

CHAPTER IV EXPERIMENTAL

4.1 Catalyst preparation

In this study we prepared Cu/MFI, Pd/Cu/MFI, H-Co-silicate, Cu/Co-silicate to study the NO removal reaction. As for H-Co-silicate catalyst, it was supported by Prof. Inui's laboratory. The amount of cobalt incorporated into this catalyst is about 0.81 wt%. All catalysts were synthesized using rapid crystallization method as shown in Figure 4.1 proposed by Inui [97]. This synthesis is the advantage for both synthesized and metallosilicate zeolite catalysts.

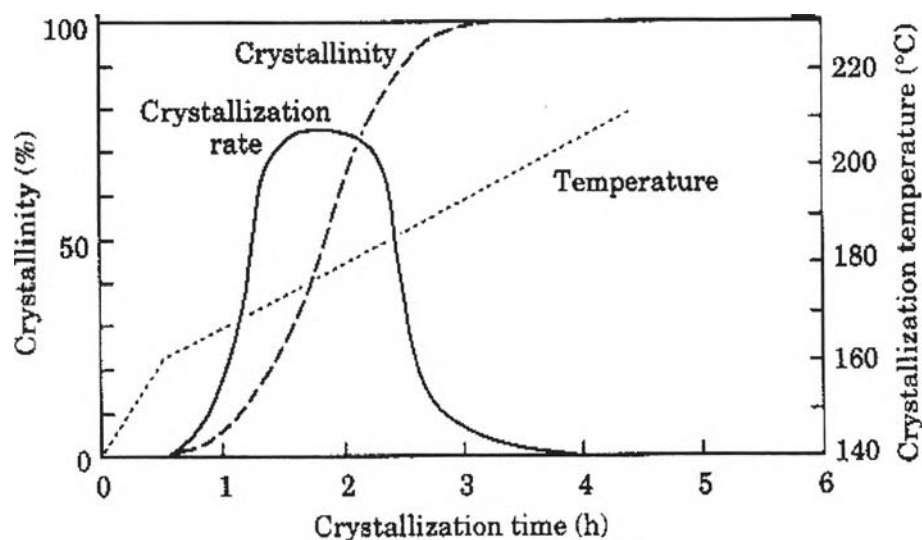


Figure 4.1 Illustration for rapid-crystallization method with a programmed temperature rise (Inui 1989 [97]).

Comparing the conventional slow crystallization method, rapid crystallization method involves in temperature programmed crystallization process that can minimize the crystallization procedure. The separation of precipitated gel from the supernatant fluid is also easy to perform by centrifuge. Furthermore, obtained crystallites by rapid crystallization procedure are uniform and small promoting high catalytic activity and

selectivity. The preparation of catalysts in this study was prepared in the following method.

4.1.1 Gel and decantation solution

For gel and decant preparation, TPABr (Tetra n-propyl Ammonium Bromide) and $AlCl_3$ were used as the source of organic template and Al, respectively. The atomic ratio of silicon to aluminium was set at 50. Two groups of solutions for gel and decant preparation were prepared separately. The compositions of reagents are described in table. 4.1 for as-synthesized Na form MFI. The details for preparation illustrated in Figure 4.2 were concisely described as follows: Continuous droplets of A-1 and B-1 were added into a solution of C-1 stirred using the stirrer with a magnetic bar at room temperature while maintaining a pH of 9-11 of the mixed compound. H_2SO_4 (conc.) or 1M NaOH is added to adjust the desired pH of solution. Then, the gel mixture was separated from the supernatant liquid by configuration. The gel mixture was milled in order to be uniform and fine crystallites as follows: milled 15 min \rightarrow centrifuged (to remove the left supernatant out) milled 15 min \rightarrow centrifuged \rightarrow milled 30 min. Finally, the gel mixture was obtained. Simultaneously, a decantation solution was prepared using solution A-2; B-2 and C-2 detailed in table 4.1 and followed the same procedure as gel preparation.

