

CHAPTER III

METHODOLOGY

In this research work, the plasma promoted catalytic partial oxidation of methane was carried out at atmospheric conditions. The well-known methanol synthesis catalyst from synthesis gas, Cu/ZnO, prepared by the coprecipitation method, was used in this study. The wire and plate electrodes made of stainless steel were used to generate an a.c. corona discharge in the quartz tube reactor where the reaction takes place. Both the feed and product streams were analyzed by two gas chromatographs with thermal conductivity detector and flame ionization detector.

3.1 Materials

3.1.1 Catalyst preparation materials

- Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) was AR grade of 99.5% purity obtained from Merck.
- Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was AR grade of 99% purity supplied from Merck.
- Potassium carbonate (K_2CO_3) was AR grade of 99.9% purity provided by Merck.
- Distilled water used in this study was from the Pharmaceutical Organization Authority of Thailand.

3.1.2 Gaseous reactants

- Hydrogen (H_2) UHP grade, 99.999%, was obtained from TIG.
- Oxygen (O_2) research grade, 99.999% was supplied by Praxair.

- Methane (CH₄) UHP grade of 99.97% purity was obtained from ATS.
- Helium (He) of 99.995% purity was obtained from TIG.

3.2 Catalyst preparation

In this research work, the 10% loading of copper on zinc oxide was prepared by the coprecipitation technique. Aqueous solutions of 0.1 M copper nitrate and 0.1 M zinc nitrate, were prepared by dissolving in distilled water. Then the two solutions were mixed together in order to get the desired copper to zinc ratio. The potassium carbonate solution was also prepared at a concentration of 0.1 M. A mixed aqueous solution of copper nitrate and zinc nitrate was added slowly and simultaneously with the potassium carbonate solution into 100 ml of distilled water with vigorous stirring. The temperature of co-precipitation was kept constant at 80°C. The pH was controlled between 6.0-7.0 by controlling the flow rate of potassium carbonate. Next, the precipitates were aged at 50°C for half an hour under gentle stirring. The precipitates were then filtered by filter paper and thoroughly washed with hot distilled water. The filtered precipitates were dried at 110°C overnight. The dried precipitates were then calcined in a muffle oven at 250°C for 3 hours and 350°C for 4 hours to obtain the catalyst.

3.3 Catalyst characterization

3.3.1 Surface area measurements

The surface of the catalyst sample was determined by the Brunauer-Emmet-Teller (BET) method. The sample was outgassed at 140°C for 3 hours before characterization. The Autosorb-1 Gas Sorption System (Quantachrome Corporation) with liquid nitrogen temperature at 77 K was employed to measure the specific surface area of the prepared catalyst.

3.3.2 Reduction temperature determination

The TPR (Temperature-programmed reduction) was used with 5% H₂/He in order to determine the temperature at which the catalyst was reduced.

3.3.3 X-ray diffraction

X-ray diffractometer supplied by Shinkaku was used to determine the crystalline phase on the catalyst. It is based on the fact that an X-ray diffraction pattern is unique for each crystalline substance. X-ray is Cu K-alpha at 40 kV and 30 mA and RINT2000 wide angle goniometer was used as a goniometer.

3.3.4 Atomic absorption spectroscopy

AAS Varian, was used to measure Cu and Zn contents in the catalyst. The sample solution was prepared by using HCl to dissolve the catalyst particle and it was then diluted with distilled water.

3.4 **Experimental setup**

Figure 3.1 shows the schematic diagram of the plasma catalytic reactor system. The system consisted of three sections, reactant make-up section, reaction section and analysis section.

