CHAPTER IV

EXPERIMENTAL WORK

This chapter describes the experimental systems and the experimental procedures applied in this research. Section 4.1 shows the scope of this study. The experimental system of catalyst characterization by FT-IR is explained in section 4.2.

4.1 The scope of this study

The following analytical grade of metal oxide, hydroxide and zeolite are used in this study.

1. MgO, a commercial product of Carlo Erba, Italy.
2. $Ca(OH)_2$, a commercial product of Daikin Brothers.,LTD..
3. NaY, a commercial product of Tosoh Corporation.
4. Na-mordenite, a commercial product of Tosoh Corporation.

4.2 The characterization of Catalyst by FTIR

4.2.1 Fourier transforn infrared spectrometer (FTIR) of pyrrole adsorption

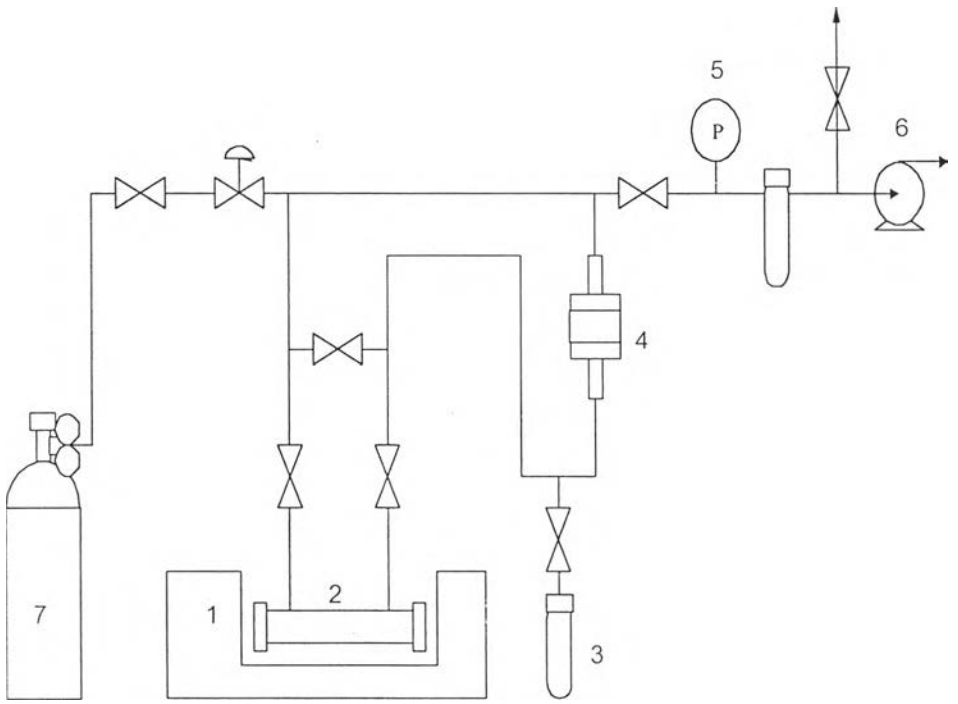
4.2.1.1 Chemical and reagents

Pyrrole, analytical grade supplied by Fluka, was used in these experiments.

4.2.1.2 Instruments and Apparatus

- **Flow diagram**

The flow diagram of the in-situ FT-IR apparatus is depicted in figure 4.1. All gas lines, valves and fitting in this apparatus are made of pyrex glass except for the IR gas cell and the sample disk 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. Nitrogen was used for purging before starting the experiment. Pyrrole was added to a glass tube connected with a valve which can be opened to the gas line system. A home-made electro-magnetic pump, fixed in the gas line, was used for circulating the gas (including the pyridine vapour) through the sample in order to accomplish the adsorption of gases or pyridine specie on the sample surface. A Labconco 195 - 500 HP vacuum pump, which theoretically has capacity at 10^{-4} Torr, was used. Furthermore, a digital pressure indicator, attached to the gas line, measured the pressure of the system and checked leaking of the apparatus as well.



1) FTIR Analyzer

2) IR quartz gas cell

3) Pyrrole tube

4) Electro magnetic circulating pump

5) Digital pressure indicator

6) Vacuum pump

7) Nitrogen gas cylinder

Figure 4.1 Flow diagram of instrument used for pyrrole adsorption experiment

- **FT-IR**

A Nicolet model Impact 400 FT-IR equipped with a 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 used in this study. The FT-IR analyzer was placed on a movable table for conveniently adjustment.

