

CHAPTER II

METHODOLOGY

2.1 Materials

For catalyst preparation materials,

- (gamma) Alumina ($\gamma\text{-Al}_2\text{O}_3$) used as catalyst support was analytical research grade (AR grade) and obtained commercially from Merck company. The size of Al_2O_3 was 70-230 mesh ASTM.

- Palladium (II) Chloride (PdCl_2) of 99 % purity from Aldrich Chemical Company.

- Concentrated Hydrochloric Acid (HCl) used as solvent obtained from J.T. Barker and has 36.5-38.0 % of concentration.

All of the gases were used without any further purification.

- Nitric Oxide (NO) 1.05 and 5.15 % in helium was obtained from Airco gases.

- 1.08 %, 5.25 % of Carbonmonoxide (CO) in helium, 3.15 % of oxygen (O_2) in helium, 3.16 % of nitrogen (N_2) in helium, and ultra high purity helium were commercially obtained from Thai Industrial Gas (TIG).

2.2 Catalyst Preparations

The palladium on alumina catalysts were prepared by the impregnation technique. Al_2O_3 was sieved to select only 180 - 70 mm. of particle size and heated to 140 °C for 20 hours to eliminate volatile matter. The palladium (II) chloride of known weight was dissolved in 10 cc of conc. hydrochloric acid. The solution was heated to 50 °C and slowly stirred until all of PdCl_2 was dissolved. This solution was diluted further to make a 50 cc solution and put

into burette. The color of this solution was red-brown. This was the “precursor” solution.

Al_2O_3 was put into a beaker and water was added to it until all Al_2O_3 was wetted. The precursor was very slowly poured onto wetted Al_2O_3 beaker which was simultaneously heated on a hot plate to 70-80 °C. This addition continued until all of precursor was used. This allowed accurate control of the amount of the active ingredient. The resulting catalyst was dried at 80 °C for overnight. Every catalyst was calcined in air at three different temperatures (500, 600 or 700 °C, programmed heating rate 10 °C/min) for 6 hrs.

The catalyst chloride ion was eliminated by washing with hot deionized water. The conductivity meter was used to detect the conductivity of washed water until the conductivity was closed to zero. The catalyst was again heated to 120 °C overnight to get rid of deionized water and kept in a desiccator under vacuum.

2.3 Catalyst Characterization

2.3.1 Surface Area Measurements

This characterization gives a surface area of porous material by using the Brunauer-Emmett-Teller method (BET). BET is the practical method that is used for determining surface area of porous materials. This method is based on the physical adsorption of an inert gas at constant temperature, -196 °C (boiling of nitrogen is -196 °C). The catalyst was outgased at 120 °C for overnight to remove volatile matter. The specific area of each catalyst was measured from five points of nitrogen adsorption isotherm at P/P_0 ratios lower than 0.3. Nitrogen was adsorbed with each catalyst until P/P_0 was closed to

unity. At P/P_0 ratios close to unity, the average pore radius and average pore volume were calculated.

2.3.2 X - Ray Diffraction (XRD)

XRD is one of the most frequently applied techniques in catalyst characterization. X-rays having wavelengths in the Å range, are sufficiently energetic to penetrate solids and are well suited to probe their internal structure. XRD is used to identify bulk phases and estimate particle. The width of diffraction peaks carries information on the dimensions of the reflecting planes. The Scherrer formula relates crystal size to line width:

$$\langle L \rangle = K\lambda/\beta/\cos(\theta)$$

in which β is the peak width at the middle height (radian)

K is a constant (often taken unity)

λ is a wavelengths (Å)

θ is the corresponding Bragg angle (radian)

In this work, X-ray measurements were measured with Rigaku Rotating with copper K- α line as the X-ray source.

2.4 Apparatus

The experimental system shown in Figure 2.1 is composed of three parts. The first part is the gas blending system, the second part is the differential flow reactor, and the last part is the gas chromatography used to analyze the concentrations.

