

## CHAPTER III

### EXPERIMENTAL SECTION

In this research work, the plasma promoted catalytic oxidative coupling of methane was carried out at atmospheric conditions. The wire and plate electrodes made of stainless steel were used to generate an AC corona discharge in the quartz tube reactor where the reaction took place. Both the feed and product streams were analyzed by gas chromatographs comprising of thermal conductivity and flame ionization detector. The purpose of this work was to determine effects of ethane partial pressure, flow rate, catalyst types, applied voltage and frequency on methane conversion and product selectivities.

#### 3.1 Materials

##### 3.1.1 Catalyst Preparation Materials

- KL zeolite
- NaX zeolite
- NaOH treated Y zeolite
- Platinum (II) acetylacetonate ( $[\text{CH}_3\text{COCH}=\text{C}(\text{O}-)\text{CH}_3]_2\text{Pt}$ ) with Pt of 97% purity manufactured by Aldrich Chemicals

##### 3.1.2 Gaseous Reactants

- Methane ( $\text{CH}_4$ ) UHP grade of 99.97% purity was obtained from ATS.
- Oxygen ( $\text{O}_2$ ) research grade of 99.99% purity was obtained from TIG.
- Ethane ( $\text{C}_2\text{H}_6$ ) research grade, 99.99% was supplied by TIG.
- Helium (He) of 99.995% purity was supplied by TIG.

- Hydrogen (H<sub>2</sub>) of 99.999% purity was supplied by TIG.

### 3.2 Catalyst Preparation

In this work, the catalysts were prepared at 1wt.% loading of platinum (Pt). Before addition of the metal, KL zeolite was dried in an oven at 110°C overnight and calcined at 400°C in a dried air with a constant flow rate of 100 ml/min g of catalyst for 5 h with a temperature ramp of 3°C/min. The incorporation of platinum metal into the zeolite was performed using the chemical vapor deposition (CVD) method. Weighed platinum (II) acetylacetonate (Pt (AcAc)<sub>2</sub>) was mixed physically with the dried zeolite under nitrogen atmosphere. The mixture was loaded into the reactor tube under a helium flow rate of 2 ml+/min. The mixture was slowly ramped to 40°C and held there for 3 h, and then ramped again to 60°C and held again for 1 h. The procedure was repeated by increasing temperature to 80, 90 and 100 °C, respectively. After further ramping to 100°C, the mixture was held for 1 h to sublime the Pt(AcAc)<sub>2</sub>. After sublimation, the mixture was ramped to 130°C and held for 15 minutes to ensure that virtually all of Pt(AcAc)<sub>2</sub> was sublimed. The reactor was cooled to room temperature, and the sample was removed. At this point, the sample was ramped to 350°C in flow of air for 2 h and calcined at that temperature for 2 h to decompose the platinum precursor. The resultant Pt/KL catalyst was stored in a desiccator. All experiments were the same as above expect for the change of new zeolites (NaX and NaOH treated Y) while the others kept constant. The percentages of platinum on three zeolites were analyzed by atomic absorption spectroscopy. The analysis results of actual platinum loadings were 1.00, 0.98 and 0.98 % for KL, NaX and NaOH treated Y zeolites, respectively.

### 3.3 Experimental Setup

The schematic diagram of the studied corona discharge system used throughout this study is illustrated in Figure 3.1. The system can be categorized into three sections i.e., the reactant gases mixing section, the reaction section and the analysis section.

#### 3.3.1 Reactant Gases Mixing Section

This section was utilized for blending gases to a desired flow rate and a given composition before being flowed to the reactor. All reactant gases used in this experiment were used without any further purification. All gases were passed through 7-micron stainless steel filters in order to trap any foreign particles in the gases. Sierra mass flow controllers were used to control a volumetric flow rate of each gas. The check valves were placed downstream of all mass flow controllers to protect from the back pressure effect.

A pressure gauge was placed downstream of the mass flow control module just prior to the inlet zone of the reactor to monitor the total pressure in the line of gaseous stream. Since all the experiments were conducted at atmospheric pressure, the gauge had to be read zero. Also, this gauge was to ensure that the pressure in the overall system was not too high to cause leakage around the reactor.

