

CHAPTER III EXPERIMENTAL



3.1 Materials

3.1.1 Chemicals

The chemicals used as metal precursor in this work were supplied by CARLO (Milan, Italy), which were cobalt (II) nitrate, iron (III) nitrate nonohydrate, ammonium molybdate (VI) tetrahydrate, and nickel (II) nitrate hexahydrate. The catalyst supports obtained from Aldrich (Milwaukee, USA) were silica gel, magnesium oxide, and alumina as shown in Table 3.1

Table 3.1 Surface area of catalyst supports

Support	Catalog Number	Size (mesh)	Surface Area (m ² /g)
Silica gel	Aldrich (28,862-4)	70–230	500
Magnesium oxide fused(99+%)	Aldrich (34,282-3)	40	4.057
Aluminum oxide	Aldrich (26,774-0)	150	155

3.1.2 Gases

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

3.2 Experimental Apparatus

3.2.1 Gas Controlling System

The mass flow controller from Sierra Instrument were used to control all of the inlet gas flow rates. One-micron filters were placed in the line prior to the mass flow controller to purify all inlet gases. Check valves were installed to prevent the back flow.

3.1.2 Catalytic Reactor

The reactor was 1-inch diameter quartz tube that was set in horizontal configuration. In order to operate the reaction, the catalysts were placed in a middle of quartz tubular reactor, and then put the reactor inside the tubular electrical furnace used to heat up the temperature until the reaction temperature. The reaction temperature was measured and controlled by K-type thermocouple and Omron PID temperature controller. The tip of thermocouple was positioned close to the outside of quartz tubular reactor.

3.3 Experimental Methods

3.3.1 Catalyst Preparation and Pretreatment

A series of metal catalysts, which were Ni, Co, Fe, Mo, Ni-Mo, Co-Mo and Fe-Mo in different ratios of 1:1, 1:2 and 2:1 on silica gel, magnesium oxide, and alumina supports, were prepared by incipient-wetness impregnation technique with 6% total metal loading on the supports. The amounts of water was kept at incipient-wetness conditions, which were 0.63 cm³ for a gram of silica gel, 0.01 cm³ for magnesium oxide, and 0.4 cm³ for alumina. After impregnation, the catalysts were dried in air at ambient temperature for a few hours, after that they were dried in an oven at 80 °C for 6 to 8 hours and then calcined for 3 hours at 500 °C in flowing dried air. The finished catalysts were left cool to ambient temperature and kept in a dessicator.

3.3.2 Catalytic Synthesis Studies

For the production of carbon nanotubes, a 0.1–0.5 g of calcined catalyst was placed at the middle of a quartz tubular reactor, supporting by quartz wools, reduced by heating in hydrogen flow of 100 sccm (standard cubic centimeter per minute) with a heating rate 10 °C/min to reach 500 °C and held at this temperature for 30 min. After that the hydrogen flow was shut off and helium flow was introduced at a constant flow rate of 100 sccm. The temperature was increased at a heating rate of 10 °C /min to reach 750–850 °C, The catalytic reactor was

operated at atmospheric pressure. Subsequently, hydrocarbon gases, such as CO, CH₄ or mixed gases (CO + CH₄) with a molar ratio of 1:1, were introduced at a total flow rate of 100 sccm, and kept under these conditions for 30 minute. In addition, CO gas was heated at around 300 °C to remove iron pentacarbonyl [Fe (CO)₅] in pretreatment furnace before feeded to the reaction. At the end of each run, the system was cool down with He to the ambient temperature.

