



CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Chemicals

- Lithium aluminum hydride (LiAlH_4), (95% purity), Acros Organics
- Nano-titanium (nano-Ti), Sigma-Aldrich
- Titanium dioxide (TiO_2), Degussa
- Titanium (III) chloride (TiCl_3), synthesis
- Nano-nickel (nano-Ni), Searle company
- Carbon aerogel (CAs)

3.1.2 Equipment

- High-energy ball-mill (Retsch ball mill, Model S100)
- Thermo-volumetric apparatus
- X-ray diffractometer (XRD) measurement (Rigaku, D/max-2200)
- Temperature program desorption (TPD) analyzer (TPDRO 1100, Thermo Finnigan)
- Glove-box filled with purified nitrogen
- Scanning electron microscope (SEM) (Hitachi, S-4800)
- Surface area analysis (SAA) (Quanta Chrome, NOVA 1200)

3.2 Experimental Procedures

3.2.1 Sample Preparation

In this study, LiAlH_4 was used without further purification. A small amount of catalysts, which were nano-Ti, TiO_2 , TiCl_3 , and nano-Ni, and carbon aerogels were also added to the systems. Composition of the mixture is shown in Tables 3.1 and 3.2. The mixtures were milled with 300 rpm for 30 min and a ball-to-powder ratio of 40:1.

Table 3.1 Mass ratio of mixed sample for carbon aerogels

Sample	Chemicals	Mass ratio (%)
1	LiAlH ₄ + CAs	95:5
2	LiAlH ₄ + CAs	90:10
3	LiAlH ₄ + CAs	85:15
4	LiAlH ₄	100

Table 3.2 Mass ratio of mixed sample for carbon aerogels and catalysts

Sample	Chemicals	Mass ratio (%)
1	LiAlH ₄ + CAs	95:5
2	LiAlH ₄ + nano-Ni	95:5
3	LiAlH ₄ + nano-Ti	95:5
4	LiAlH ₄ + TiO ₂	95:5
5	LiAlH ₄ + TiCl ₃	95:5
6	LiAlH ₄ + CAs + nano-Ti	90:5:5
7	LiAlH ₄ + CAs + TiO ₂	90:5:5
8	LiAlH ₄ + CAs + TiCl ₃	90:5:5
9	LiAlH ₄ + CAs + nano-Ni	90:5:5

Note: All the materials handlings (including weighing and loading) were performed in a glove-box filled with purified nitrogen to keep a low moisture concentration and oxygen concentration during operation using a gas recycling purification system, and avoid exposing the samples to air.

3.2.2 Experimental Set Up

The thermo-volumetric apparatus was used to study the gas-solid interaction. The schematic of the experimental set-up is shown in Figure 3.1.

- The set-up consisted of a high pressure stainless reactor, which held the sample and part of stainless steel tube as a gas reservoir.

- Pressure transducers were used to measure the system pressure in the range of 0 – 3,000 psig with 0.13% global error.
- A pressure regulator with 4,000 psig maximum limit was installed to control gas flow rate into the whole system.
- Inside the reactor, a K-type thermocouple was placed to measure the temperature.
- The high pressure stainless steel reactor was heated from room temperature to 250°C with the heating rate of 2°C/min via a furnace controlled by a PID temperature controller.