Table 4.1 Reagents prepared for the synthesis of Na/MFI

Solution for gel preparation		Solution for decant preparation	
A1 solution		A2 solution	
AlCl ₃	0.8998 g	AlCl ₃	0.8998 g
TPABr	5.72 g	TPABr	7.53 g
H ₂ O	60.00 ml	H ₂ O	60.00 ml
conc.H ₂ SO ₄	3.4 ml		
NaCl	1.0 g		
B1 solution		B2 solution	
Na ₂ OSiO ₂ H ₂ O	69.00 g	Na ₂ OSiO ₂ H ₂ O	69.00 g
H ₂ O	45.00 ml	H ₂ O	45.00 ml
C1 solution		C2 solution	
TPABr	16.00 g	NaCl	26.27 g
NaCl	51.54 g	H ₂ O	104.00 ml
NaOH	2.39 g		
H ₂ O	208.00 ml		
conc.H ₂ SO ₄	1.55 ml		

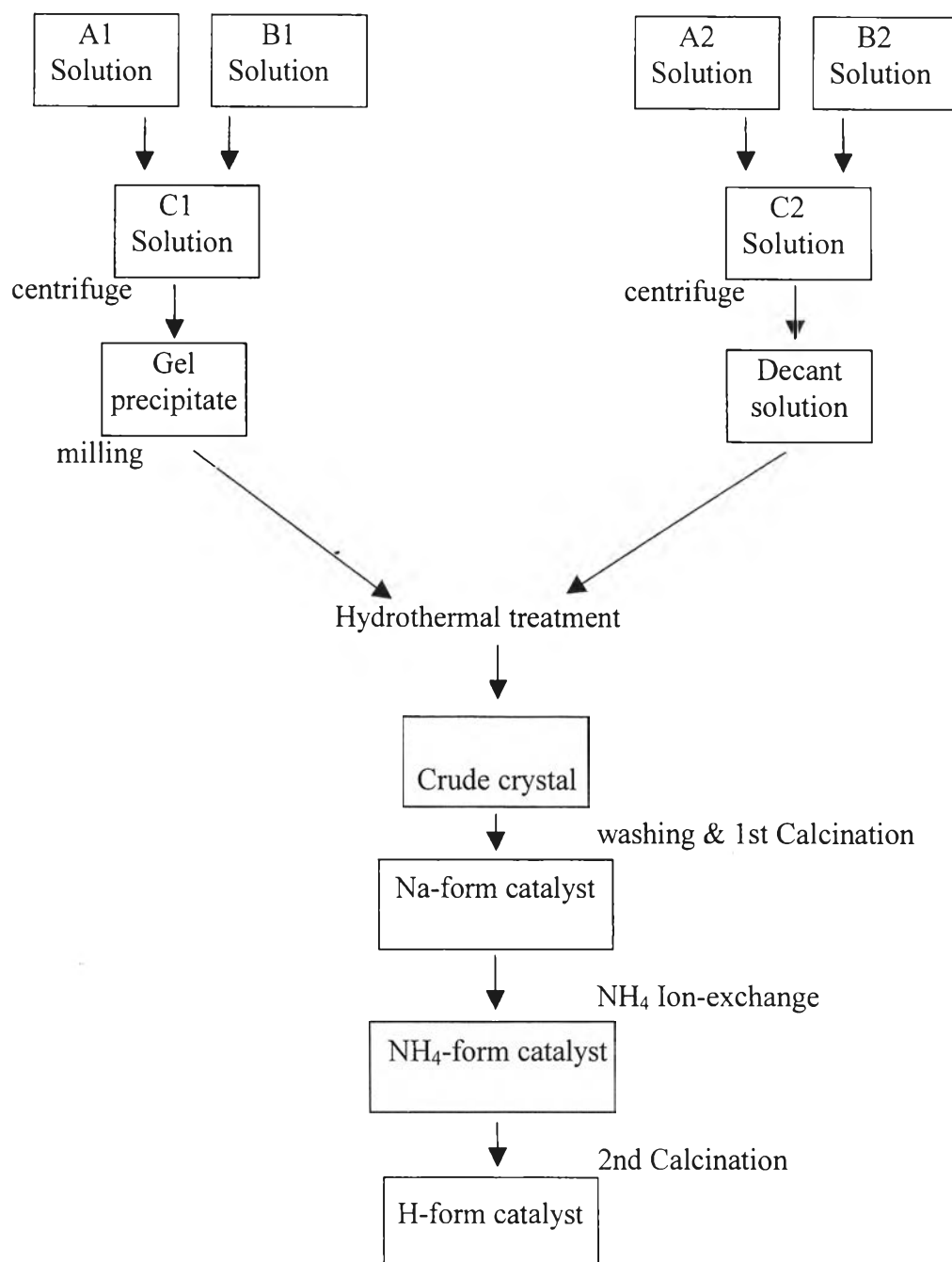


Figure 4.2 Preparation procedure of as-synthesized MFI by rapid crystallization method

