



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Gases

All gases used in this experiment were obtained from Thai Industrial Gas Public Co., Ltd. (Thailand) which were the air zero grade, high purity hydrogen, high purity helium and methane-compressed grade.

#### 3.1.2 Chemicals

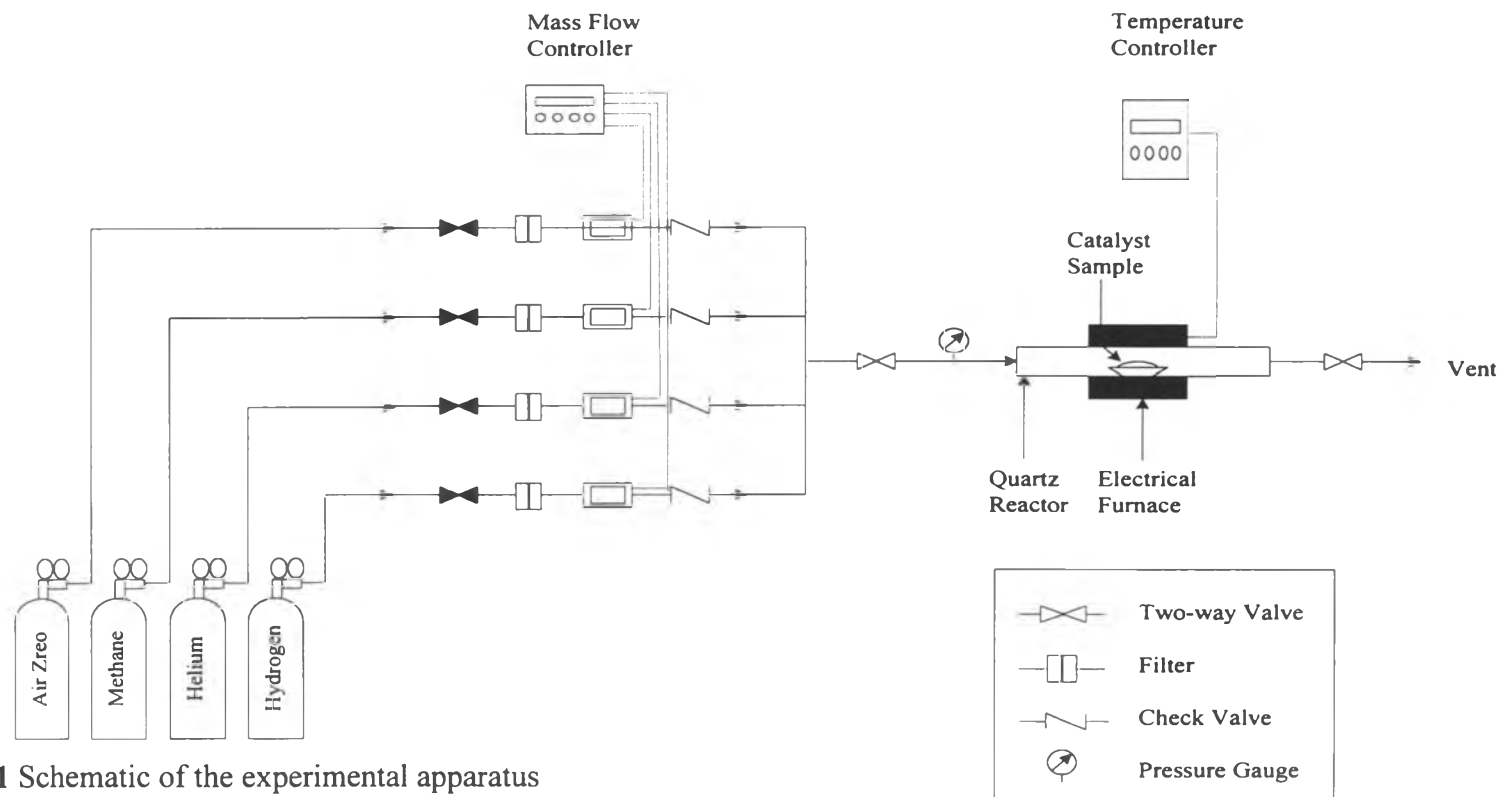
The chemicals used as metal precursor in this work were supplied from CARLO (Milan, Italy), which were cobalt (II) nitrate, iron (III) nitrate nonahydrate and ammonium molybdate (VI) tetrahydrate. The catalyst supports obtained from Aldrich (Milwaukee, USA) were silica gel and magnesium oxide.

### 3.2 Experimental Apparatus

The experimental apparatus was set as schematically shown in Figure 3.1 that consists of gas controlling system and catalytic reactor.

#### 3.2.1 Gas Controlling System

The gas flow rates of all inlet gases were controlled by the Sierra Instrument mass flow controllers. To prevent any small particles that may get into the mass flow controllers, one-micron filters were put in the line prior to the mass flow controllers to purify all inlet gases. Check valves were also installed to prevent the back flow of gasses.



**Figure 3.1** Schematic of the experimental apparatus

### 3.2.2 Catalytic Reactor

The catalytic reactor was a 1-inch diameter quartz tube that was set in horizontal configuration. In operation, the catalyst was placed in a ceramic boat and then inserted into the middle of reactor. The reactor was heated by an electrical furnace, and its temperature was controlled by Omron PID temperature controller with K-type thermocouple. For monitoring temperature, the tip of thermocouple was in the position close to the catalyst in quartz tube reactor.