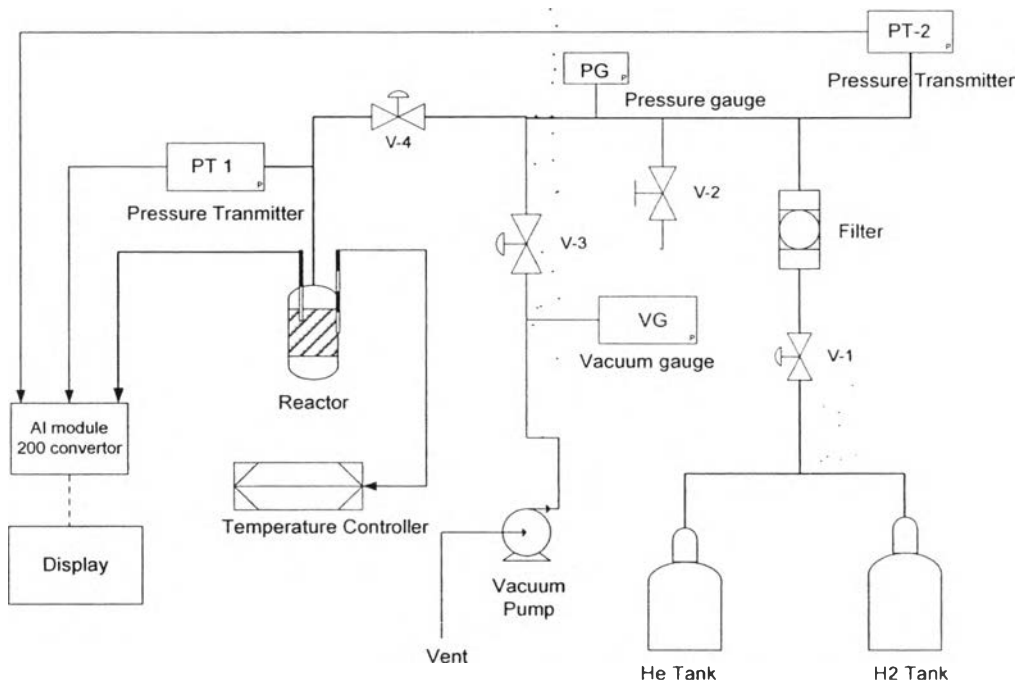


Figure 3.1 Schematic of the experimental set-up.

3.3 Hydrogen Sorption Data Collection

3.3.1 Desorption

The pressure transducers must be calibrated for each desorption experiment. Atmospheric pressure, 14.7 psi, was used as the reference pressure to set the zero span on the transducer to vacuum or set it to 14.7 psi.

- The amount of mixture sample used in each experiment was about 300 mg depending on the molecular weight of a loading metal.
- A sample was then placed into the sample holder and V_s is determined.
- The degassing procedure at about 10^{-3} torr and 25°C was conducted to remove the remaining gas for at least an hour.
- The sample holder was initially pressurized with hydrogen gas at 30 psig. Hence, the valve between the manifold and the sample holder was closed.
- The dehydrogenation was performed by a stepwise increase in the heating rate of $2^\circ\text{C}/\text{min}$ from room temperature to 250°C via a furnace controlled by a PID temperature controller. A sample was held at this condition until no further desorption was observed.
- While the above processes were continuing, the pressure values were recorded every minute until the pressure in the sample holder was constant. The observed pressure values were treated by the deduction method as followed:

$$\text{Hydrogen pressure} = \text{Observed pressure} - \text{Helium pressure} \quad (3.1)$$

The hydrogen capacities are estimated by the equation of state as stated in Equation (3.2):

$$P_H V_s = Z n_H R T_H \quad (3.2)$$

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

V_s = volume of the sample holder, cm^3

Z = compressibility factor (Table 3.4)

n_H = mole of desorbed hydrogen, mol

R = $82.06 \text{ cm}^3 \cdot \text{atm} / \text{mol} \cdot \text{K}$

T_H = temperature of the sample, K

Table 3.3 Compressibility factors at different temperature ranges

Temperature ($^{\circ}\text{C}$)	Z
20-44	$0.00004P+0.9991$
45-70	$0.00004P+0.9993$
71-90	$0.00004P+0.9994$
91-114	$0.00004P+0.9995$
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	$0.00002P+1$
341-535	$0.00002P+1.0001$
531-727	$0.00001P+1.0002$

where,

P = pressure of hydrogen gas inside the sample holder at that temperature, psi

$$\text{Hydrogen capacity, wt\%} = \frac{\text{Released hydrogen} \times 100}{\text{Amount of sample}} \quad (3.3)$$

Subsequently, the hydrogen gas in the sample holder was purged out to the ventilation system. The sample holder was cooled down to room temperature, and introduced to the vacuum condition (10^{-3} torr) for at least 1 h. The use of the high vacuum pressure helped in the regeneration of the substrate.

3.3.2 Absorption

Hydrogen was fed into the sample holder until the pressure reaches approximately 1.200 psig. The sample was heated with the rate of 2°C/min until the desired absorption temperature. Hereafter, the hydrogen uptake began and further extended for the next 12 h. The pressure values were recorded every minute.

3.4 Characterization

In order to identify phase transformation during hydrogen desorption and absorption of LiAlH₄, X-ray diffraction (XRD) measurement was used at the room temperature over a range of diffraction angles from 20 to 70° with CuK- α radiation (40kV, 30 mA). The desorption temperature was measured by temperature program desorption (TPDRO 1100, Thermo Finnigan). The TPD was carried out from the room temperature with a heating rate of 10 °C/min to 250 °C, where the sample was held for 1 h under a nitrogen flow. Surface morphology of CAs was investigated by using scanning electron microscope (SEM), Hitachi S-4800, with an accelerating voltage of 20 kV. Samples were coated with platinum under vacuum before observation. A surface area analyzer, Quantachrome NOVA 1200, was used to determine surface area of CAs. Samples of CAs were degassed at 300 °C for 12 hours in heating bags before analysis. N₂ adsorption-desorption isotherms were determined at -196 °C to obtain surface area, pore volume, and average pore size diameter of CAs.