CHAPTER III
EXPERIMENTAL

3.1 Hydrogen desorption/absorption in NaAlH$_4$

3.1.1 Materials

1. Sodium aluminium hydride (90% NaAlH$_4$ from Aldrich Chemical)
2. TiCl$_3$ (from Riedel-de Haën)

   TiCl$_3$ powder was obtained from drying 12% TiCl$_3$ in hydrochloride solution. About 30 ml TiCl$_3$ solution was stirred in an enclosed glassware bottle, which was connected with a high vacuum pump. The solution was sucked to remove hydrochloric acid out at 50°C. The suction was conducted until TiCl$_3$ solution became TiCl$_3$ powder (violet powder) and leaved it under the vacuum atmosphere overnight.

3. ZrCl$_4$ (99.5% from Aldrich Chemical)
4. HfCl$_4$ (99.5% from Aldrich Chemical)
5. VCl$_3$ (99%, from Merck)
6. TiO$_2$ (from JJ-Degussa-Hüls)
7. Ti (99.98% 325 mesh from Aldrich Chemical)
8. Graphite (99.99% from Aldrich Chemical)
9. Activated carbon (20-40 mesh, from CALGON, BPL)
10. Carbon nanotubes were obtained from synthesis (see sectionxxx).
11. Hydrogen (UHP from TIG)
12. Argon (UHP from TIG)

3.1.2 Sample preparation

In each experiment, as-received NaAlH$_4$ was combined with one of transition metals (TiCl$_3$, ZrCl$_4$, HfCl$_4$, VCl$_3$, Ti, and TiO$_2$) or co-dopants (graphite, activated carbon, and carbon nanotubes) by centrifugal ball milling (Retsch ball mill model S100, stainless steel vial size 250 ml, stainless balls with 1 cm and 2 cm diameters) for 20 min. An amount of used dopants in each experiment was 4 mol%

while the amount of added co-dopant was 10 wt%. Figure 3.1 displays the sample preparation in each experiment.

3.1.3 Experimental set up

The thermovolumetric apparatus (Servert's experimental) was used to study the gas-solid interaction between hydrogen and metal hydrides ($NaAlH_4$). The schematic of the experimental set-up is shown in Figures 3.2. The pressure regulator with 3,000 psig maximum limit was purchased from Concoa (Model BU-2581-AQ) and installed to control the gas flow rate fed to the system. The set-up consisted of a high pressure stainless reactor (Swagelok 316SS, ~25 cm^3), which was used to hold the sample and part of stainless steel tube as a gas reservoir (~30 cm^3). The pressure transducer was utilized to measure pressure of the system changing from the desorption or absorption, and obtained from Cole-Parmer (Model 68073-68074) capable for measuring in the range of 0-3,000 psig with 0.13 % global. error. Temperature was measured inside the reactor by a type K thermocouple (error $\pm 2°C$) and controlled by a PID temperature controller. A online data logger program was utilized to record temperature and pressure every minute.