4.1.2 Crystallization

After mixing the gel mixture with decant solution in a glass vessel contained in an autoclave. Nitrogen gas was introduced to replace the atmosphere in the autoclave and pressurized up to 3 kg/cm² gauge for 2 h to check the leak in the line. The autoclave was heated from room temperature to 160°C with the heating rate of 1.5°C/min and then up to 210°C with the heating rate of 12°C/h, followed by cooling the hot mixture to room temperature overnight. The produced crystallites were washed with de-ionized water several times until the amount of Cl⁻¹ was removed. Dechloride crystallites were separated from the mixture by centrifuge and dried at 110°C using an oven machine for around 3 h.

4.1.3 First Calcination

After drying at 110°C, the dried crystallite sample was calcined in an air stream with temperature programmed method. The heating rate used for calcination is about 8.75°C/min from room temperature to 540°C in about 1 h. The objectives of this procedure is to burn off the organic template and to leave the cavities and channels in the crystals. The catalysts after calcination was abbreviated as Na/MFI.

4.1.4 Ammonium ion-exchange

To transform Na into NH₄ form of zeolite crystals, the catalysts was ion-exchanged with 1M NH₄NO₃ at 80°C for 1 h. Subsequently, the mixture was cooled down to room temperature and ion-exchanged twice. The ion-exchanged crystal was washed with deionized water and dried at 110-120°C for at least 3h in an oven. After ammonium ion-exchange method, the catalyst obtained was NH₄/MFI.

4.1.5 Second Calcination

NH₄/MFI catalyst was calcined up to 540°C in order to remove NH₃ and nitrocompound species using the same temperature heating program as first calcination technique. Therefore, the NH₄ form zeolite was transformed into a H form that can be designated as H/MFI catalyst.

4.1.6 Metal ion exchange method

In this study amine complex salts and acetate compound were used as the sources of platinum group metals and copper, respectively. Approximately 1g of H-form catalyst

was ion-exchanged in an aqueous solution of the salts at 80°C (for copper source) or 90°C (for platinum source) all day. It was washed with deionized water, dried at 110°C overnight and calcined at 540°C for 3.5 h. The metal ion-exchanged H/MFI is designated as Me/MFI. And for Pd/Cu/MFI, Pd/MFI was ion-exchanged twice in an aqueous solution of copper acetate by the same method mentioned above. Then, the sample was dried overnight and calcined at 540°C by air.

4.2 Nitric oxide removal

4.2.1 Nitric oxide mixture

The feed gas compositions with a GHSV of 30,000 h⁻¹ introduced for the reaction of NO removal in this study are as followed;

NO	1,000 ppm
n-Octane	1,000 ppm
O ₂	2 mol%
He	balanced

4.2.2 Pretreatment condition

The pretreatment procedure used in this study concerns the hydro-treatment, thermal-treatment and hydrothermal-treatment conditions. Helium was used as carrier gas for all pretreatment. The effect of steam was carried out using 0-10mol% H₂O. As for thermal-treatment, the temperature studied is varied from 600-1,100°C. The heating rate was approximately 9.6°C/min from room temperature to 600°C and then about 1.67°C/min from 600°C to 1,100°C. Hydrothermal-treatment condition is more severe condition to be investigated. The condition is set with 10mol% of H₂O and varied in temperature conditions from 600 to 1,000°C. The heating rate for hydrothermal-treatment is similar to that used for thermal-treatment. Catalysts were pretreated by varied pretreatment conditions after introduction of metal species on the catalysts but Cu/Co-silicate pretreated at 1,000°C. At first, H-Co-silicate was pretreated at 1,000°C using the heating rate cited above. Then, copper as an acetate source was introduced in H-Co-silicate pretreated at 1,000°C by ion-exchange method. The advantage of this

procedure is to protect the transformation of active Cu^{2+} species to be inactive forms by the pretreatment at $1,000^\circ\text{C}$.