#### 3.3.2 Reaction Section

##### *3.3.2.1 Power Supply Unit*

The schematic diagram of the power supply unit in series is illustrated in Figure 3.2. The domestic AC input of 220 V, 50 Hz was connected to the DC power supply converter to convert to relatively low DC current, then pass through a function generator for varying frequency in range 0-800 Hz. The output pass through a 500 watt amplifier, in order to amplify

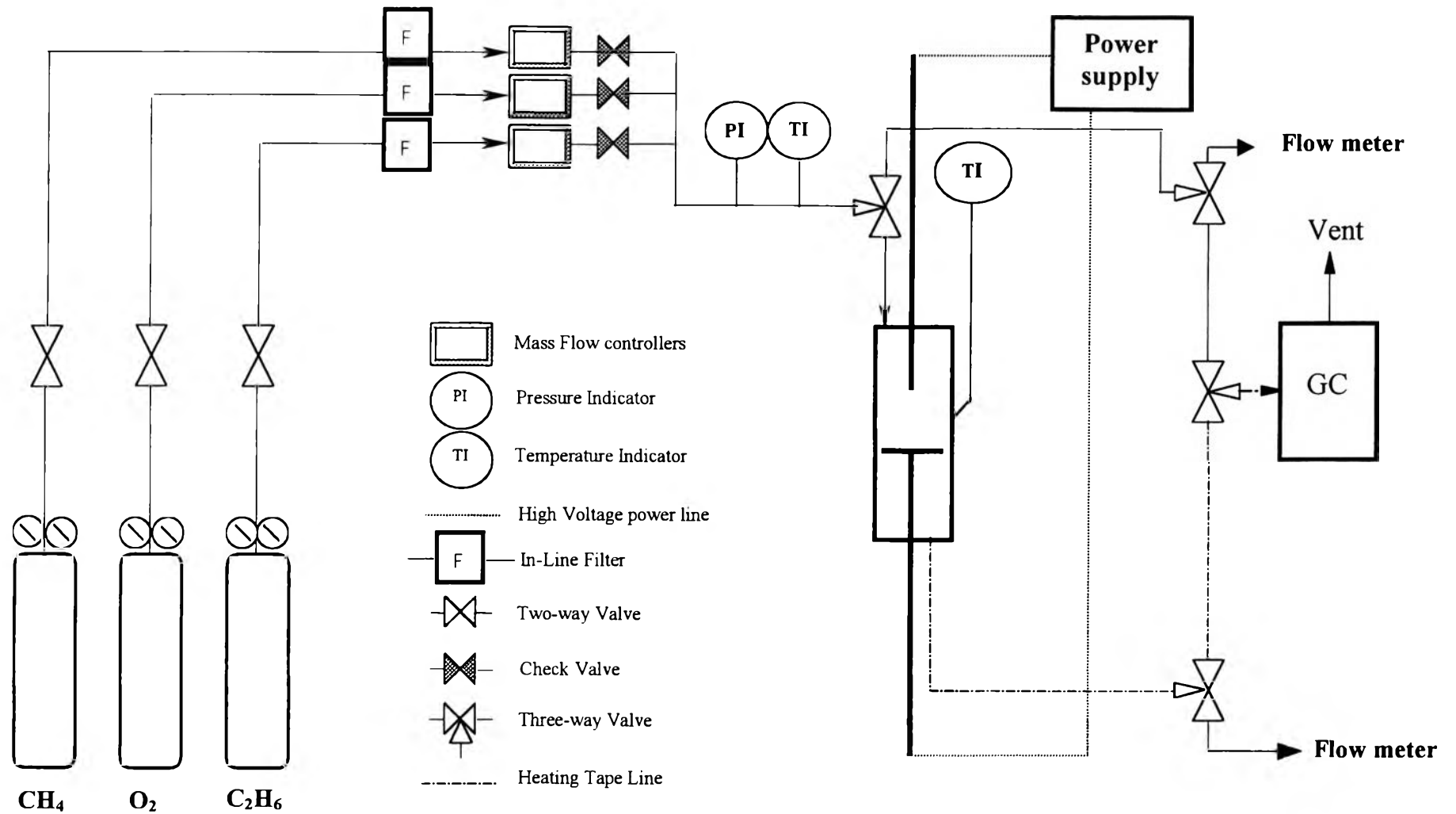
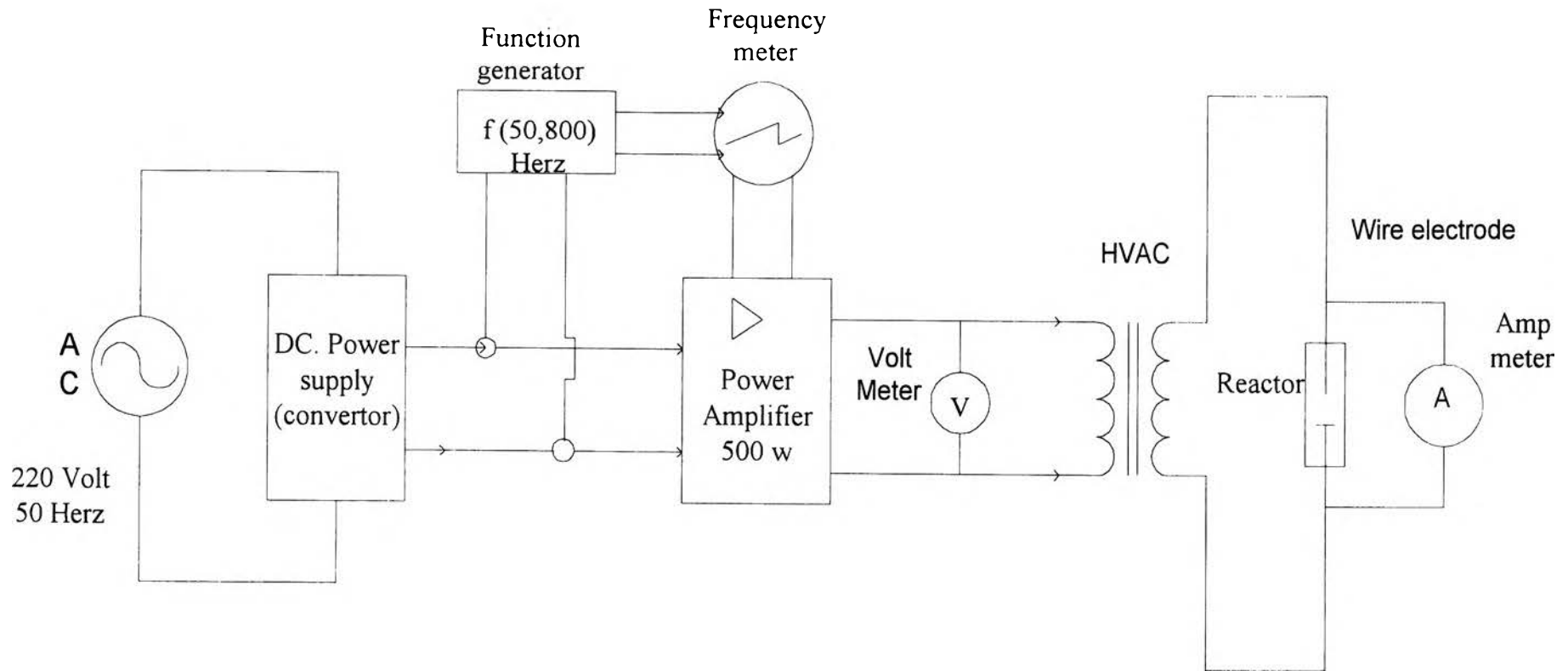