3.1.4 Hydrogen desorption/absorption

Immediately after mixing, approximately 1 g of a sample was placed into the thermovolumetric apparatus. For hydrogen desorption, the high pressure stainless steel reactor (316SS) was heated from room temperature to 280°C via a furnace controlled by a PID temperature controller. The K-type thermocouple was placed inside the reactor to measure the temperature. The pressure transducer (Cole Parmer, model 68073-68074) was used to measure the pressure change resulting from hydrogen desorption from the sample. For the absorption experiments, hydrogen (99.9995%) was used to pressurize the high pressure vessel at about 120°C and 10 MPa for 10 h. Once the pressure reading was constant over a period of time, the data was used to calculate the amount of hydrogen absorbed on the sample. Amount of the released hydrogen shown in the results (H/M) was calculated with respect to the amount of $NaAlH_4$ in the sample. The same procedure was repeated to investigate their reversibility.
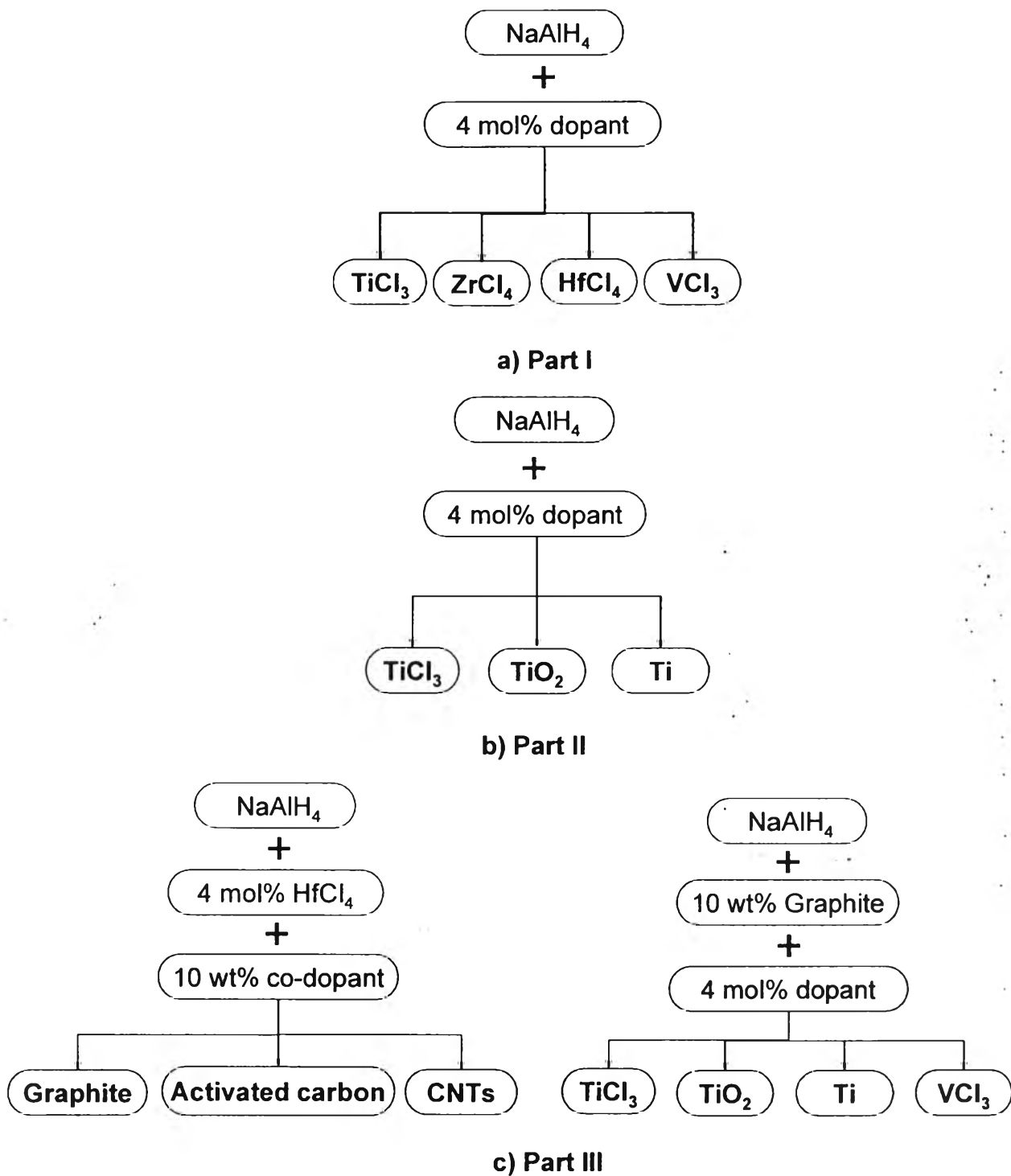
a) Part I

