CHAPTER III
EXPERIMENTAL SECTION

3.1 Materials

A commercial bimetallic palladium-silver catalysts supported on alpha alumina (Pd-Ag/α- Al$_2$O$_3$) manufactured by United Catalysts Inc. (UCI) has been used for this study. Table 3.1 summarizes characterization data for this catalyst provided by the manufacturer.

Table 3.1 Catalysts characterization data

Pd-Ag/α- Al$_2$O$_3$ sphere	egg-shell type
Nominal size	2$^\times$4 mesh
Pd (wt%)	0.030 ± 0.005
Ag (wt%)	0.235 ± 0.025
Al$_2$O$_3$ (wt%)	99.6 ± 0.1
Density (g/cm^3)	0.70 ± 0.05
Surface area (m^2/g)	30
Pore volume (cm^3/g)	0.45 ± 0.05

Blank studies were conducted on α-alumina pellets, 2.4 mm in diameter, obtained from Nissan Girldler Catalyst CO., Ltd.

The following reactant gases were used:

- Acetylene 5.01 ± 0.10 % balanced with N_2

- Ethylene 41.96 ± 0.20 % balanced with N_2

- Hydrogen 5.17 ± 0.10 % balanced with N_2 (used in acetylene hydrogenation)

- Ultra high purity (UHP) hydrogen (used in ethylene hydrogenation).

For constructing GC calibration curves of all reactants and product gases, a standard gas mixture with the following composition was used:

Hydrogen	3.05 ± 0.08%
Ethane	10.10 ± 0.20 %
Acetylene	3.95 ± 0.08%
Ethylene	23.11 ± 0.20%

Ultra high purity (UHP) nitrogen served as dilution gas.

3.2 Preparation of Pd-Ag/Al$_2$O$_3$ and alumina pellet mixture

In order to achieve a differential reactor operation, the conversion of reactant gases has to be low (i.e., less than 15%). Since the catalyst gave very high conversions, the catalyst used in these experiments had to be diluted with blank alumina. Pd-Ag/Al$_2$O$_3$ pellets and blank alumina pellets as dilutant were ground together in a high speed centrifugal ball mill to obtain intimate mixing. The centrifugal ball mill operated at a speed of 40 rpm for 15 minutes. After that, the mixture was sieved with a 80/120 mesh screen.

3.3 Catalyst characterization

3.3.1 Transmission electron microscopy (TEM)

The size and shape of metal particles were observed by transmission electron microscopy using a JEOL 2000FX instrument operated at 200 kV. When the impinging electrons interact with the solid, two types of scattering occur, i.e., elastic and inelastic scattering. Although both of them can be used in the interpretation of the results, the imaging techniques are mainly based on the elastic scattering process. In the bright field imaging method, strongly scattered electrons are stopped by the objective aperture. As a result, the more strongly scattering parts of the specimen, for example metal particles, appear darker on the image. Prior to TEM characterization, the catalyst was ground into fine powder. Then the catalyst powder was dispersed in inert solvent using an ultrasonic suspender. After that, a drop of the suspension was deposited on a thin carbon film supported on a standard grid and allowed to dry. This specimen was applied to TEM and each grid was surveyed to obtain an area that relates to the catalyst surface of interest.

3.3.2 Oxygen-hydrogen titration

Hydrogen titration of adsorbed oxygen was applied in a Quantasorb pulse chemisorption systerm to determine the metal dispersion, defined as the ratio of surface metal atoms to the total metal atoms in a given sample. First, pulses of oxygen were injected into the catalyst until no further oxygen uptake was observed. Then oxygen in the instrument was flushed out with helium at room temperature for 15 minutes. Then hydrogen pulses were injected to the catalyst until no further uptake of hydrogen was detected. The catalyst was flushed with helium at room temperature for 2 hours in order to remove the ß- phase hydride

hydrogen from the Pd bulk. Then, the adsorbed hydrogen left on the surface was titrated with oxygen by applying pulses of oxygen until no further oxygen uptake was observed. The latter oxygen uptake data was used to determined the amount of adsorbed hydrogen on the surface.

### 3.3.3 Temperture program desorption (TPD)

Temperature program desorption was carried out in micromeritcs TPD/TPR 2900 instrument with the temperature range of 40-600 $^\circ$ C. The Pd-Ag/ Al_2O_3 catalyst was reduced in pure hydrogen for 2 hours and then was exposed to 55 ml/min of hydrogen for 15 minutes. The catalyst was flushed with nitrogen and the baseline was allowed to be steady. Then the catalyst was heated with the heating rate of 5 $^\circ$ C/sec in nitrogen.

3.4 Apparatus

The experimental system is shown in Fig. 3.1. The system comprises of three main parts, i.e., gas blending system, a differential flow through reactor, and an effluence gas analyzer.