3.4.1 Reactant make-up section

All gases used in this work were used without any further purification. The mass flow controllers, supplied by SIERRA Instrument, Inc., were installed to control the flow rates of the gases which were fed into the reactor. The error of this instrument was reported to be less than 1%. The pressure of the gases before the mass flow controllers was regulated by the gas regulators and kept constant at 25 psia in order to make sure of the reliable

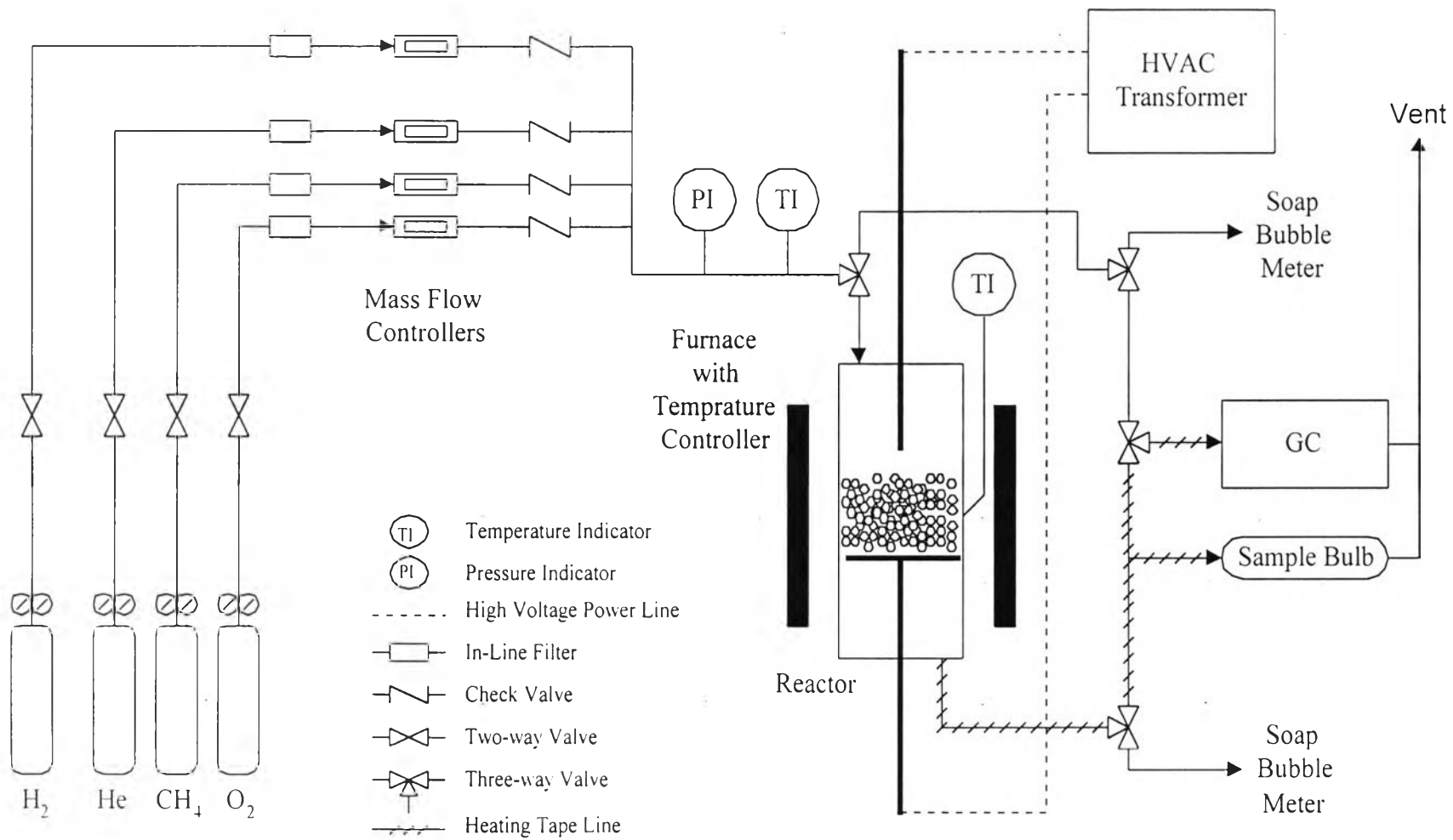


Figure 3.1 Flow diagram of plasma catalytic reactor system

function of the transducers. Moreover, 0.7 μm in-line filters were installed upstream of all mass flow controllers to separate all foreign particles in the feed gases. Check valves were placed downstream of all mass flow controllers to protect them from any back pressure effects.