- IR gas cell

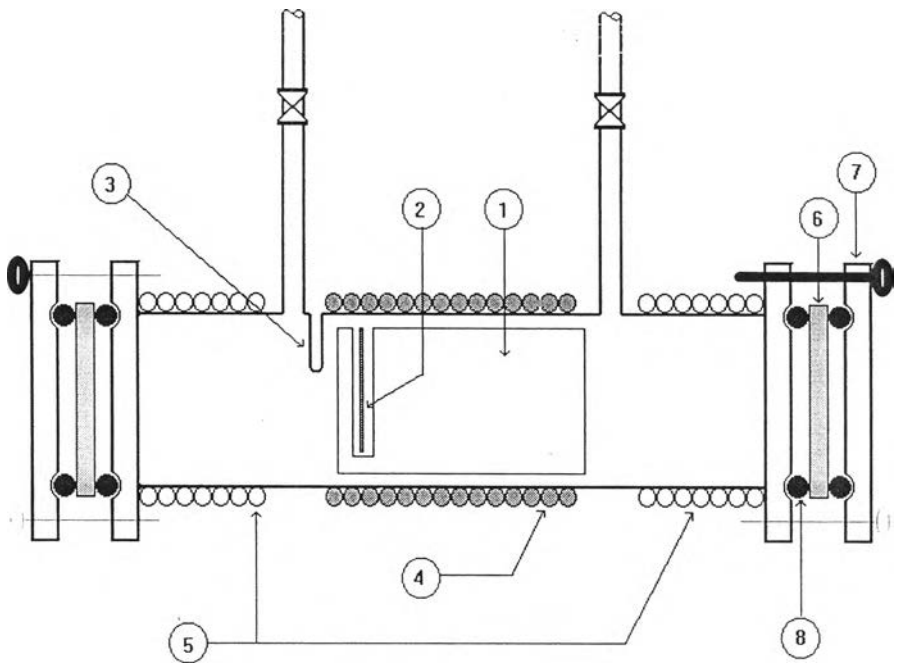
IR gas cell used in this experiment (figure 4.2) was made of quartz glass and covered with a 32 × 3 mm KBr windows at each end of the cell. Each window was sealed by two O-rings and a stainless flange fasten by a set of screws.

The cell is roughly divided into two zones; heating and cooling with respect to the temperature. The function of the heating zone at the middle of the IR cell is to increase the temperature for the sample disk. The quartz sample holder for the sample disk to keep it perpendicular to the IR beam, is arranged inside the IR cell in the heating zone. A thermocouple is used to measure the sample disk temperature. The temperature is controlled by a variable voltage transformer and a temperature controller. Water cooling was run at both ends of the IR cell in orded to reduce the excessive heating, which may damage O-ring seals and the windows.

4.2.1.3 Sample disk preparation

To produce a self-supporting catalyst sample disk for an IR experiment, the catalyst was milled throughly in a small quartz motar to obtain a very fine powder. This minimized the scattering of infrared radiation and provided a high quality of spectrum.

The die used was made of stainless steel and is shown in figure 4.3. The most important part of the die, which is directly in contact with the sample is so –called the support disks. The support disks are composed of upper and lower disks, each 20 mm. in diameter. The support disks are highly polished to a mirror like finish in order to overcome the sticking of sample to the surface of the die, the main problem in pressing disks. The powder sample, about 0.06 - 0.065g, was spreaded to totally cover the surface of the lower support disk placed in the die to make a sample having a weight of 15-20 mg/cm^2. If a thick sample disk was used, a poor IR scan would result and if a too thin sample disk was employed, it would be easily cracked by thermal treating. All parts of die were put together and were pressed by a manual hydraulic press at the pressure of 140 -180 kg/cm^2 for 5 minutes. The pressure should not be too low so that a self-supporting disk cannot form. After pressing, the well-formed disk was carefully removed from the die and mounted in the IR cell.



1. Sample holder
2. Sample disk
3. Thermocouple position
4. Heating rod
5. Water cooling line
6. KBr window
7. Flange
8. O-ring

Figure 4.2 IR gas cell used for pyrrole adsorption experiment.

