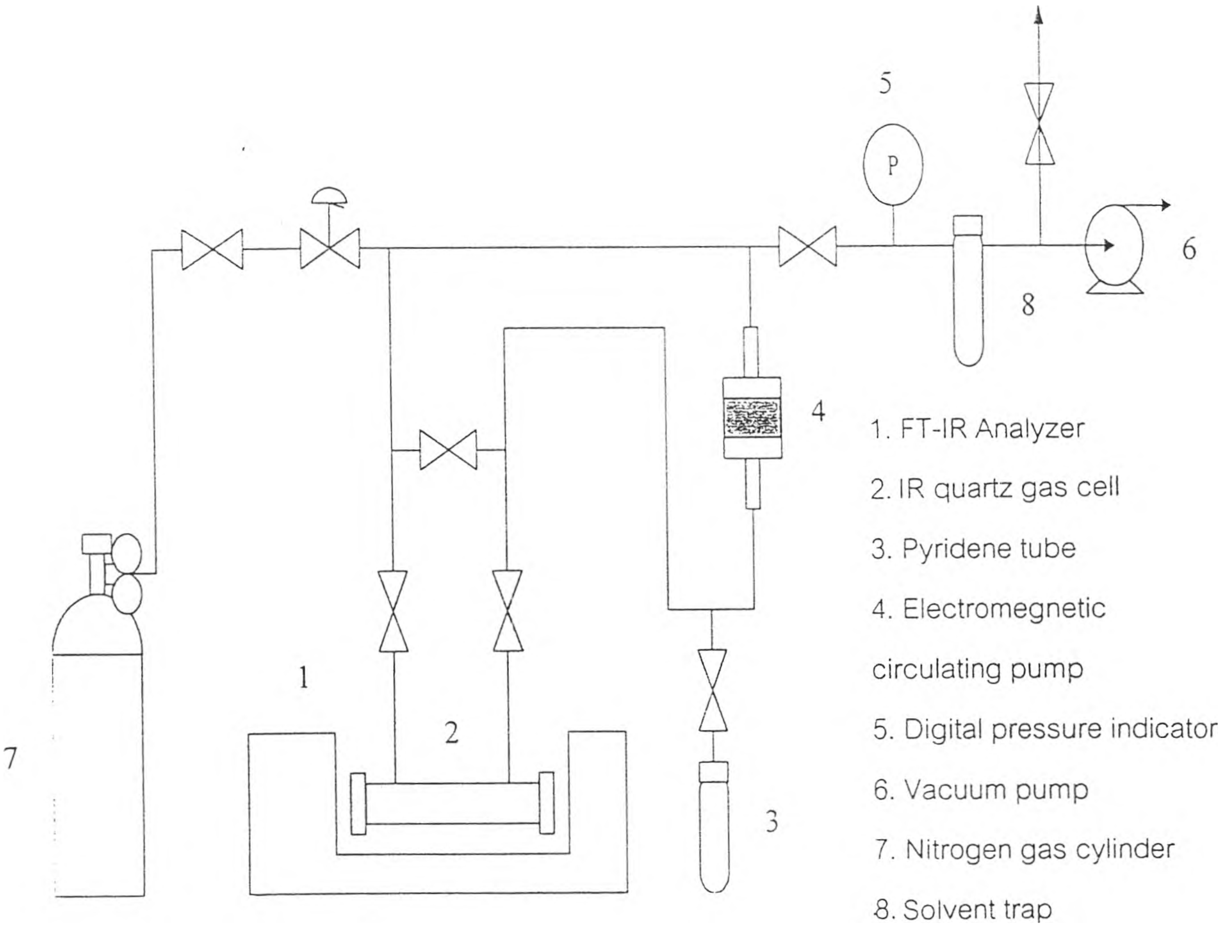


Figure 4.3 Flow diagram of instrument used for pyridine adsorption experiment.

4.3.4 CO adsorption

The active sites of catalyst were measured by CO adsorption technique on the basis that one CO molecule adsorbed on one active site. The amount of CO was measured by a thermal conductivity detector. The operating condition of the TCD is illustrated in table 4.3

Table 4.3 Operating condition of the TCD for CO adsorption

Helium carrier gas flow rate	30 ml/min
Detector temperature	80 °C
Detector current	80 mA

0.1 g of catalyst was placed in the stainless tubular reactor. Hydrogen gas was introduced into the reactor at the flow rate of 40 ml/min. The reactor was heated with an increasing rate of 2°C/min until the temperature reached 450°C and hold at this temperature for 1 hr. After cooling down to room temperature in Argon stream, the catalyst was ready to measure active site. 50 μl of CO was injected to reactor at the injection port located before the catalyst bed. The CO gas injection was repeated until the sample did not adsorb CO any more. The amount of active sites of catalyst was calculated by the amount of adsorbed CO gas (see Appendix B).