b) Part II

c) Part III

Figure **3.1** Sample preparation of each experimental part: a) effect of different transition metals, b) effect of different Ti-precursors, and c) effect of carbon materials on the hydrogen desorption/absorption in $NaAlH_4$.
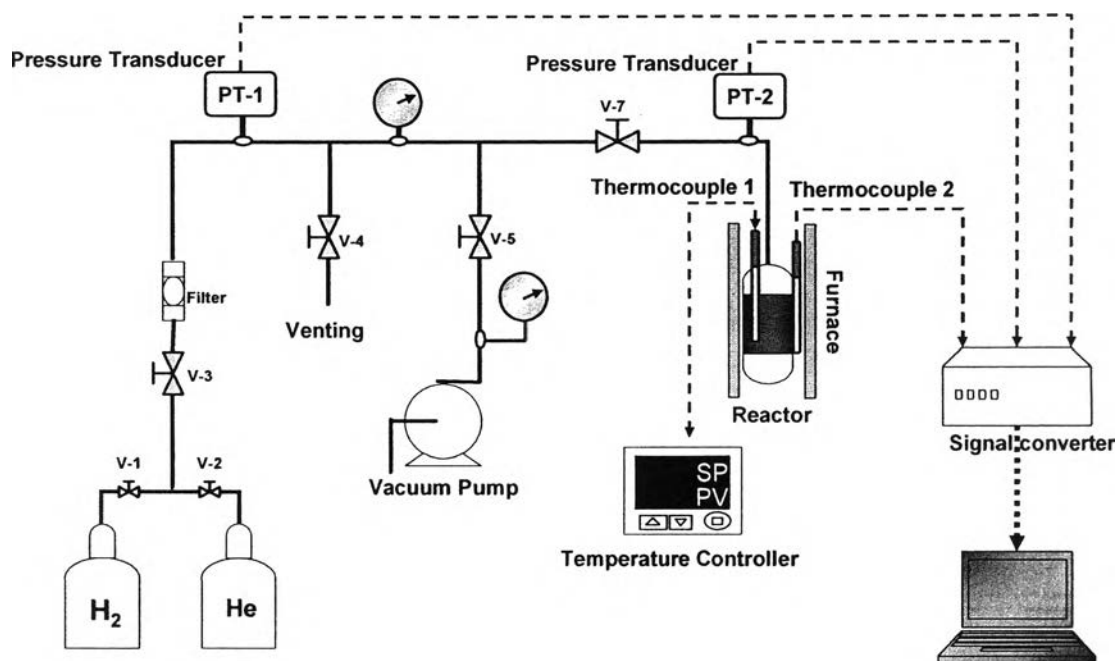
Figure 3.2 Schematic diagram of the experimental set-up for hydrogen desorption/absorption of NaAlH₄ systems.

The hydrogen capacities were estimated by the equation of state as stated in Eq. (3.1). The compressibility factor (Z) used in this relation was given in Table 3.1.

$$P_H V_s = Z n_H R T_H \tag{3.1}$$

where,

P_H = pressure of hydrogen gas inside the sample holder after correction, atm

n_H = mole of desorbed hydrogen, mol

T_H = temperature of the sample in reactor, K

Z = Compressibility factor

R = gas constant, 82.056 atm cm³ mole⁻¹ K⁻¹

Vs = volume of sample holder, cm³

$$Re\,leased\ hydrogen, wt\%(H\,/\,M) = \frac{Amount\ desorbed\ hydrogen}{Amount\ of\ metal\ hydride} \times 100 \tag{3.2}$$

Table 3.1 Compressibility factor at different temperature ranges (Perry *et al.*, 1995)

Temperature (°C)	Z
20-44	0.00004P+0.9991
45-70	0.00004P+0.9993
71-90	0.00004P+0.9994
90-114	0.00004P+0.99995
115-139	0.00003P+0.9997
140-165	0.00003P+0.9998
166-214	0.00003P+0.9999
215-300	0.00003P+1
301-340	0.00002P+1

3.1.5 X-ray diffraction

The samples were characterized using a Rigaku x-ray diffractometer system equipped with RINT 2000 wide angle goniometer from 28-90 with CuK-alpha radiation (40 kV, 30 mA). To protect the samples exposed to air and moisture, they were covered with a Kapton tape and prepared in the glove box under nitrogen atmosphere.