Pressure and temperature of the feed gas were read out directly from a pressure gauge and thermocouple type-K was installed downstream of the reactant make-up section.

3.4.2 Reaction section

3.4.2.1 Power supply unit

Figure 3.2 illustrates the schematic diagram of the power supply unit. Domestic AC power, 220 V and 50 Hz, was connected to the variable transformer in order to vary the output voltage from 0 to 110 V. The output of this variable transformer was then transmitted to the high voltage alternating current transformer (HVAC) which increased the output voltage by 125 times. The HVAC could then step up the voltage to a maximum value of 12,500 V.

3.4.2.2 Reactor

The quartz tube reactor used in this study is shown in Figure 3.3 and the reactor tube had an inside diameter of 8 mm. The wire electrode was made of 1/16 inch diameter stainless steel rod. The plate electrode had the shape of a circular disk made of stainless steel plate that has thickness of 1 mm. It was drilled with 8 holes and each hole had a diameter of 1 mm. On the top of the plate electrode, stainless steel cloth was attached in order to prevent the catalyst particles from falling through the holes. The clearance between these two electrodes was 9 mm. The catalyst, which was packed in the reactor, had a height of 7 mm. Therefore, the gap between the wire electrode and the catalyst was 2 mm. The corona discharge occurred in

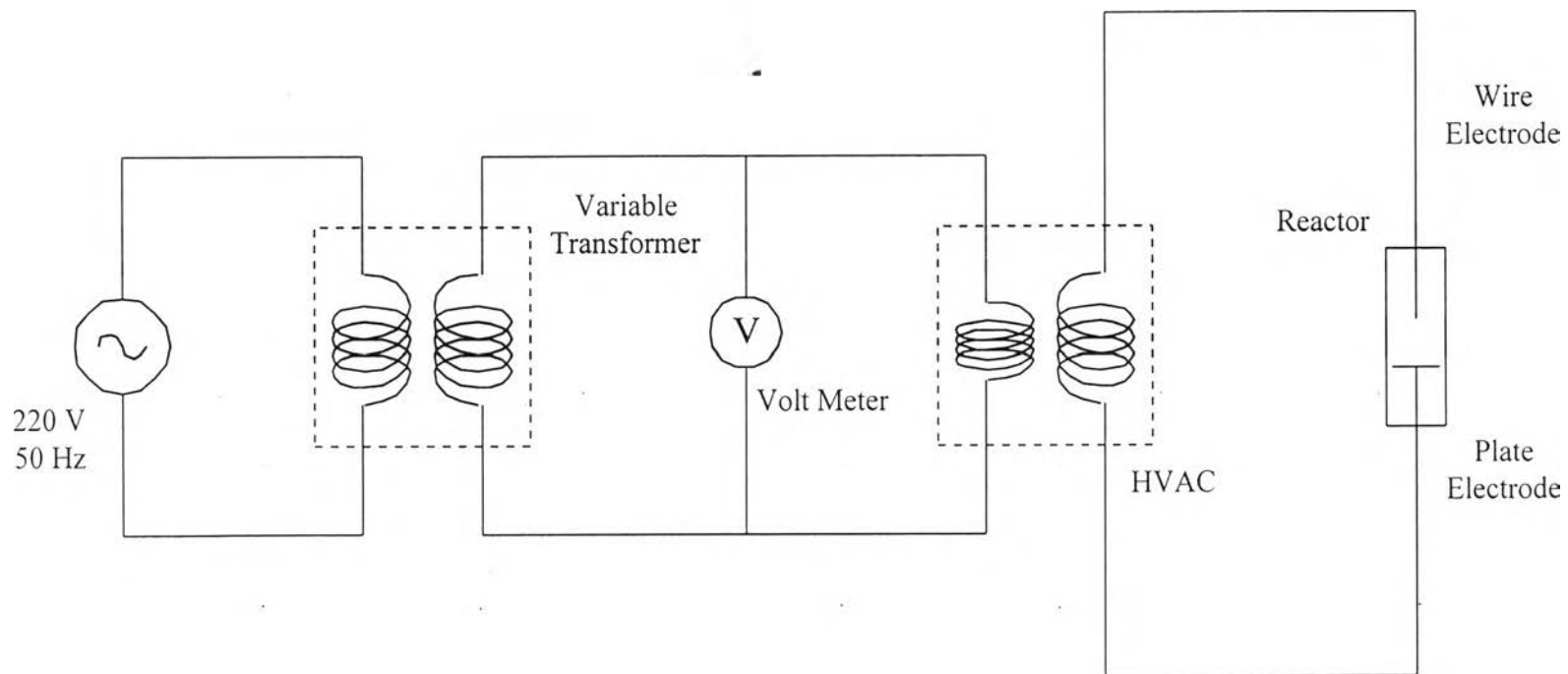


Figure 3.2 Schematic diagram of power supply unit

this area of the gap space. A type-K thermocouple was connected outside the reactor wall for monitoring the wall temperature.