Figure 3.1 Flow diagram of plasma reactor system

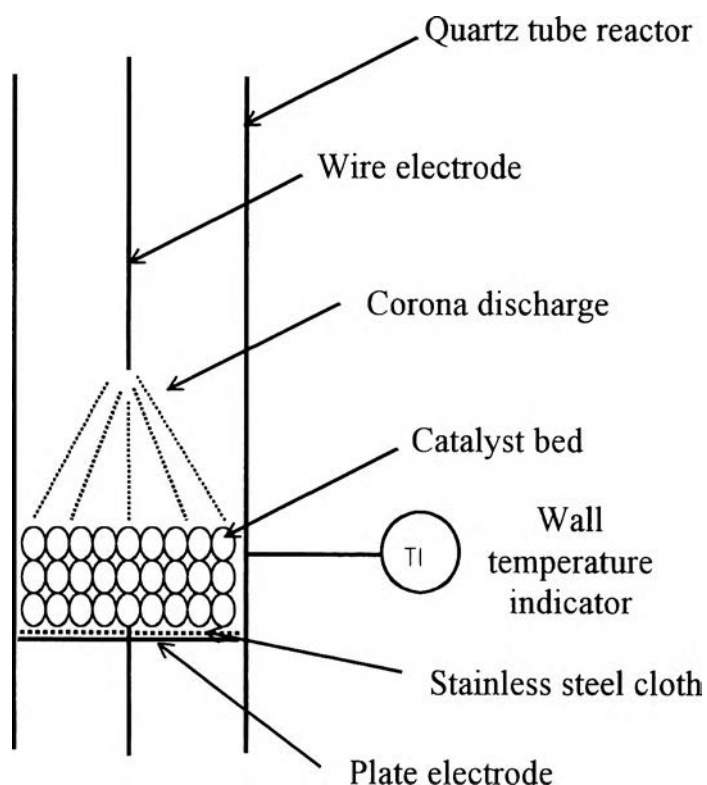


**Figure 3.2** Schematic diagram of power supply unit

voltage in range 0 to 80 V. Thereafter, the output was transmitted to the high voltage (HVAC) transformer having the power multiplying factor of 125. The final output obtained from the HVAC transformer was then sent to the reactor for the generation of electric discharges.

### 3.3.2.2 Reactor Unit

The corona discharge reactor is shown in Figure 3.3. The reactor was constructed of an 8-mm I.D. quartz tube. A lower plate electrode was mounted perpendicular to the tube axis with 8 holes in it to allow gas flow. Studied catalyst was placed on this electrode. The upper electrode made of 1/16-inch diameter stainless steel rod is a wire suspended above the catalyst bed and the distance between the electrodes is 1.3 cm. A type- K thermocouple was placed against the middle of outside wall of the reactor to measure the wall temperature.



**Figure 3.3** The configuration of the corona discharge reactor in this study

### 3.3.3 Analysis Section

The product gas stream was heated along the line to the on-line GC in order to prevent any liquid condensation in the line before reaching the GC. A Perkin-Elmer GC with a thermal conductivity detector (TCD) and a flame ionization detector (FID) was used as an on-line GC. The quantitative analysis of the percent volume of all gaseous components was carried out by correlating their peak-area responses derived from the GC chromatograms. The Perkin-Elmer GC was installed with a 10-port valve in order to separate the analyzed gas into two parts with independent sample loops. The first part was introduced to HayeSep-T column connected with FID allowing the separation of methanol and formaldehyde. The second part was sent to Carbonxen-1000 column connected with the TCD allowing the separation of H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. The GC conditions are summarized as follows:

#### Perkin-Elmer GC

Injector type:	Automatic sampling 10-port valve
Injector temperature:	120 °C
Oven temperature:	120 °C hold for 5 minutes, then rised to 170 °C at constant rate of 10 ° C/min and eventually hold for 20 minutes.
Detectors:	Thermal conductivity detector (TCD) and Flame ionization detector (FID)
Detector temperature:	190 °C
Columns:	HayeSep-T (5' x 1/8'') and Carbonxen-1000 (15' x 1/8'')
Carrier gas:	High purity helium

Carrier gas flow rates: 28.4 ml/min for HayeSep-T column  
and 28.4 ml/min for Carbonxen-  
1000 column

### 3.4 Experimental Procedure

The experiment was divided into two parts. The first part was a study on the plasma system without catalyst to determine the effects of ethane partial pressure, flow rate, frequency, and voltage on oxidative coupling of methane. The second part was to introduce catalysts into the plasma system in order to study the catalytic effect. All of experiments were operated at atmospheric pressure and room temperature.

#### 3.4.1 The Plasma System with the Absence of Catalyst

For the absence of catalyst, the effects of ethane partial pressure, gas flow rate, frequency and voltage on conversions and products selectivities were determined.

##### *3.4.1.1 Study of Ethane Partial Pressure Effect*

The feed stream consisted of methane, oxygen and ethane. All the feed gas species were maintained at constant flow rates by using mass flow controllers. The bubble flow meter was used to check the readings of the mass flow controllers. In this experiment,  $\text{CH}_4/\text{O}_2/\text{C}_2\text{H}_6$  ratios were varied; 4:2:1, 4:2:0.75, 4:2:0.50, 4:2:0.25 and 4:2:0 corresponding to ethane partial pressures of 0.14, 0.11, 0.08, 0.04 and 0 atm, respectively. The total flow rate was kept constant at 100 ml/min. The gap width of the electrodes was set at 1.3 cm. After the desired flow rates of all feed gases were obtained, the feed mixture gas was introduced to the on-line Perkin-Elmer GC for measuring the exact feed gas composition. Next, the feed gas was fed into the reactor and the supply power was turned on at the desired voltage and



frequency. The applied voltage and frequency were held constant at 8,000 V and 400 Hz, respectively. The GC was then employed to determine the product gas composition every 30 minutes. Once, the product gas reached a steady-state condition, the steady-state product gas chromatograms were collected and analyzed by the on-line Perkin-Elmer GC. Afterwards, the experiment was repeated by changing another  $\text{CH}_4/\text{O}_2/\text{C}_2\text{H}_6$  ratio while the others kept constant.

