CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Catalysts

The catalysts used in this research are Pt, Pd and Rh, loading on commercial ceramic-honeycombed monolith. Catalyst samples were provided by Johnson Matthey Co.,Ltd. Platinum catalyst contains 196 cells per square inch (cpsi) while the cell densities of palladium and rhodium catalysts are both 200 cpsi. The catalysts used for the laboratory reactor were in the form of cylindrical with 5 mm in diameter and 10 mm in length.

3.1.2 Volatile Organic Compounds

Diethylamine (DEA) represented for nitrogenated volatile organic compound was used in this research. This compound presents environmental hazards as referred in the previous chapter. Anhydrous liquid amine was vaporized in a vapor saturator and then its vapor was carried through the system by He. The composition of amine in feed was adjusted at a desired value by controlling the vapor saturator temperature and He flow.

3.1.3 Gases

The gases used in this study were high purity helium and oxygen obtained from Praxair (Thailand) Co., Ltd and Thai Industrial Gases Ltd. All gases were supplied with an initial pressure of 2000 psig and the outlet pressure was controlled by a pressure regulator.

3.2 Experimental Apparatus and Setup

The experimental apparatus is schematically shown in Fig. 3.1. It consists of three sections: (i) gas mixing system, (ii) catalytic reactor, and (iii) analytical instrumentation.

3.2.1 Gas Mixing System

This section is used for mixing gases before being introduced to the reactor. It consists of helium, oxygen, and vapor of amine. Helium was used as dilute carrier gases for amine vapor. Oxygen was used as an oxidizing gas. All gas streams were equipped with valves, filters to remove dust and particles before pass through the flow measurement. A calibrated mass flow controller and rotameters were set up to control the flow rate of the gas streams. Anhydrous liquid diethylamine was vaporized as saturated vapor. Its vapor pressure was controlled in the water bath and then was carried by the helium flow into the feed stream. All gas streams were controlled to flow in one direction by using check valves. Each feed stream was mixed in a mixing chamber and delivered to the reactor.

3.2.2 Catalytic Reactor

The reactor was made of a pyrex glass tube with a inside diameter of 6 mm. The reactor could be electrically heated in the furnace with an on-off temperature controller. A type-K thermocouple inserted into the reactor was connected to the temperature controller for measuring the reaction temperature. A variable voltage transformer was used for controlling electrical current to the heating coil in the furnace. By appropriate adjustment of the variac and the temperature controller, isothermal conditions can be achieved with a maximum variation of $\pm$ 1 ^{o}C at steady state.

3.2.3 Analytical Instrumentation

The effluent gas leaving the reactor was sampled by a manual gas-sampling valve and immediately analyzed on a Shimadzu 14A gas chromatograph equipped with a thermal conductivity detector (TCD). The column utilized in the chromatograph was Porapak Q, 80/100 mesh, 2 mm ID x 2 ft in stainless steel. The temperature of the column was maintained at 30 $^{\circ}$C and the flow rate of carrier gas was controlled at 25 ml/min throughout the analysis. The output of chromatograph was recorded by a Shimadzu C-R4A Chromatopac. The observed peaks were identified by comparison of the retention times obtained from injection of standard gas samples. The composition of oxygen and carbon dioxide in the effluent gas was determined by comparison of the calibrated peak area of standard gas samples. In order to increase the accuracy, the conversion of amine to CO_2 was measured at least 3, usually 4 or 5 times, under each set of steady state condition and the results were averaged.

3.3 Methodology

3.3.1 Catalyst Characterization

The total surface area and cell densities of three commercial-honeycombed monolith catalysts were characterized prior to experimental run. To measure total surface area, nonspecific physical adsorption has generally been used. This common method is used routinely in most catalyst studies and it is developed by Brunauer, Emmett, and Teller, so called BET surface area analysis (Satterfield, 1991). The measurements were performed by using a Micromeritics Autosorb as an analyzer. The catalysts were degassed at 150 $^{\circ}$C for 2 hours prior to measurement of surface area. A standard procedure for determining the total surface area is based on the adsorption of N_2 at liquid N_2 temperature onto the surface of the catalysts. In comparison of different