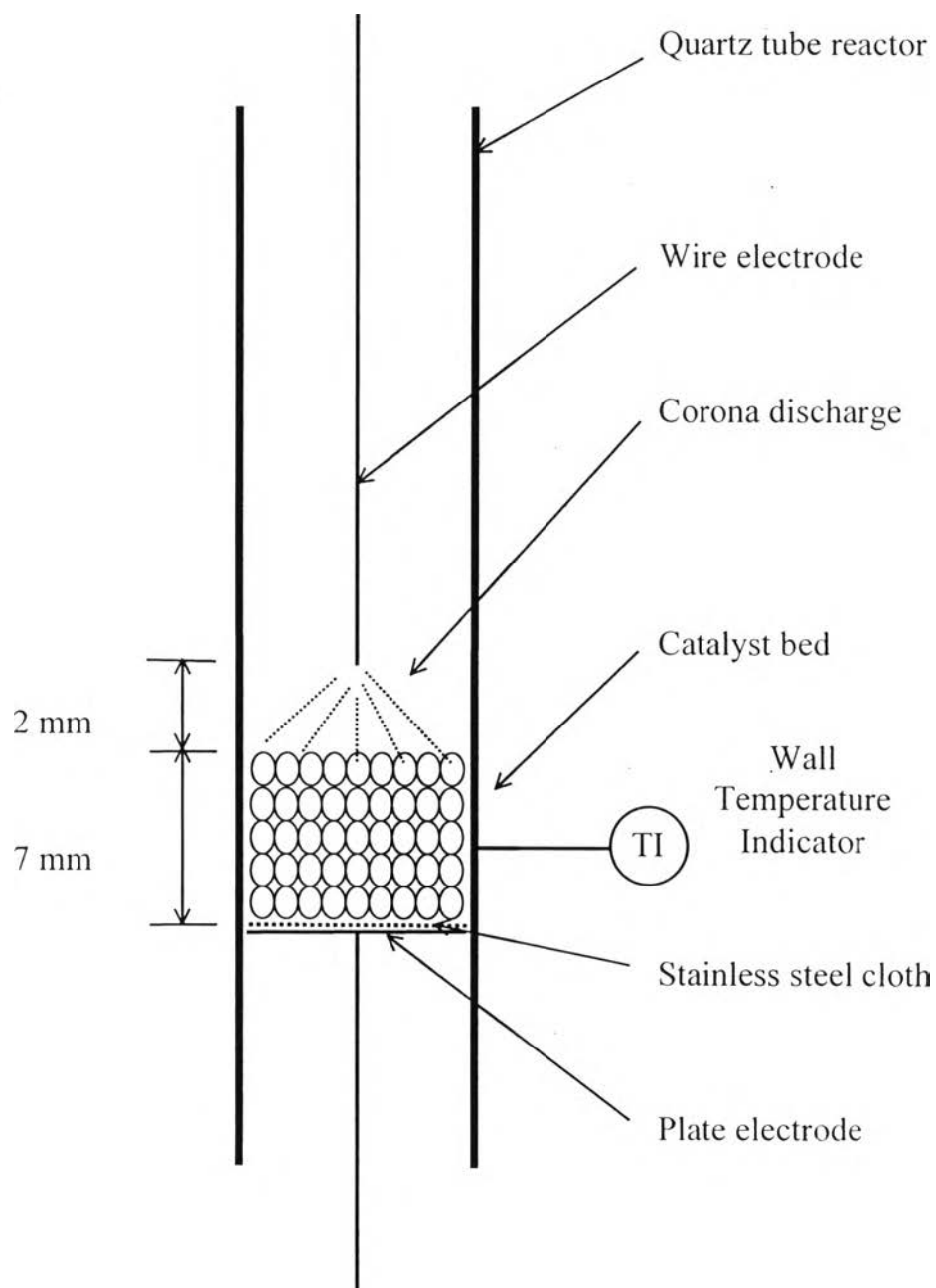


Figure 3.3 Configuration of plasma catalytic reactor

3.4.3 Analysis section

The product gas stream was heated along the line to the on-line GC. This prevented any liquid condensation in the line before the GC. The volumetric flow rates of the product stream and feed stream were measured by using a bubble flow meter during each experiment. It was found that the difference in both flow rates was very small, so the flow rate through the reactor was assumed constant. The product gas was also collected in a sample bulb for analysis with a stand-alone GC.

A Perkin-Elmer GC with a thermal conductivity detector (TCD) and a flame ionization detector (FID) was used as an on-line GC. A Fisons GC with thermal conductivity detector (TCD) was used as a stand-alone GC. The quantitative analysis of the percent volume of all the gaseous components was carried out by correlating their concentrations to 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 the FID allowing the separation of formaldehyde and methanol. The second part was sent to a HayeSep-DB column connected with the TCD allowing the separation of