#### *3.4.1.2 Study of Flow Rate Effect*

The applied voltage used in this study was 8,000 V. The frequency of 400 Hz and a gap width of 1.3 cm were set in the experiment. The mixture of  $\text{CH}_4/\text{O}_2/\text{C}_2\text{H}_6$  of 4:2:1 at different total flow rates were achieved by using the mass flow controllers. Four different total flow rates were used: 50, 75, 100, and 125 ml/min. After the desired composition of the feed gas was obtained, the supply power unit was then turned on at the desired voltage and frequency. Then, the similar procedure was taken as described before.

#### *3.4.1.3 Study of Frequency Effect*

It was found that the coke deposit on the electrode surface appeared when the system was operated under the frequency below 400 Hz. Therefore in this experimental study, the frequency had to be varied from 400 to 700 Hz. The mixture was kept constant at a  $\text{CH}_4/\text{O}_2/\text{C}_2\text{H}_6$  of 4:2:1 while the total flow rate of 50 ml/min and a gap width of 1.3 cm were set in this experiment. In addition, the voltage was fixed at 8,000 V. The similar procedure was taken as described before.

#### *3.4.1.4 Study of Voltage Effect*

The feed gas was a mixture of methane, oxygen, and ethane having a constant ratio of  $\text{CH}_4/\text{O}_2/\text{C}_2\text{H}_6$  of 4:2:1. The total flow rate of the feed gas kept constant at 50 ml/min and the gap width of the electrode was set at 1.3 cm. The frequency of 500 Hz was selected in this experiment and the

applied voltage was varied from 5,500 to 8,000 V. Thereafter, all of experimental procedures above were followed again except for the change of new voltage while the others kept constant.

### 3.4.2 The Plasma System with the Presence of Catalyst

In this experimental study, different zeolite catalysts were introduced in order to determine their effects on the oxidative coupling of methane. It was necessary to carry out a pretreatment of the catalyst by reduction before studying the reaction experiment.

#### 3.4.2.1 *Catalyst Reduction Procedure*

For catalyst reduction, 60 mg of catalyst was packed in the reactor on the plate electrode as shown in Figure 3.3. Next, the catalyst bed was slowly ramped flowing hydrogen at 100 ml/min · g of catalyst for 2 h to a temperature of 350°C and reduced for 1 h at such temperature. Finally, the catalyst was ready to be used for the reaction experiment.

#### 3.4.2.2 *Study of Frequency Effect*

60 mg of 1%Pt/KL zeolite catalyst was packed in the reactor and then reduced with hydrogen. The frequency had to be varied from 400 to 700 Hz. The mixture was kept constant at a CH<sub>4</sub>/O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratio of 4:2:1 while the total flow rate of 50 ml/min and a gap width of 1.3 cm were set in the experiment. In addition, the voltage was fixed at 8,000 V. All experimental procedures were the same as explained before.

#### 3.4.2.3 *Study of Voltage Effect*

60 mg of 1%Pt/KL zeolite catalyst was also used in this experiment. The catalyst was packed in the reactor and reduced with hydrogen. The applied voltage was varied from 5,500 to 8,000 V. The mixture of methane, oxygen and ethane with a CH<sub>4</sub>/O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> ratio of 4:2:1 at total flow rate 50 ml/min, gap width 1.3 cm and frequency 500 Hz were applied. Thereafter, all of experimental procedures were followed again.

#### 3.4.2.4 Study of Catalyst Types

60 mg of 1%Pt/KL zeolite catalyst was used in this experiment. The catalyst was packed in the reactor and then reduced with hydrogen. The mixture of methane, oxygen and ethane with a  $\text{CH}_4/\text{O}_2/\text{C}_2\text{H}_6$  ratio of 4:2:1 at the total flow rate of 50 ml/min was continuously fed into the reactor until no other peaks appeared on the GC chromatograms. The applied voltage of 6,000 V and the frequency of 500 Hz were applied to the reactor. When a steady state condition was attained, all the analysis data were collected. After that, the power supply was shut off. Again, all of these experimental procedures were carried out again by using 1%Pt/NaX and 1%Pt/NaOH treated Y zeolite catalysts instead of 1%Pt/KL zeolite catalyst.