4.2.3 Reaction condition of SCR of nitric oxide

The catalytic reaction was carried out using an ordinary flow microreactor under atmospheric pressure. To reduce the pressure drop during the reaction test, the catalyst powder was tabletted, crushed, and sieved into

12 - 22 mesh. In order to investigate the activity for NO removal, catalyst was heated in a He stream from room temperature to 600°C and maintained at 600°C for 30 min. After that, a feed gas composed of 1,000 ppm NO, 1,000 ppm n-octane, 2mol% O_2 , and 0-10 mol% H_2O balanced with He was allowed to flow with a GHSV of $30,000\text{ h}^{-1}$. Every 10 min after the feed gas was introduced to ensure the steady state catalytic activity, the reactants and products were analyzed by gas chromatographs (Chrompack, Micro GC CP 2002 with MS-5A and porapak Q column) equipped with integrators. The reaction test was undertaken every 50°C diminishing from 600°C to 200°C followed the same procedure as mentioned above. The catalytic activity of nitric oxide reduction and n-octane combustion were investigated as the amount of N_2 and carbon oxides(CO_x ; CO_2+CO) produced, respectively. Figure 4.3 illustrated the reaction scheme for NO and n-octane conversion in this study.

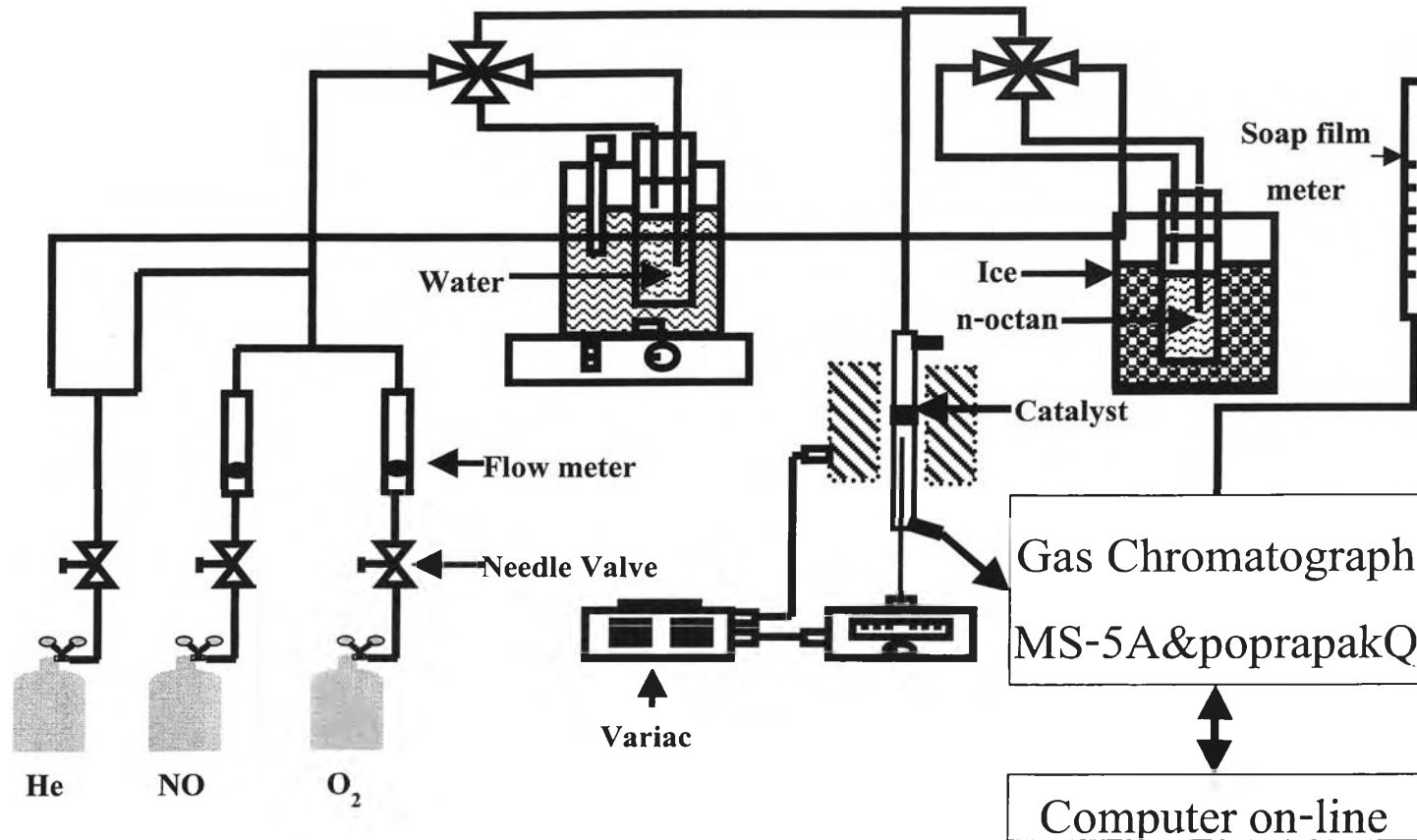


Figure 4.3 Schematic diagram of the reaction line for NO and n-octane conversion analyzing by gas chromatograph consisting of molecular sieve-5A and porapak Q columns

4.2.4 Decomposition of NO

In this study the reaction was carried out to investigate the capability of catalyst on NO decomposition in order to imply the Cu^{1+} species on the catalyst. A mixed flow of 1,000 ppm NO balanced with He to obtain a GHSV of $30,000 \text{ h}^{-1}$ was carried out for this purpose. The temperature program of NO decomposition was operated as same method as reaction test.

4.2.5 Stability test

The durability test of catalyst was taken into account at the reaction temperature of 400°C , the optimum temperature for NO conversion of 200%Cu/MFI, during NO conversion. At first, the reaction test was operated in a dry condition for 1 h and then 10mol% H_2O was introduced in the inlet reaction gas mixture for 1 h and subsequently the reaction test was changed back to a dry condition. Every 1 h, the reaction test was changed into dry and wet conditions as a cycle. This test was lasted 9 h to investigate the stability of catalyst.