3.4.1 Gas blending system

All the reactant gases were first passed through a 7 micron filter in order to remove any small particles. In addition, N_2 gas was further purified by a Cole-Parmer drying tube to trap moisture. The flow rate of each gas was controlled by Sierra Instrument mass flow transducers to achieve the desired feed stream composition. Check valves were installed to prevent the back
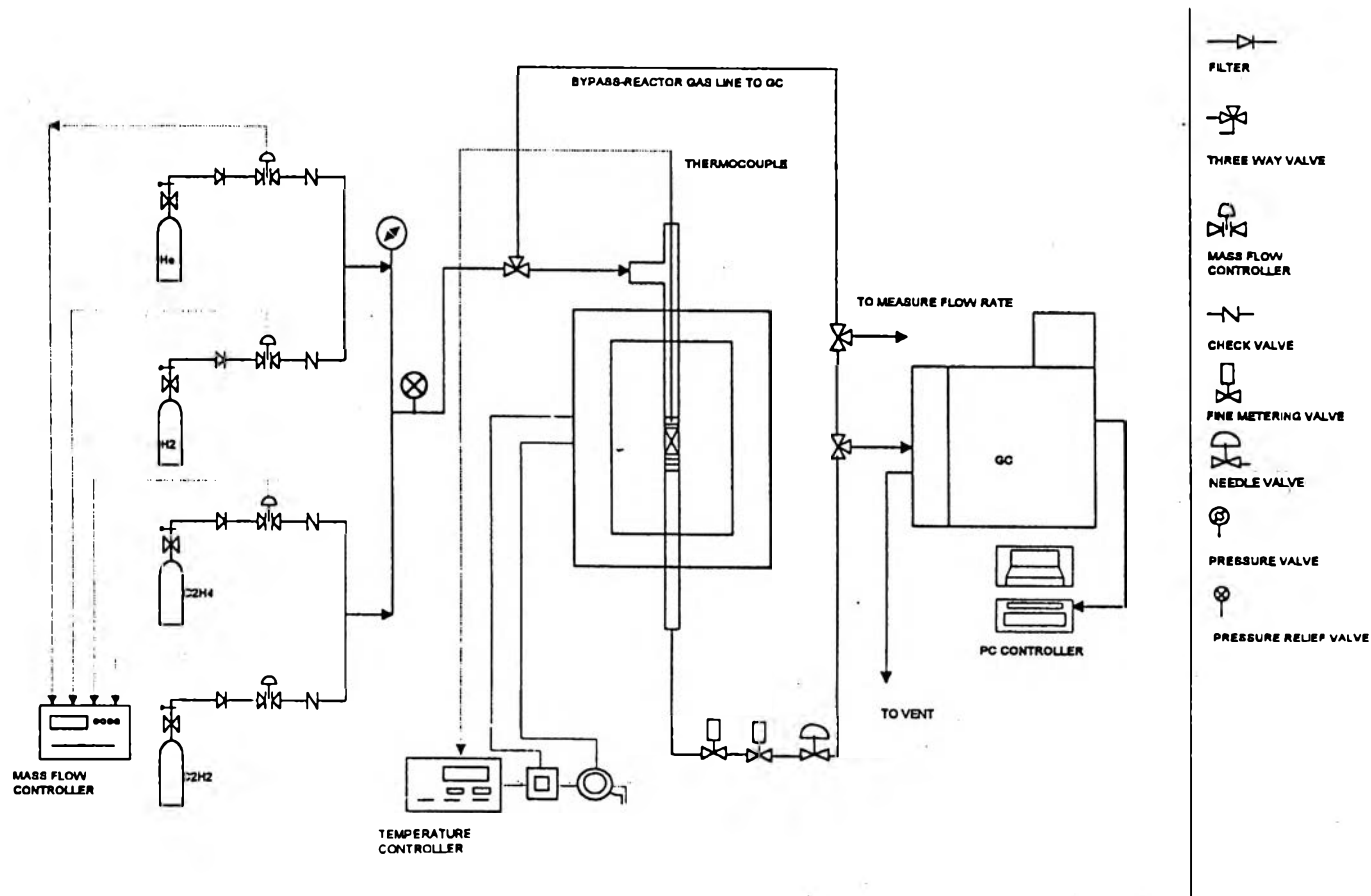
Figure 3.1 Schematic flow diagram of the instrument.

flow of gases. The feed stream was mixed and then fed to the reactor. At the inlet of reactor, a pressure relief valve was set at 20 bar maximum.