3.2 Synthesis of Pd or V deposited MWNTs and their hydrogen storage capacity

3.2.1 Materials

1. LaNi$_5$ (from Guangzhou Research Institute for Non-Ferrous Metals, China)

2. PdC$_{10}$H$_{11}$O$_4$ (98%, Aldrich Chemical)

3. VC$_{15}$H$_{21}$O$_6$ (98%, Aldrich Chemical)

4. LPG (from Afrox South Africa)

5. 10% H$_2$ gas balanced with Argon (99.9995%, Afrox South Africa)

3.2.2 CNT synthesis and treatment

CNTs were synthesized by the chemical vapor deposition using LPG and $LaNi_5$ as a carbon sources and a catalyst. About 2 g of treated $LaNi_5$ powder was loaded into a quartz combustion boat and placed inside a quartz tube located inside a tube furnace. The system was sealed and flushed with nitrogen for 10 min, and then the temperature was ramped to 800°C. Once the temperature was stabilized, the nitrogen flow was cut off and liquid petroleum gas (LPG) flow was initiated at a flow rate of 5.8 cm^3 min^{-1}. After 60 min, the LPG flow was terminated and the nitrogen flow was re-initiated. The sample was then cooled under nitrogen. To purify CNTs obtained from the synthesis, 2 g of CNTs were added to 100 ml of 10 M HCl. The mixture was sonicated (ultrasonic bath, integral systems, model UMC-20, 50 kHz, 400 watts) for 1 h and refluxed at 120°C for 3 h. The solid was filtered and washed with deionized water until pH value of the rinsed water was around 6-7, and dried in an oven at 90°C overnight. Before metal deposition, the purified CNTs were modified through oxidation by concentrated HNO_3 under ultrasonication for 1 h.

3.2.3 Metal deposition on CNTs

Metal deposition on CNTs was prepared by two methods. The first method was the reflux method for Pd deposition. 0.001 M $PdC_{10}H_{11}O_4$ in toluene was added in 0.5 g purified CNTs. The mixture solution was stirred and sonicated for 30 min, and then 10% H_2 gas balanced with Argon was bubbled through the former mixture under the reflux condition at 130°C. The filtered solid was washed with toluene and dried in a vacuum oven at 120°C overnight. For V deposition, 0.5 g purified CNTs were mixed with $VC_{15}H_{21}O_6$ using mortar. The powder was loaded in a reactor, vacuumed and heated to 450°C for 1 h. The amount of deposited metal on CNTs is approximately 10%.

3.2.4 Hydrogen storage experiment

Hydrogen adsorption on samples were measured by Sievert's apparatus, as shown schematically in Figure 3.3, equipped with a vacuum pump, vacuum gauge, three pressure transducers in different pressure range (0.3% accuracy, Gem Sensors), digital read out and record set (34970A data acquisition and switch

unit, Agilent). All reactors, valves, and fittings were purchased from Swagelok. Some parts of the apparatus were put into a temperature controlled unit in order to prevent errors due to the change in the ambient temperature. Approximately, 900 mg of a sample were used for each measurement. Before starting the hydrogen adsorption experiment, the degassing procedure was conducted at vacuum condition $\sim 10^{-2}$ mbar, from room temperature to 400°C for 1 h to remove remaining gases. Subsequently, hydrogen (purity >99.999%) was fed into the sample holder at 400°C and hydrogen pressure of $\sim$ 65 bar. The system was held under this condition until the pressure was stable in order to activate the sample. Then, the system was cooled down to room temperature. Hydrogen adsorption was operated at the liquid nitrogen temperature (-196°C) and room temperature (20°C) with an initial hydrogen pressure $\sim$ 65 bar. After the hydrogen adsorption, hydrogen gas was released from the system by heating up to 380°C. The same procedure was repeated to investigate the reversibility. Hydrogen adsorption data obtained were calculated as mass of adsorbed hydrogen/mass of adsorbent materials (weight percent). All the calculations were carried out using real gas law with precise calculations of H_2 compressibility factor, Z(P,T), similarly to the one described in elsewhere (Zhou *et al.*, 2001). The correction of internal reactor volume (by subtracting sample volume) was done starting from the estimated sample density of $\sim$ 1.4 g cm^{-3}.