4.3 Characterization

4.3.1 X-ray diffraction (XRD) analysis

The crystallinity, arrangement and spacing of atom in crystalline materials can be analyzed using X-ray diffraction analysis. The refraction or diffraction of the x-rays was monitored at various angles with respect to the primary beam x-ray diffraction analysis was carried out using an x-ray refractometer, Shimadzu XD-D1, with Ni-filtered $\text{CuK}\alpha$ radiation.

4.3.2 Scanning Electron Microscopy (SEM) analysis

The surface morphology of the catalyst was studied by scanning electron microscopy analysis. In this study we used Scanning Electron Micrograph model ISM-6400 operated.

4.3.3 BET method

BET method was applied to measure the surface area of sample. Shimadzu Flow Sorb II 2300 using liquid nitrogen as a probe molecule was operated in this study.

4.3.4 Inductively Coupled Plasma analysis (ICP)

The bulk metal composition of catalyst was analyzed by Inductively Coupled Plasma analysis, ICP Shimadzu ICPS-1000 III was applied in this study.

4.3.5 Infrared (IR) technique

In this work an IR technique as both exsitu IR and insitu FT-IR analyses were used. We used the exsitu IR method to characterize the structural properties of zeolite by the lattice vibration [112]. The vibration bands between 400 and 1200 cm^{-1} can indicate the structural framework of MFI type zeolite [113]. Supporting wafer mixed by KBr and sample at the weight ratio of 100:1 was recorded IR spectra by Nicolet mode Impact 400 equipped with a deuterated triglycine sulfate (DTGS) detector and supported with omnic version 1.2a on windows software. Before preparing the sample disk, the mixture of sample was milled into fine powder to avoid the scattering of IR spectra and be enable to make disk. Then, fine powder was compressed by hand in a mold to become a thin film attached to the mold. The mold containing a thin film was placed on the holder which IR spectra can penetrate the thin film thoroughly and directly. On the other hand, we adopted insitu FT-IR for pyridine adsorption to investigate the acidity of the sample [114].