3.4.2 Differential flow reactor

Acetylene and ethylene hydrogenation reactions were carried out in a differential flow reactor. The reactor was constructed from three Swagelok unions (1/4" in diameter) loaded with 0.1000 g of catalyst mixture packed between two plugs of 0.15 g of zirconia wool. Inlet and outlet lines were 1/4" stainless steel tubes. The reactor was placed in an electrical heater equipped with a PID controller. The reaction temperature was monitored and controlled by a Yokogawa instruments model UP27 temperature controller which can hold the reaction temperature within ± 0.2 °C from a set point. Two fine metering valves and one needle valve were installed at the outlet of reactor. The pressure in the reactor was built up by adjusting the needle valve and maintained at the desired value of 18 kg/cm^2 (255 psi) by the 2 fine metering valves. The reactor pressure was measured by a pressure gauge at the effluence of the reactor.

3.4.3 Analytical instrumentation

Gas chromatograph was used to measure the composition, qualitatively and quantitatively, of feed stream and reactor effluence. A Hewlett Packard 5890 series II gas chromatograph equipped with thermal conductivity detector (TCD) was used. The analysis was conducted using a Carboxen 1004 micro-packed column at constant temperatures of 170, 350, and 150 °C for column, detector, and injector, respectively.

The compositions of feed stream and effluence gases were analyzed, both qualitatively and quantitatively, from the chromatograms. The retention time and peak areas of the analyzed gases were compared with those of the standard gas mixtures of known compositions. From the retention time, the type of gas was identified, while the relative concentration of each gas was obtained from integration of peak areas.

A sampling valve equipped with a 100 μl sampling loop was used to inject the reactor effluence gas every 15 minutes into the GC for analysis. From the decrease in concentration of acetylene and ethylene between reactor inlet and outlet, the conversions of these two gases were determined.

3.5 Reaction rate studies

After loading 0.1 g of fresh catalyst (0.00625 g of actual catalyst mixed with 0.09375 g of blank alumina as diluent) into the reactor , the catalyst bed temperature was raised to 200 °C in pure nitrogen stream at a flow rate of 35 ml/min. Once the bed temperature reached 200 °C, 6 ml/min of hydrogen was added to the nitrogen stream to achieve a hydrogen concentration of 15 %. The temperature was held at 200 ° C for 2 hours, and then the hydrogen stream was cut off and the bed was cooled down in a flow of pure nitrogen over a period of 3 hours at a cooling rate of 0.67 ° C/min to the reaction temperature of 80 °C. After that, the reactor was bypassed, with the catalyst remaining under pure, static nitrogen. Reactant gases and dilutant, set at the desired compositions, were allowed to flow for 15 minutes in order to stabilize the mass flow controllers. Then all the gases in the feed stream were cut off except the gas whose composition was assigned to be constant for that set of experiments. For instance, in case of hydrogen dependence of ethylene

hydrogenation experiments, in which hydrogen content was fixed at 3 mol %, ethylene and nitrogen gas were cut off. Then the valve was switched to allow the measuring of gas flow rate. The flow rate was measured and adjusted to the desired value. Then the other reactant gas was allowed to enter the system and the accumulated flow rates of these two gases were measured. The latter reactant gas was adjusted to achieve the desired accumulated flow rate. Finally, the nitrogen gas was added and its flow rate was adjusted to reach the expected total flow rate of 300 ml/min. The needle valve, installed at the position in front of the GC-vent selection valve was closed to keep the pressure in the system at 18 kg/cm^2. After that, the feed stream was injected into the GC to analyze the composition of each reactant gas in order to ensure that the desired feed stream compositions were obtained. A series of three needle valves between the reactor and the GC inlet line were set at fully closed position. Then the reactant mixture was switched to the reactor. When the pressure was built up to around 18 kg/cm^2, all the valves were adjusted to achieve and maintain the reactor pressure at the desired value through the experiment. The reactor effluence gas was injected into the GC every 15 minutes starting at 5 minutes from the time that the reactant was applied to the catalyst bed. When the reactant conversion rate reached the steady state, the time on stream was prolonged for at least another half hour and then the feed stream was cut off. Each run was reproduced to achieve the repeated steady state rate of reactant conversion, and then the experiments at other conditions were conducted.

The differential flow through reactor was used to find power rate laws. In order to achieve the differential reactor conditions and to avoid the effect of heat transfer limitations, the conversions were kept below 15% for the kinetic experiments. Since the catalyst mixture contained very small particles, it was assumed that the effect of internal concentration and temperature gradients

could be neglected. External transfer resistances depend strongly on the actual gas velocity over the catalyst bed. Tests of external limitations were conducted to find the flow rate in the region of no external limitation. Series of experiments were conducted at constant reactant feed compositions and constant temperature with various feed stream flow rates. For ethylene hydrogenation experiments, the compositions of the feed streams were fixed at 3 mol% hydrogen, 30 mol % of ethylene and balanced with nitrogen and the reaction temperature was fixed at 80 ° C while the total feed rates were varied, i.e., 150, 200, 300 and 400 ml/min . In case of acetylene hydrogenation experiments, the reactants fed to the reactor were 2 mol% of hydrogen and 1 mol % of acetylene. The reaction temperature was 80 ° C for each run. The feed flow rates used were 150, 200 and 300 ml/min, respectively. The reactant conversion rates were then plotted as a function of the feed stream flow rates. The flow rate in the region of no external limitation was determined from the region where the curve became horizontal, i.e., the region where the reactant conversion rate did not change with flow rates.