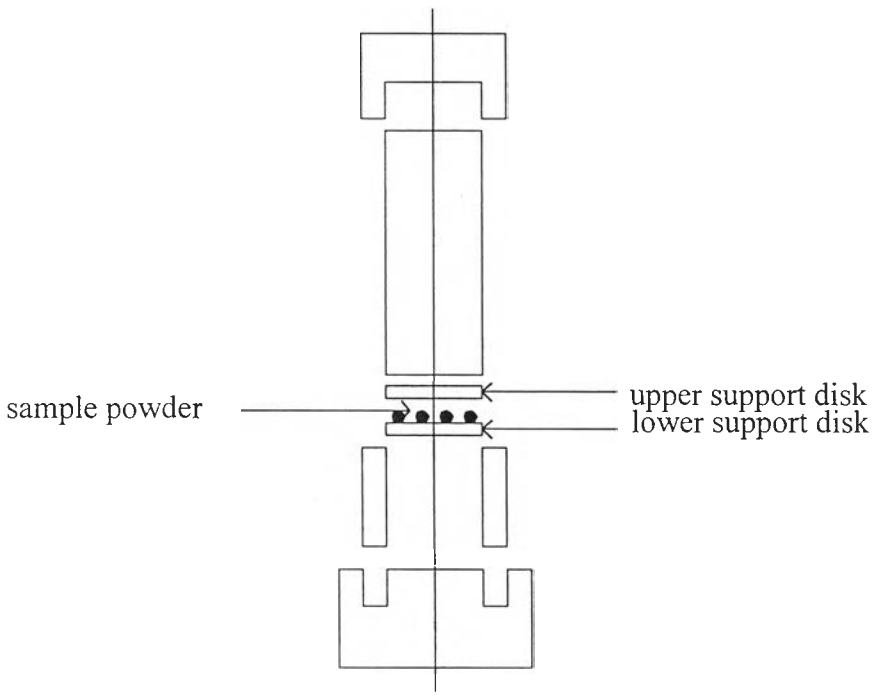


Figure 4.3 Body of the die for preparation of a self-supporting catalyst disk.

4.2.1.4 Experimental procedure

After a well-formed sample disk is obtained, it was placed in the sample holder and then the sample holder, including sample disk, was placed into the middle of the IR gas cell. The sample disk is located as close to the thermocouple probe hole as possible. Once the KBr windows were sealed at both ends of the IR gas cell and leaks were not observed, the IR gas cell was evacuated by a vacuum pump through the gas line to place the system under vacuum. The sample disk was kept in vacuum at room temperature. Pyrrole vapour was brought into contact with the disk at room temperature. Under vacuum, liquid pyrrole evaporates from the pyrrole tube into the gas line leading to the IR gas cell. To achieve the optimum adsorption of pyrrole, pyrrole vapour was flowed through the IR gas cell. After that, the IR cell and gas line were evacuated to remove not only pyrrole vapour remaining in the cell and gas line but also the physisorbed pyrrole

from the catalyst surface too. The vacuum pump was operated till the IR spectra peaks of pyrrole vapour and physisorbed pyrrole totally vanished and there was no change in any other peaks of the spectra. Then, FT-IR measurement of the spectra of the pyrrole-adsorbed sample started at room temperature.

The vacuum pump was kept running while the sample disk and the IR gas cell were heated to remove all species desorbed from the sample surface out of the system in order to avoid disturbing the result spectra by such species. On the other hand, since the vibration would occur and bring about bad scans, the vacuum was switched off while the temperature was held constant for IR detection. The measurement was completed when all peaks of adsorbed pyrrole disappeared so that the IR spectra of the sample was identical to the one before pyrrole dosing.

4.2.2 Adsorption on catalysts surface by GC

4.2.2.1 Adsorption of Carbon dioxide

The basicity measurement of the catalyst using CO_2 adsorption was shown as follows:

In each experiment, 0.1 g of catalyst sample was placed in a stainless steel tube. At room temperature, 20 μl of CO_2 gas was injected, using a micro syringe, above the catalyst bed. The injection was repeated until the sample did not adsorb CO_2 anymore. The amount of CO_2 adsorbed on the catalyst during each injection was measured by thermal conductivity detector gas chromatograph(Shimadzu 8A). The operating conditions were listed below.

GC model	: Shimadzu 8A
Detector	: TCD
Detector temperature	: 80°C
Detector current	: 80 mA
He flow rate	: 30 ml/min

4.2.2.2 Pyrrole adsorption measurement by Flame Ionization Detector

Adsorption of pyrrole by using Flame Ionization Detector was performed by packing catalyst sample in a stainless steel tube. The tube was then placed inside a Gas Chromatograph. At 65°C, the vapour of pyrrole was injected at constant value. The injection was repeated until the sample did not adsorb pyrrole anymore. The amount of pyrrole adsorbed on the catalyst during each injection was meausred by flame ionization detector gas chromatograph Shimadzu 9A. The operating conditions are described below.

GC model	: Shimadzu 9A
Detector	: FID
Injection temperature	: 140°C
Column temperature	: 65°C
N_2 flow rate	: 30 ml/min