Fig. 3.1 Schematic of the experimental setup.
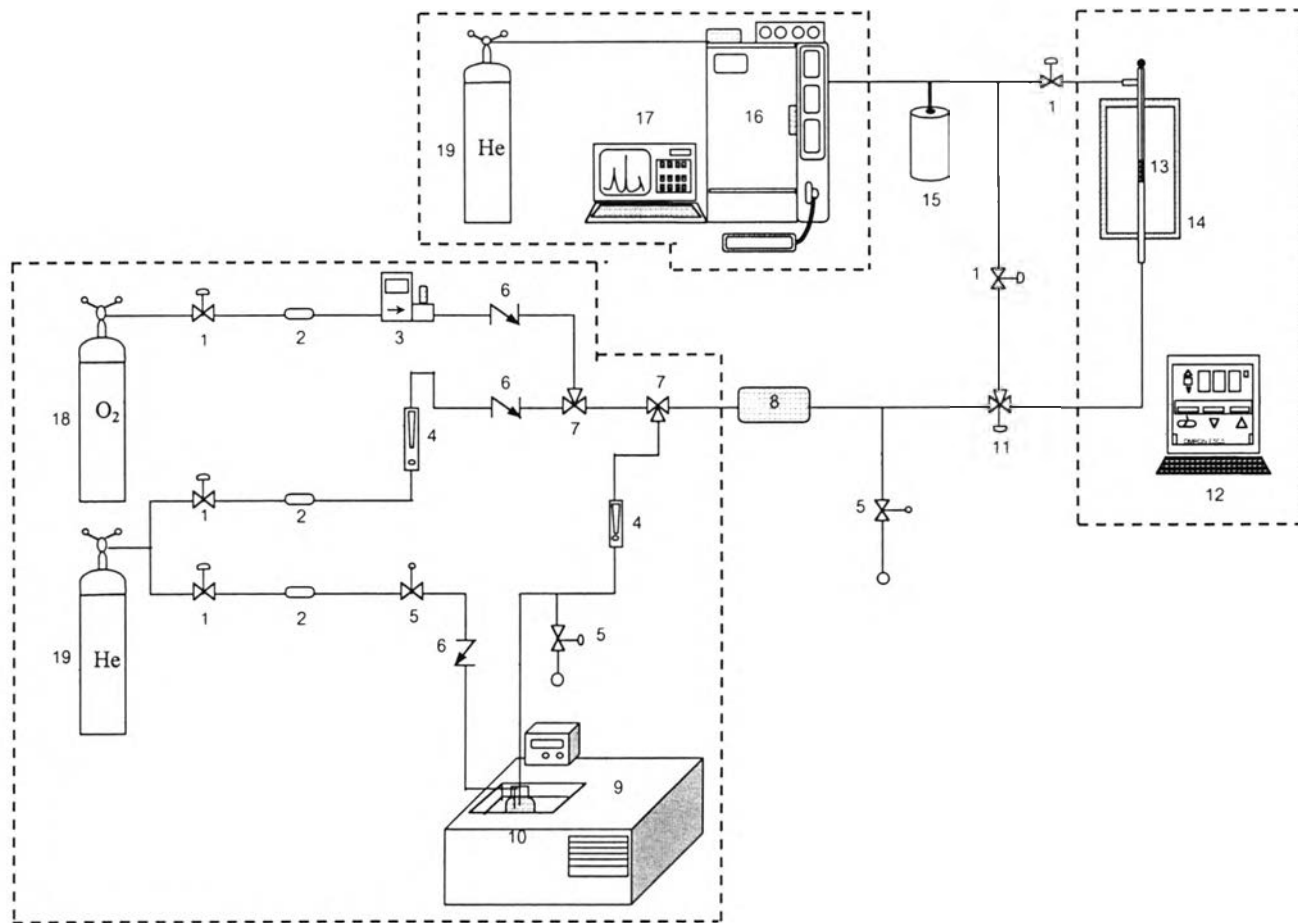
Description:

1: Ball valves

2: Filters

3: Calibrated mass flow controller

4: Rotameters

5: Needle valves

6: Check valves

7: Tees

8: Mixing chamber

9: Water bath

10: Vapor saturater

11: Three-way valve

12: Temperature controller

13: Reactor

14: Furnace

15: Trap Unit

16: Gas chromatograph

17: Data processor

18: High purity O_2 gas tube

19: High purity He gas tubes

catalysts or the effect of various treatments on catalytic activity, it is necessary to know the extent to which a change in activity is caused by a change in the surface area of a catalyst.

The number of channels, in terms of cell densities, was also characterized. It was measured by counting the number of channels per square inch and then was recorded in the unit of cells/in^2 (cpsi).

3.3.2 Activity Measurement

The catalytic activity of all catalysts was measured in terms of "light-off temperature". Three types of commercial monolith catalyst were prepared in the cylindrical form and then were placed into the center of glass tube reactor. The experiments were carried out by running the steady state amine oxidation in a fixed bed glass tubular reactor with the feed composition of 0.2 vol% (2,000 ppm) amine vapor, 21 vol% O_2 and balanced in helium. The temperature of the catalyst bed was increased continuously from 200 to 400 °C. The product sampling began after the reactant gases had passed through the catalyst bed for 30 minutes to allow the system to reach the steady state. The product was analyzed by a gas chromatograph to find the conversion of amine to CO_2. The plots of CO_2 formation as a function of reaction temperature were represented the activity curves. These activities were measured in terms of the temperature corresponding to 50 percents CO_2 formation. The lower the temperature for 50 percents CO_2 formation, the greater the catalytic activity. In this present study, the most active catalyst will be further studied in the next experimental part. The effects of reactant concentration and reaction temperature on the reaction rate will be studied over the most active catalyst. The kinetic parameters will also be evaluated by taking the reactions over the most active catalyst in order to establish the kinetic model.