## 3.3 Experimental Methods

### 3.3.1 Catalyst Preparation

All catalysts were prepared by using incipient wetness impregnation technique with 6% total metal loading on the support. The metal precursors were weighed and dissolved in deionized water. The amount of water was kept at incipient-wetness conditions, which are 0.63 and 0.1 cm<sup>3</sup> of water to a gram of a silica and magnesium oxide respectively. The metal aqueous solution was introduced to the dry support and then the mixture was continuously ground with a mortar and pestle. The mixture was left to dry in ambient air at room temperature for a few hours, and then dried in an oven at 80 °C for 6 hours. The catalysts were calcined in a dried airflow of 100 sccm. The calcined temperature was linearly increased to 500 °C at a heating rate of 10 °C/min. The catalysts were held at 500 °C for 3 hours. The finished catalysts were left cool to room temperature and then kept in a dessicator.

### 3.3.2 Catalytic Synthesis Studies

This thesis considered two approaches for catalytically synthesize carbon nanotubes by methane. The first method is methane alone as a feeding gas and reaction temperature is fixed. The second one is a mixture of hydrogen and methane, and the reaction temperature is programmed.

Approach 1: Methane alone with fixing reaction temperature

Generally, a 0.1-0.5 g of calcined catalyst was loaded into the ceramic boat and placed at the middle of reactor. The catalyst was reduced by heating in 100 sccm of hydrogen stream up to 500 °C and held at this temperature for 30 minutes. Then, the hydrogen stream was cut off and the helium was fed at flow rate of 100 sccm while the reactor temperature was linearly increased at rate of 10 °C/min up to reaction temperature, typically 700-1000 °C. Once the reaction temperature was reached, helium was replaced by 100 sccm of methane. The catalysts were held at this condition for 30 minutes. Then methane flow was turned off and the reactor was cooled down in a flow of helium.

Approach 2: A mixture of hydrogen and methane with scanning reaction temperature

Typically, a 0.1-0.5 g of calcined catalyst was loaded into the ceramic boat and placed at the middle of reactor. Then, a mixture of hydrogen and methane with flow rate of 100 and 25 sccm, respectively was passed over the catalysts while the reactor temperature was linearly increased at rate of 5 °C/min up to 1000 °C and held at this temperature for 2 min. Until the reaction time was reached, methane flow was turned off and the reactor was cooled down to room temperature with the hydrogen flow.

The summary of all studies conditions is shown in Table 3.1.

**Table 3.1** Summary of all catalytic synthesis of carbon nanotubes

Catalyst	Approach	Reaction Temperature (°C)
Co-Mo (1:1)/SiO <sub>2</sub>	1	1000
Co-Mo (2:1)/MgO	2	1000
Co-Mo (1:1)/MgO	2	1000
Co-Mo (1:2)/MgO	2	1000
Fe-Mo (2:1)/MgO	2	1000
Fe-Mo (1:1)/MgO	2	1000
Fe-Mo (1:2)/MgO	2	1000
Co-Mo(1:1)/MgO	1	700
Co-Mo(1:1)/MgO	1	800
Co-Mo(1:1)/MgO	1	900
Co-Mo(1:1)/MgO	1	1000

### 3.4 Carbon Product Characterizations

The combinations of Raman, Transmission Electron Microscopy (TEM), and Temperature Programmed Analysis techniques were used to characterize both of qualitative and quantitative of produced carbon. The Raman technique allows for a systematic screening the types of overall carbon products. The TEM technique provides the structure details of carbonaceous deposits on catalysts. The Temperature Programmed Analysis was used to confirm the forms of carbon present in sample, and also contributed the amount of total carbon products.

#### 3.4.1 Raman Spectroscopy

The spent catalysts with deposited carbon were studied by the laser Raman spectra model JASCO TRS-600SZ-P single monochromatic spectrophotometer, equipped with a CCD (charge-couple device) with the detector cooled to about 153 K with liquid nitrogen. The excitation source was the 514.5 nm Spectra 9000 Photometrics Ar ion laser.

#### 3.4.2 Transmission Electron Microscopy (TEM)

The two dimensional image of size and shape of carbon nanotubes were observed by TEM using JEOL-2010 electron microscope operated at the accelerating voltage of 200 KeV. The bright-field images were taken at magnifications between 50K to 300K with an objective aperture in place. The TEM samples of carbon nanotubes were prepared by sonicating in ethanol for a few minutes followed by deposition of a few drops of the suspension on the lacy carbon grid.

#### 3.4.3 Temperature Programmed Analysis

##### 3.4.3.1 *Temperature programmed oxidation (TPO)*

To conduct the TPO experiment, a continuous flow of 10 % O<sub>2</sub>/He was passed over the catalyst containing the carbon deposits while the temperature is linearly increased at 12 °C/min. The evolution of CO<sub>2</sub> and CO produced by the oxidation of carbon species is completely converted to methane and

then the amount of methane is monitored by a Gas Chromatograph using GC-17A, Shimadzu. Quantification of methane was achieved by calibrating with 50  $\mu$ l pulses of pure methane.

#### 3.4.3.2 *Thermal gravimetric analysis (TGA)*

The quantity of carbon products was tested by Thermal Gravimetric Analysis using DUPONT Instrument TGA 2950. The prepared material was burned out in a flow of 10% oxygen in helium gas with a heating rate of 10  $^{\circ}$ C/min. The total weight gain of carbon materials is define as  $(W_{\text{initial}} - W_{\text{final}})/W_{\text{final}} * 100\%$ , where  $W_{\text{initial}}$  and  $W_{\text{final}}$  are the weight of sample at 200  $^{\circ}$ C and 750  $^{\circ}$ C respectively.