CH₄, C₂H₄, CO, CO₂, O₂, and H₂. But this column was not suitable for the separation of O₂ and CO. So the Fisons GC, with a MoleculaSieve 13X column, was used to separate these two components. The GC conditions are summarized as follows:

Perkin-Elmer GC

Injector type:	Automatic sampling 10-port valve
Injector temperature:	160°C
Oven temperature:	120°C
Detectors:	Thermal conductivity detector (TCD) Flame ionization detector (FID)

Detector temperature:	160°C
Column:	HayeSep-T (5'×1/8'')
	HayeSep-DB (30''×1/8'')
Carrier gas:	High purity Helium
Carrier gas flow rate:	27.5 ml/min for HayeSep-DB column
	30 ml/min for HayeSep-T column

Fisons GC

Injector type:	Manual injection with 6-port valve
Injector temperature:	160°C
Oven temperature:	32°C
Detector:	Thermal conductivity detector (TCD)
Detector temperature:	140°C
Column:	MoleculaSieve 13X (5'×1/8'')
Carrier gas:	High purity Helium
Carrier gas flow rate:	4.5 ml/min

3.5 Experimental procedure

The operation of the reactor is divided into two parts, first to carry out the catalyst reduction and second, to perform the plasma promoted catalytic partial oxidation of methane at atmospheric pressure and room temperature.