3.3.3 Reaction Rate Studies

The experiments were carried out over the most active catalyst under the atmospheric pressure. Differential method was applied for the reaction rate measurement in this present study. The effects of diethylamine and oxygen concentrations on the reaction rate will be studied as well as the effect of reaction temperature.

3.3.3.1 Effect of Diethylamine Concentration

The dependence of reaction rate with respect to DEA concentration was determined under the constant temperature at 250 °C. The reactant mixtures consisted of 2,000, 5,000, and 8,000 ppm of DEA concentrations and 15, 20, 25, and 30 vol% of oxygen concentrations balanced in helium. All experimental runs were conducted with the total flow rate of 260 ml/min under the atmospheric pressure. The reaction rate as a function of DEA concentration was investigated at different oxygen concentrations.

3.3.3.2 Effect of Oxygen Concentration

The effect of oxygen concentration was examined under the constant temperature at 250 °C. The concentrations of 15, 20, 25, and 30 vol% were tested and the experiments were conducted with three different DEA concentrations of 2,000, 5,000, and 8,000 ppm, respectively. The total flow rate of 260 ml/min was used and the reactions were performed under the atmospheric pressure. The relationship between the reaction rate and oxygen concentration was studied.

3.3.3.3 Effect of Reaction Temperature

The reactions were examined at the DEA concentrations of 2,000, 5,000, and 8,000 ppm. The effect of reaction temperature on the reaction rate

was studied by varying the reaction temperatures of 250, 265, and 275 $^{\circ}$C, respectively. All experimental runs were conducted with the total flow rate of 260 ml/min under the atmospheric pressure.

3.3.4 Kinetic Studies

3.3.4.1 Reaction Order with respect to Diethylamine and Oxygen Concentrations

A series of experiments was carried out with the oxidation of diethylamine (DEA) over the most active honeycomb monolith catalyst using a differential reactor. Conversion was kept below 10% in every experiment. The steady state reaction rates of CO_2 formation measured in these experiments were later used for modeling the kinetics of the DEA oxidation. According to the relationship between the reaction rate and the concentration, the reaction order can be determined by using the differential method (Fogler, 1992). Determination of the reaction order with respect to the DEA concentration was performed at a given temperature and oxygen concentration. The range of DEA concentration studied was 1,000 - 10,000 ppm and O_2 concentration balanced in helium was kept constant at 21 vol%. In the case of the reaction order with respect to the O_2 concentration, O_2 concentration studied was in the range of 10-35 vol% and DEA concentration balance in helium was kept constant at 2,000 ppm. The mixed reactant gas was passed through the reactor packed with the catalyst. The total volumetric flow rate under reaction conditions was approximately 260 ml/min. The oxidation reactions were investigated in the chemical kinetic regime at the temperatures of 250 and 265 $^{\circ}$C.

3.3.4.2 Apparent Activation Energies

The apparent activation energies of the reactions were determined experimentally by using a feed of 2,000 ppm diethylamine(DEA), 21 vol% O_2

balanced in helium. The rate of CO_2 formation was measured at different temperatures. A series of experiments were carried out over the most active catalyst and performed under the atmospheric pressure with a total flow rate of 260 ml/min. The reaction temperatures were varied in the range of 250 to 400 °C. It can be seen that a plot of (ln r) versus (1/T) should be a series of straight lines whose slopes are proportional to the apparent activation energies.

3.3.5 Data Evaluations and Calculations

After the results from the quantitative analysis are evaluated, the CO_2 formation is calculated using the stoichiometric balance of the oxidation reaction of diethylamine (DEA) as shown in Eq. (3.3):

$$CO_2 \text{ Formation (\%)} = \frac{0.25[CO_2] * 100}{[DEA]} \qquad (3.3)$$

In kinetic measurements, since the CO_2 formation is kept below 10%, the rate of CO_2 formation can be determined in terms of initial reaction rate. The initial reaction rate is directly measured by the differential method according to Eq. (3.4):

$$r_o = \frac{F_o.X}{W} \qquad (3.4)$$

where r_o =   the initial reaction rate of CO_2 production, gmoles.sec^{-1}.g^{-1}catalyst;

            F_o =   the total molar volumetric flow rate, gmoles.sec^{-1};

            X   =   the conversion of DEA to CO_2;

            W   =   the catalyst weight, g.

For kinetic model, the kinetic parameters such as reaction order and apparent activation energy can be determined from the Arrhenius equation.

The reaction order with respect to diethylamine (DEA) can be determined by varying the DEA concentration as kept constant O_2 concentration. On the other hand, the reaction order with respect to O_2 can be determined in the opposite way. The most general way to establish which step is the rate limiting is also use of the Arrhenius equation from which activation energies can be determined.

$$k = k_o \exp (- E_a / RT) \qquad (3.5)$$

$$\ln k = \ln k_o - \frac{E_a}{R} (1/T) \qquad (3.6)$$

where
k = the rate constant, depends on the temperature;

k_o = the pre-exponential factor;

E_a = an apparent activation energy, kcal/mole;

R = the universal gas constant = 1.987 cal mole^{-1}K^{-1};

T = the absolute temperature, K.