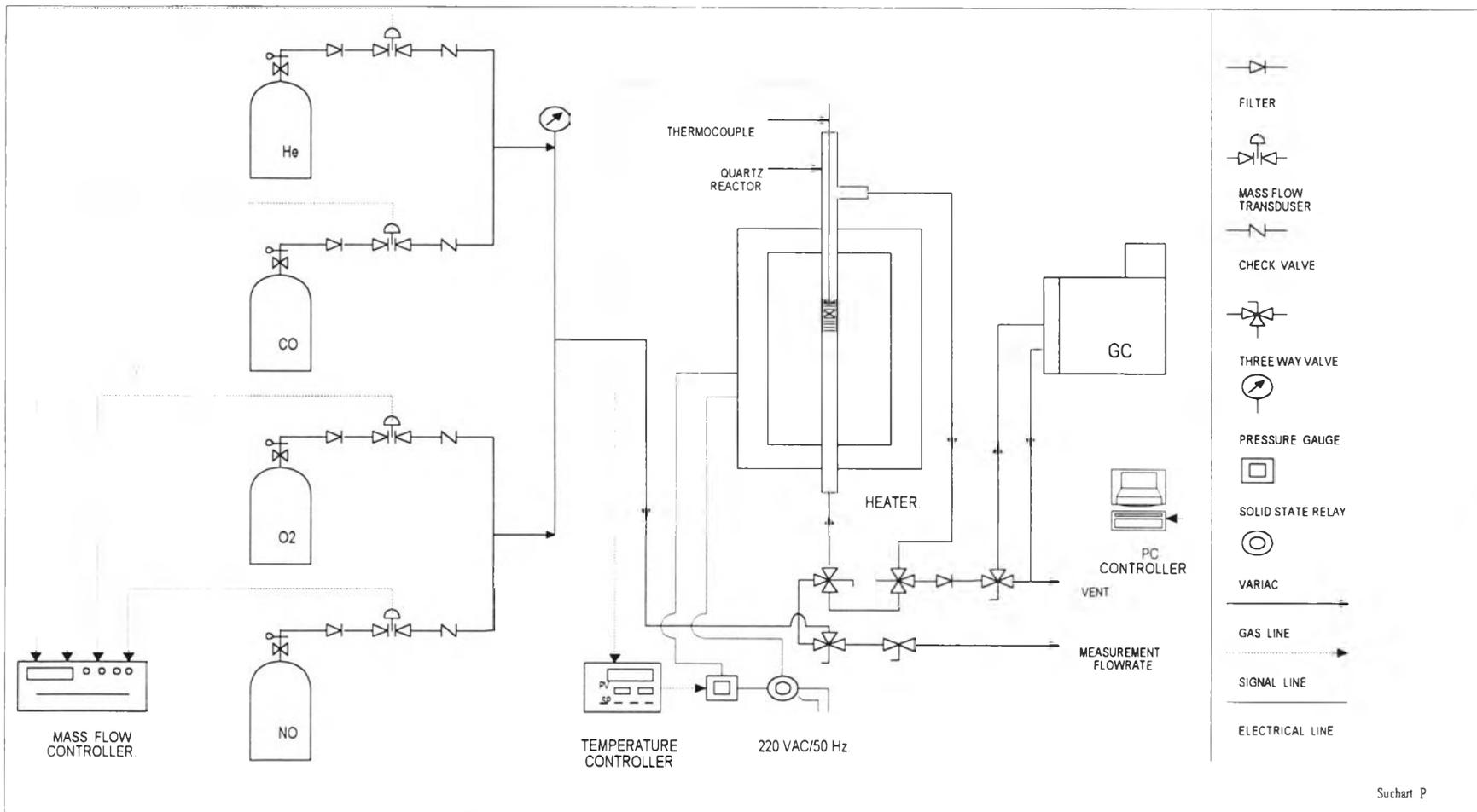


Figure 2.1 Schematic flow diagram.