3.5.1 Catalyst reduction procedure

For catalyst reduction, 100 mg of catalyst was packed in the reactor on the plate electrode as shown in Figure 3.3. Next, the bed was heated to 110°C with flowing helium at 30 ml/min for half an hour. After that, the temperature of the bed was raised again to the reduction temperature of 250°C and the hydrogen was introduced at the flow rate of 10 ml/min with the helium. This gives the H₂/He ratio of 25%. The reduction step took 10 hours.

After the reduction, the furnace was shut down and the hydrogen was shut off. The helium was still fed into the reactor in order to cool the bed down to room temperature. Finally, the catalyst was ready to be used for the reaction experiment.

3.5.2 Variation of oxygen partial pressure experiment

100 mg of 10% Cu/ZnO catalyst was used in these experiments. The catalyst was packed in the reactor and then reduced. The feed stream consisted of CH₄, O₂ and He. 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. There were three different CH₄ to O₂ ratios used in these experiments; 8:1, 4:1 and 2:1 (CH₄/O₂/He = 24/3/73, CH₄/O₂/He = 20/5/75 and CH₄/O₂/He = 16/8/76). The total flow rate was kept constant at 100 ml/min. After the desired composition of the feed gas was obtained, the feed 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 HVAC transformer to supply power to the electrodes was turned on. The applied voltage was held constant at 5,000 V. The product gas composition was then determined by the GC every 16 minutes. Once, the product gas reached a steady-state condition, the steady-state product gas chromatograms were collected and analyzed by on-line Perkin-Elmer GC. The product gas was also collected by using the sample bulb. This sample gas was then injected to the Fison GC using a gas-tight syringe in order to determine the exact composition of O₂ and CO. Afterwards, the experiment was repeated with fresh catalyst and a new CH₄ to O₂ ratio, while the total flow rate and applied voltage were kept constant.

3.5.3 Variation of applied voltage experiments

The reactor was packed with 100 mg of 10% Cu/ZnO catalyst and reduced. The applied voltage was varied from 5,000 to 10,000 V. The mixture of CH₄ to O₂ of 4:1 (CH₄/O₂/He = 20/5/75) at 100 ml/min was prepared by using the bubble flow meter and mass flow controllers. This feed gas composition was measured by on-line Perkin-Elmer GC. After a CH₄ to O₂ ratio of 4:1 was obtained, the feed gas was then continuously fed to the reactor and the supply power was turned on at the desired voltage. Next, the product gas was examined by the GC every 16 minutes. When the product gas reached a steady-state condition, the steady-state product gas chromatograms were collected and analyzed by on-line Perkin-Elmer GC. The product gas was also collected by using the sample bulb. This sample gas was injected to the Fison GC by gas-tight syringe in order to determine the exact composition of O₂ and CO. Afterwards, the experiment was repeated by changing to fresh catalyst and the new applied voltage while the CH₄ to O₂ ratio and total flow rate were kept constant.

3.5.4 Variation of total flow rate experiments

100 mg of 10% Cu/ZnO catalyst was also used in this experiment. The catalyst was packed in the reactor and reduced. The applied voltage used in this study was 5,000 V. The mixture of CH₄ to O₂ of 4:1 at different total flow rates were prepared by using the bubble flow meter and mass flow controllers. Four different total flow rates were used; 50 ml/min (CH₄/O₂/He = 10/2.5/37.5), 100 ml/min (CH₄/O₂/He = 20/5/75), 150 ml/min (CH₄/O₂/He = 30/7.5/112.5) and 200 ml/min (CH₄/O₂/He = 40/10/150). After the desired total flow rate of feed gas was obtained, the feed 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 HVAC transformer to supply power to the electrodes was turned on. The applied voltage was maintained at 5,000 V. After that, the product gas was determined

by the GC every 16 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. The product gas was also collected by using the sample bulb. This sample gas was injected into the Fison GC by gas-tight syringe in order to determine the exact composition of O₂ and CO. Afterwards, the experiment was repeated by changing to new fresh catalyst and the new total flow rate, while the CH₄ to O₂ ratio and applied voltage were kept constant.