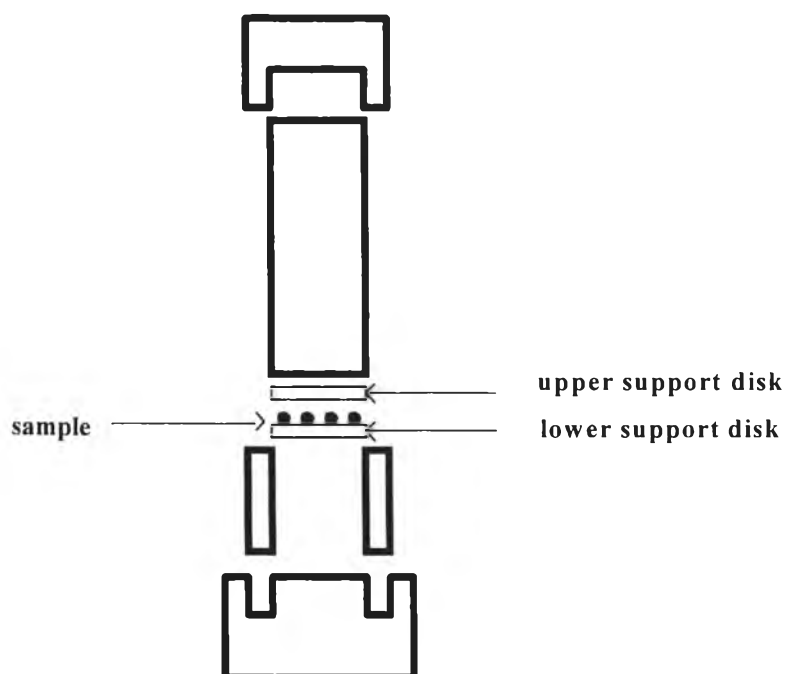


Figure 4.4 Body part of the die for preparing self-supporting sample disk.

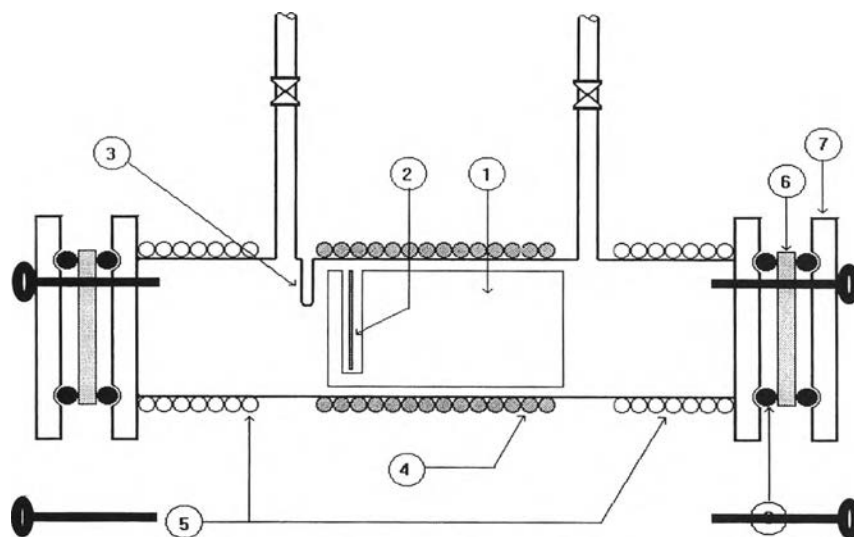
In this method, we used a pure sample at the weight of approximately 0.06 g that is depended on the difficulty of sample disk preparing and the ease of penetration of IR spectra. The pure sample was weighted and milled using the supporting disk method mentioned above. Then, it was poured and spread in the die as demonstrated in Figure 4.4. The sample was compressed using a manual hydraulic press at the pressure of 140-180 kg/cm² for 5 min. Subsequently, the thin film of sample was moved from the die and set in the holder of IR gas cell depicted in Figure 4.5.

The procedure of acidity measurement was described below. After setting the thin film of self-supporting sample in the gas cell, both ends of the gas cell were sealed with KBr windows applied to be a closed system. The sample was evacuated using a vacuum pump model Labconco 195-500 HP at 10⁻¹ torr for approximately 1 h to remove physisorbed species on the surface of sample. Pyridine vapor was circulated in the system by an electromagnetic circulating pump for about 1 h to ensure the whole surface of sample was adsorbed by pyridine vapor. Subsequently, the system was evacuated again to remove pyridine species in the gas phase. Temperature programmed desorption was carried out to investigate the amount and strength of pyridine adsorbed on the surface of catalyst from room temperature to 500°C using 50°C increasing step by step. The evacuation was continued while heating the sample and recording IR spectra at each temperature.