2.4.1 Gas Blending System

We used mass flow controllers to control the flowrate of reactants. The massflow transducer and controller model 840 were commercially obtained from Sierra Instruments.

The gases used in this work consisted of helium, nitric oxide, carbonmonoxide, and oxygen. Oxygen was used to oxidize the active metal to form metal oxide. All of gases passed through micron filters and flowed through the massflow controller at a constant pressure of 20 psig. Downstream of massflow transducer, check valves were installed to prevent back flow. Each feed stream was mixed and then sent to the reactor.

2.4.2 Differential Flow Reactor

The catalytic test of NO reduction and CO oxidation was carried out in a 1/4 inch diameter quartz reactor at atmospheric pressure. 0.1 gm of zirconia was packed above the catalyst to prevent catalyst loss by entrainment in the gas and 0.2 gm of zirconia was packed at the bottom of the catalyst for support and preheating of the feed stream. The catalyst was placed in the middle of the reactor. The reactor was heated by an electrical heater and the temperature was controlled by a PID controller. The temperature of reaction was measured by a type K thermocouple made from chromel-alumel and located at the top of zirconia plug. The thermocouple was connected to the temperature controller. This controller was Yokogawa Instruments model UP 27. The controller was automatically self-tuned to setup the best proportional, integral and derivative control parameters. At steady temperature, the variation of temperature was +/- 0.1 °C.

2.4.3 Analytical Instrumentation

Gas Chromatography (GC) was used to measure both qualitative and quantitative composition of effluent gas up and downstream of the reactor. A Fisons 8340 model GC was used in this work with a thermal conductivity detector (TCD). The oven of GC was maintained at 60 °C. A molecular Sieve 5 °A packed column from Alltech was installed in the oven to separate the gases of interest using helium gas as carrier with 25 cc/min of flowrate. The TCD temperature was 120 °C and the bridge filament temperature was 210 °C. The signal from the detector was analyzed by the Chrom-Card program.

Both qualitative and quantitative analyses were obtained from the chromatogram. Qualitative analysis was obtained by comparison of the retention times with standard gases. Quantitative analysis was obtained using the calibration factors obtained with known concentration gases. The calibration used the external standard technique. The cycle of each measurement was about 20 minutes. N₂ and CO peaks in the outlet were used to observe the rate of NO reduction, selectivity to N₂ and CO oxidation rate, respectively.

2.5 Activity Measurements

The reduction of nitric oxide with carbonmonoxide on Pd/Al₂O₃ catalysts was studied at atmospheric pressure. After the catalyst was heated to the desired reaction temperature by a linear ramp of 10 °K/min in flowing helium, the catalyst was pretreated under oxidizing conditions using 150 cc/min of 0.2 % of O₂ in helium for 2 hrs. We assumed that all of the Pd on alumina was converted to PdO after the oxygen treatment. The pretreated catalyst was contacted with the reactant gas at constant total flowrate. The

conversion was calculated every 20 minutes by measuring the amount of N_2 and CO until the reaction reached steady-state. The results were plotted as rate of reaction versus time to obtain the NO reduction selectivity to N_2 and CO oxidation activity curve.

2.6 Reaction Studies

For NO reduction with CO, the rate of reaction depends on both NO and CO concentrations. One of the effective methods used to determine reaction orders specific rate constants is the method of excesses. A differential reactor was used to determine the rate of reaction as a function of concentration for heterogeneous systems. Because of the small amount of catalyst used, the conversion of the reactants in the bed was extremely small, as was the change in reactant concentration through the bed. As a result, the reactant concentration through the reactor was essentially constant and approximately equal to the inlet concentration. The reactor was considered to be gradientless and the reaction rate was considered spatially uniform within the bed.

To accomplish gradientless operation, the conversion was kept below 15 % in each experiment for kinetic measurements. The series of experiments were examined by varying the concentrations of both NO and CO.