3.2.5 Sample characterization

1. Transmission electron microscopy (TEM, Hitachi 600).

2. Thermogravimetric analysis (TGA, Rheometric Scientific STA 1500 TGA/DSC, room temperature to 850°C, air flow rate of 14.5 cm^3 min^{-1}, heating rate of 5°C min^{-1}),

3. X-ray diffractometer (Rigaku, Cu-Kα radiation, 40 kV, 30 mA).

4. FT-Raman spectroscopy (Perkin Elmer, Spectrum GX, 40 mW, resolution of 16 cm^{-1})

5. Nitrogen adsorption/desorption at 77K (Micrometrics Tristar Surface analyzer) with Brunauer-Emmet-Teller (BET) analysis.

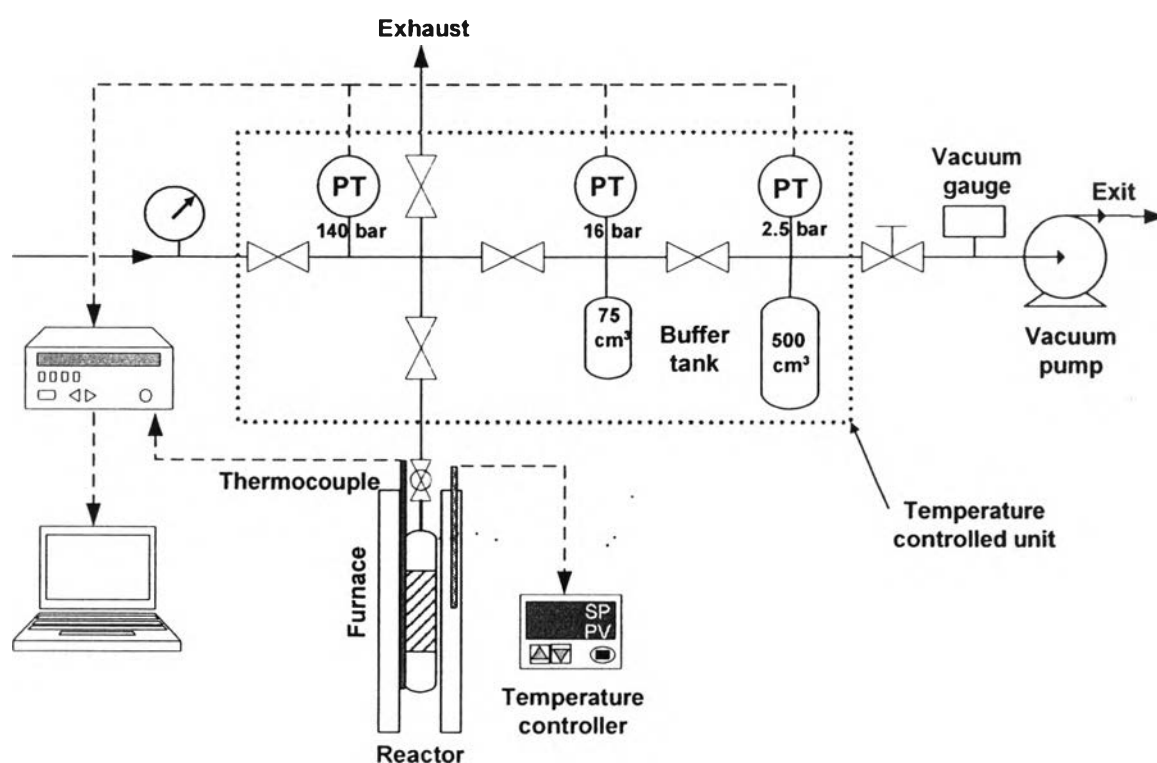6. Inductively coupled plasma spectrometry (ICP, Optima 4300DV, Perkin Elmer Instrument).

Figure 3.3 Schematic diagram of the experimental set-up for hydrogen desoprtion/adsorption of MWNTs system.