4.3.6 Temperature Programmed Reduction using H₂ as a probe molecule (H₂ TPR)

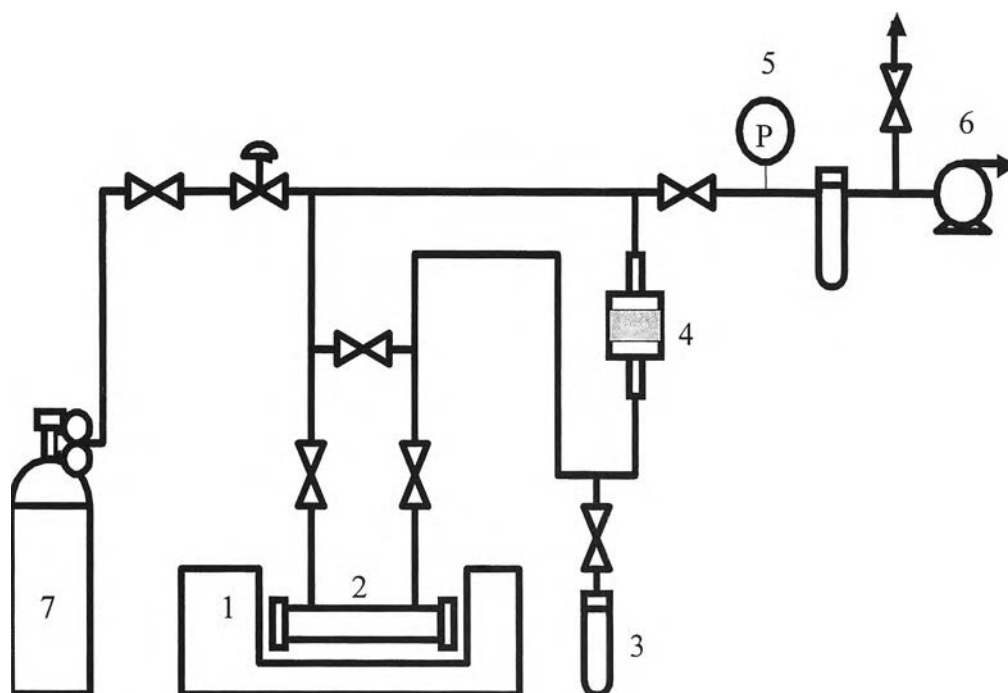
To investigate the reducibility of the catalyst, Temperature programmed reduction using H₂ as a probe molecule (H₂TPR) was carried out. At first, a 0.2 g of catalyst was oxidized at 500°C for around 2 h. Then 50 cc/min of 5%H₂/Ar stream was introduced to reduce the sample from room temperature to 750°C. The heating rate used in this study is 10°C/min. The concentration of hydrogen in the effluent gas was recorded by a thermal conductivity detector, TCD, after water vapor removing by a cold trap at methanol-dry ice temperature. The operating condition for H₂ TPR was fixed at:

carrier gas and flow	5%H ₂ /Ar, 50 cc/min
temperature of detector	80°C
detector current	80 mA



- | | |
|--------------------------|-----------------------|
| 1. Sample Holder | 5. Water Cooling Line |
| 2. Sample Disk | 6. KBr Window |
| 3. Thermocouple Position | 7. Flange |
| 4. Heating Rod | 8. O-ring |

Figure 4.5 Set of IR gas cell applied for the pyridine adsorption experiment



- | | |
|--------------------------------------|-------------------------------|
| 1) FT-IR Analyzer | 5) Digital pressure indicator |
| 2) IR quartz gas cell | 6) Vacuum pump |
| 3) Pyridine tube | 7) Nitrogen gas cylinder |
| 4) Electro magnetic circulating pump | |

Figure 4.6 Flow diagram of In situ FT-IR for acidity measurement by pyridine adsorption.

4.3.7 ^{29}Si Magnetic Angle Spinning Nuclear Magnetic Resonance (^{29}Si MAS NMR)

^{29}Si MAS NMR was tested to observe the structural Si in the sample as solid form. In this study we used JEOL 270SGX to operate and record the spectra.

4.3.8 Electron spinning resonance (ESR) analysis

Electron Spinning Resonance (ESR) analysis was chosen to study the presence or absence of the specie or metal component which has unpaired electron. In this study it is worth to investigate high spin Co^{2+} and Cu^{2+} on the sample using X-band JEOL mode JES-RE 2X spectrometer equipped with a JEOL microwave power 0.1 mW. The sample

was tested in both room temperature and liquid nitrogen temperature. Before ESR analysis, the sample was calcined at 500°C for 2 h to remove adsorbed species. Figure 4.7 showed diagram for ESR apparatus.