Series of experiments with various feed compositions and reaction temperatures were performed to obtain the rate expression of ethylene and acetylene hydrogenation reactions. For the ethylene hydrogenation part, the experiments were first conducted at fixed 3 mol % of hydrogen and a reaction temperature of 80 ° C, with ethylene concentration of 15, 20, 25 and 30 mol %, respectively, for each run to find the ethylene order. Secondly, ethylene concentrations were set at 30 mol% and the reaction temperature was kept at 80 ° C while the hydrogen concentration was varied from 2, 3, 4 to 5 mol % , repsecively. In order to determine the activation energy, various reaction temperatures, i.e., 60, 70, 80 and 90 ° C, were used while the hydrogen concentration was kept fixed at 3 mol % and the ethylene concentration at 30 mol %.

Similarly, for the acetylene hydrogenation part, first, hydrogen concentrations and reaction temperature were maintained constant at 2 mol % and 80 ° C, respectively. The acetylene concentration was varied from 0.6, 1, 1.5 to 2 mol%, respectively, to find the reaction order with respect to acetylene. Then, the acetylene concentration was set at 1 mol % and the reaction temperature was fixed at 80 ° C, while the hydrogen concentrations were varied from 1, 2, 3 to 4 mol % , repectively. To determine the activation energy, the experiments were conducted at reaction temperature of 70, 80, 90 and 100 ° C at constant concentrations of 2 mol % hydrogen and 1 mol % acetylene.

3.6 Evaluation of the experimental data

In case of ideal mixing and negligible influence of transfer limitation, the experimental conversion rates of a reactant j, per unit mass of catalyst can be evaluated from

$$R_j = (y_{j, in} F_{in} / W) \zeta_j \qquad \ldots\ldots (1)$$

where $y_{j,in}$ = mole fraction of reactant j in the feed stream

F_{in} = total feed stream flow rate

W = weight of catalyst

ζ_j = degree of conversion of component j defined as

$$\zeta_j = (F_{j, in} - F_{j, out}) / F_{j, in} \qquad \ldots\ldots (2)$$

where $\qquad F_{j,\,in}$, $F_{j,\,out}$ = input and output reactant j flow rate,

respectively

The rate of conversion of acetylene R_{C2H_2} can be evaluated from

$$R_{C2H2} = (F_{C2H2,\,in} - F_{C2H2,\,out})/W \qquad \ldots\ldots (3)$$

The calculated rates were used to determine the order of hydrogen, ethylene and acetylene as well as the apparent activation energies of the ethylene hydrogenation reaction and acetylene hydrogenation reaction.

The determination of reactant kinetic order

For the following reaction;

$$A + B \longrightarrow C \qquad \ldots\ldots (4)$$

the typical power rate law is;

$$r = k\,A^a\,B^b \qquad \ldots\ldots(4)$$

where

$\qquad r$ = reaction rate

$\qquad A,B$ = concentration of reactant A and B, respectively

$\qquad a,b$ = kinetic order of reactant A and B, respectively

$\qquad k$ = apparent rate constant

Equation (4) expressed in the logarithmic form is;

$$\log(r) = \log k + a \log A + b \log B \quad ....(5)$$

Equation (5) is a linear function between rate and concentration of all the reactants. Since the apparent rate constant, k, is assumed to be a function of temperture only, the first term in equation (5) becomes a constant as long as the temperture remains constant. In order to determine the kinetic order of one of the reactants, the temperature and the concentration of one of the reactants must be kept constant while the concentration of the other reactant is systematically varied. The plot of eqution (5) using the data obtained from the experiments is a straight line and its slope provides the kinetic order of that reactant.

To determine the apparent activation energy.

The rate constant, k, is usually expressed with the following equation;

$$k = A_0 \, e^{(Ea/RT)} \qquad ....(6)$$

Where

A_0 = constant value

Ea = apparent activation energy

R = gas constant

T = absolute temperature

Equation (6) can be expressed in logarithmic from as the following equation

$$\ln k \;=\; \ln A_0 \;+\; Ea/RT \qquad \text{........(7)}$$

The plot between the value of $1/T$ and $\ln k$ yields a straight line. The apparent activation energy is determined from the slope of the plot times the value of gas constant, R.