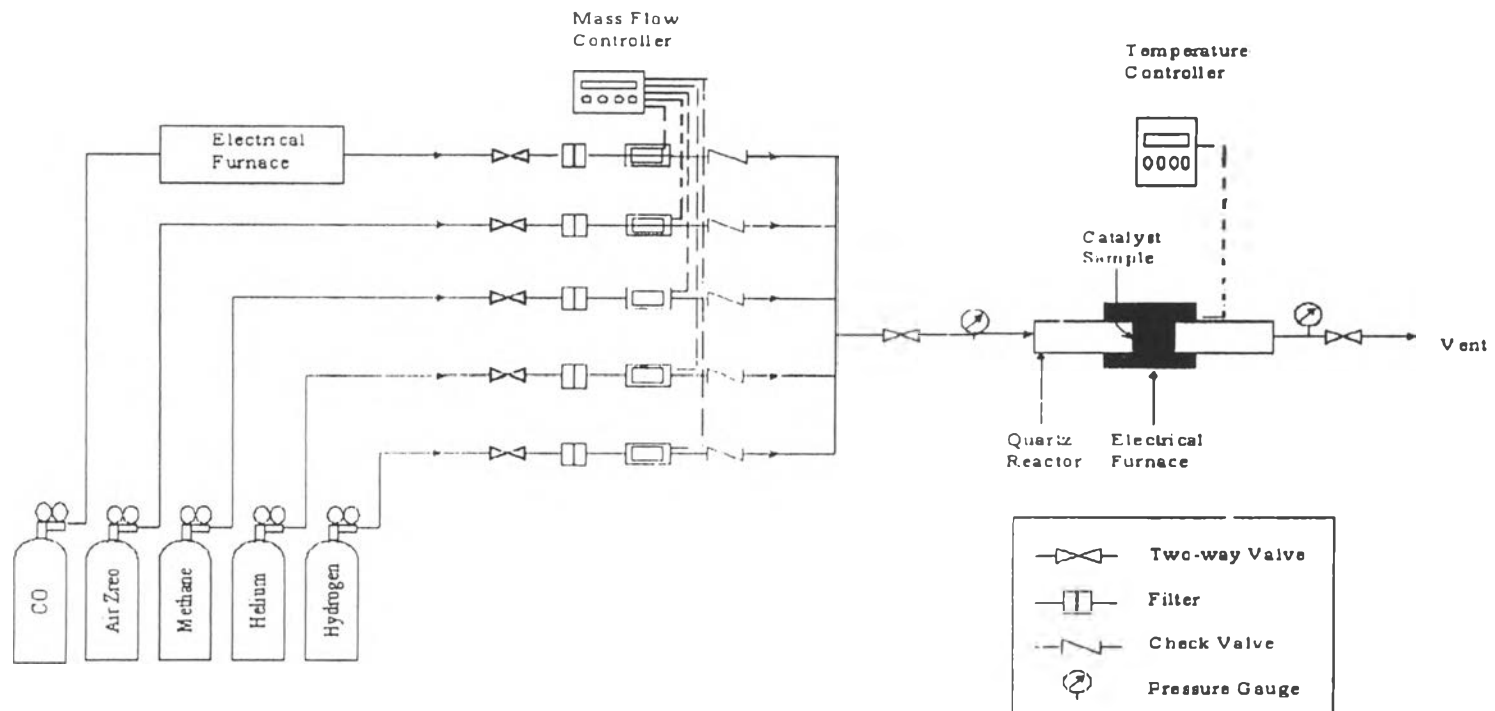


Figure 3.1 Schematic of the experimental apparatus.

3.4 Carbon Product Characterizations

The characterizations of carbon products were carried out by a number of techniques including Raman spectroscopy, TEM, and TPO which were used to characterize both qualitatively and quantitatively of produced carbons.

3.4.1 Raman Spectroscopy

The spent catalysts with deposited carbon were studied by a laser Raman spectra (Yvon-Horiba LabRam 800) equipped with a CCD (charge-couple device) detector and with three different laser excitation sources having wavelengths of 632 (He-Ne laser), 514, and 488 nm (Ar laser). The laser powers used were in the range of 3.0 to 5.0 mW.

3.4.2 Transmission Electron Microscopy (TEM)

TEM were used to observe the two dimensional image of size and shape of carbon nanotubes. The electron microscope (JEOL JEM-2010) was operated at the accelerating voltage of 200 KeV and the bright-field images were taken at 50K to 300K with an objective aperture in place. The samples were prepared by using sonication technique, which uses noise to disperse the particles. It was dissolved in ethanol, and followed by deposition of a few drops of suspension on a lacey carbon grid.

3.4.3 Temperature Programmed Oxidation (TPO)

This technique can investigate for both qualitative and quantitative properties of carbon nanotubes. To conduct this experiment, a continuous flow of O₂/He with a flow rate of 40 sccm was passed to the quartz tube which contained the carbon sample, meanwhile the temperature was linearly increased with a constant rate of 13 K/min. At the oxidation temperature, the carbon sample was reacted with O₂ and released the oxidation products such as H₂O and CO₂. After this reaction, CO₂ and H₂ gases were passed to the methanator containing Ni/Al₂O₃ catalyst, which convert CO₂ to

CH₄. Consequently, CH₄ was detected with Flame Ionization Detector (FID) and showed the signal in the monitor. The area under the curve determines the total of carbon yield. Moreover, the shape of the curve predicted the type of carbon formation.