4.3.9 UV-Vis technique

Diffuse reflectance UV-visible spectra were analyzed to investigate Co species using a Shimadzu MPS-2000 spectrometer installed with a multi-purpose reflectometry attachment, RTA-2000 using BaSO₄ as a reflectance standard.

BLOCK DIAGRAM OF ESR (JES-RE2X)

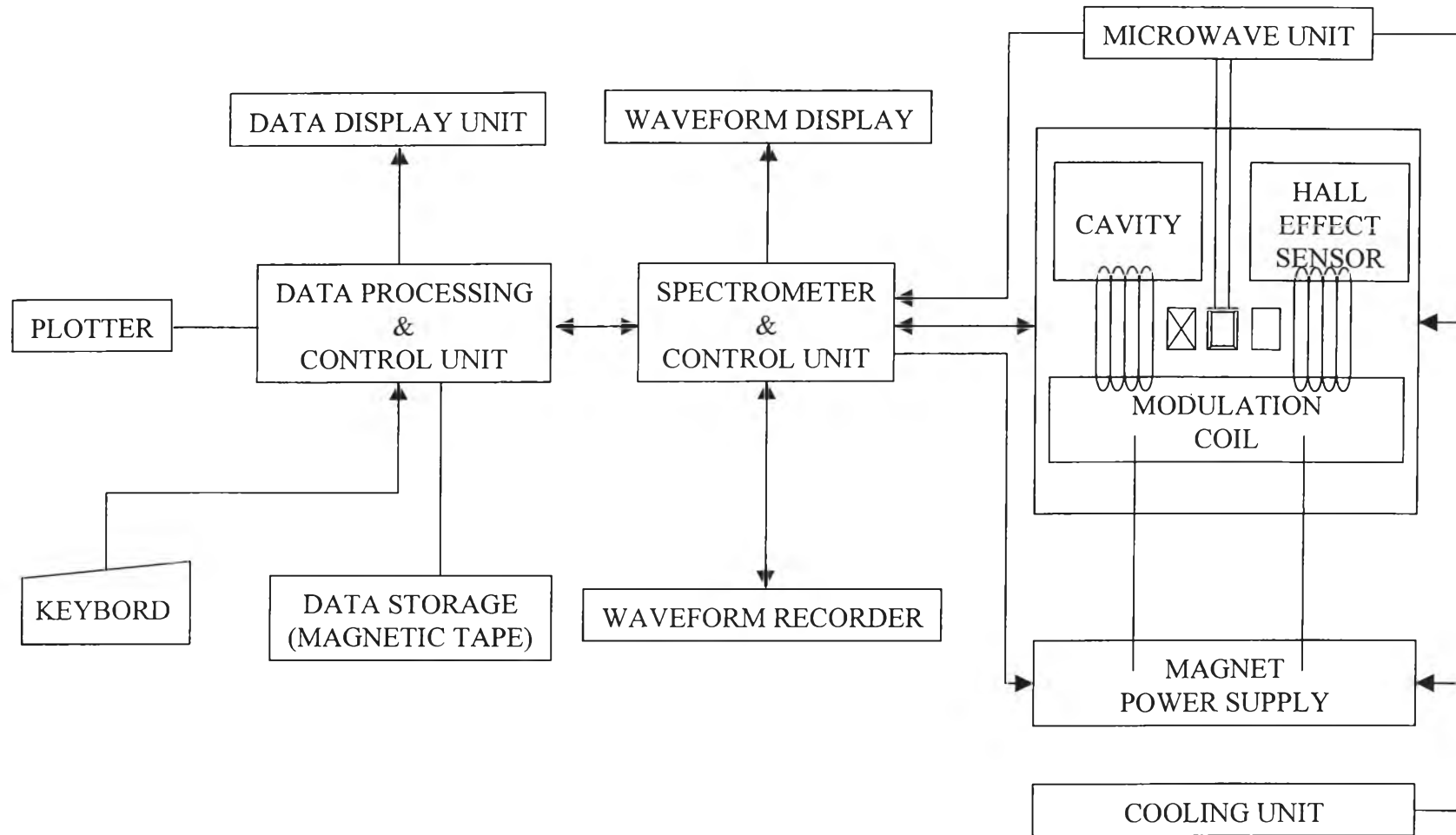


Figure 4.7 Block diagram of ESR (JES-RE2X)