



## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

In this study, various molar ratios of the  $\text{LiAlH}_4$ – $\text{LiBH}_4$  mixture and the effect of transition metals were investigated. Lithium aluminum hydride (95%  $\text{LiAlH}_4$ ), titanium dioxide ( $\text{TiO}_2$ ), vanadium (III) chloride (>99%  $\text{VCl}_3$ ) were obtained from Acros, Degüssa, and MERCK, respectively. Lithium borohydride (95%  $\text{LiBH}_4$ ), and zirconium (IV) chloride (99.5%  $\text{ZrCl}_4$ ) were purchased from Aldrich Chemicals. Titanium (III) chloride ( $\text{TiCl}_3$ ) powder was prepared by evaporation of titanium (III) chloride solution 12% in hydrochloric acid, obtained from Riedel-de Haën. The preparation took place at ambient condition—the solution was heated to  $60^\circ\text{C}$ , while it was stirred and then kept at this condition until the solid was formed. Centrifugal ball mill was used in order to mix the starting materials and the catalysts. All sample handlings (weighing and loading) were done in a nitrogen-filled glovebox to keep the sample under inert atmosphere during operation. Hydrogen gas (>99.999%) was used in the absorption experiment.

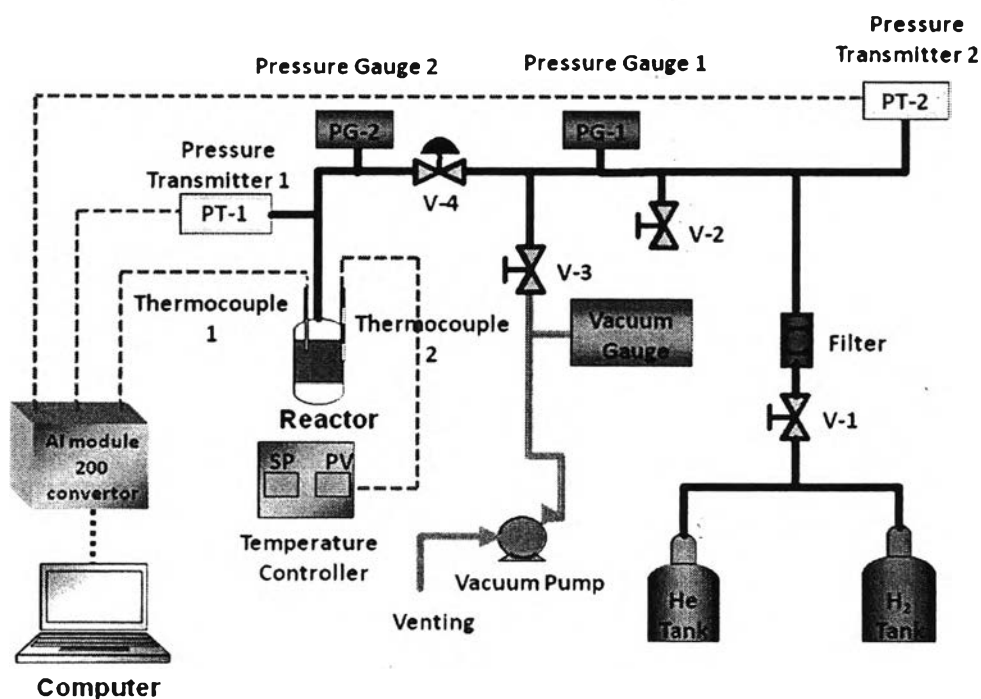
#### 3.2 Sample Preparation

All starting materials were used as-received in the powder form without further purification. In order to investigate the effect of using different molar ratios of the  $\text{LiAlH}_4$ – $\text{LiBH}_4$  mixture on the amount of desorbed hydrogen and the desorption/absorption temperature, various molar ratios of  $\text{LiAlH}_4$ : $\text{LiBH}_4$  (1:1, 2:1, 3:1, 4:1, and 1:2) were prepared using an agate pot and balls. The mixtures were mixed by high-energy ball milling with 300 rpm for 120 min and a ball-to-powder ratio of 100:1. Effect of metal catalysts on the hydrogen desorption/absorption of the mixture was also studied. The transition metals such as  $\text{TiO}_2$ ,  $\text{TiCl}_3$ ,  $\text{VCl}_3$ , or  $\text{ZrCl}_4$  were added to the mixture with a small amount of 1 mol%, and then it was mixed together with the hydride mixture by centrifugal ball milling. Approximately 350 mg

of sample was immediately loaded into the high-pressure stainless reactor after milling before it was placed into the thermo-volumetric apparatus.

### 3.3 Experimental Set-up

The thermo-volumetric apparatus was used to study the desorption and absorption of the  $\text{LiAlH}_4\text{-LiBH}_4$  systems. The schematic of the experimental set-up and actual set-up are shown in Figures 3.1 and 3.2, respectively. The set-up consists of a high-pressure stainless steel reactor. The pressure transducer was used to measure pressure of the system in the pressure range of 0–3,000 psig with 0.13% global error. The pressure regulator with 4,000 psig maximum limit was installed to control gas flow rate of the whole system. The K-type thermocouples were inserted into the reactor and the furnace to measure the temperature. The reactor was heated from room temperature to the target decomposition temperature depending on the hydride systems, which was about 300–350°C with a heating rate of 2°C min<sup>-1</sup> via a furnace controlled by a PID temperature controller.



**Figure 3.1** Schematic of the experimental set-up.



**Figure 3.2** Photograph of the experimental set-up.

### **3.4 Hydrogen Sorption Data Collection**

#### **3.4.1 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. About 350 mg of a sample was loaded in each batch of experiments depending on the molecular weight of a loading metal. The sample was then placed into the sample holder and  $V_s$  (volume of the sample holder) was determined. The degassing procedure at about  $10^{-3}$  torr and  $25^\circ\text{C}$  was conducted to remove the remaining gas for at least an hour. The sample holder was initially pressurized with hydrogen gas at about 100 psig. Then, the valve between the manifold and the sample holder was closed. The dehydrogenation was performed by stepwise increasing of a heating rate of  $2^\circ\text{C min}^{-1}$  from room temperature to desired temperature ( $300\text{--}350^\circ\text{C}$ ) via a furnace controlled by a PID temperature controller. The samples were held at this condition until no

(about 5 h). While the above processes were continuing, the pressure values were recorded every minute until the pressure in the sample holder was rather 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 were estimated by the equation of state as stated in Eq. (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,  $\text{cm}^3$

$Z$  = compressibility factor

$n_H$  = mole of desorbed hydrogen, mol

$R$  =  $82.06 \text{ cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$

$T_H$  = temperature of the sample, K

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

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.

**Table 3.1** Compressibility factors at different temperature ranges (Perry *et al.*, 1997)

Temperature (°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

#### 3.4.2 Absorption

Hydrogen was fed into the sample holder until the pressure reached approximately 1,200 psig. The sample was heated until the desired absorption temperature. Hereafter, the hydrogen uptake began and further extended for the next 6–12 h. The pressure value was recorded every minute.

### 3.5 Characterization

In order to identify phase transformation during the hydrogen desorption and absorption of the hydride systems, X-ray diffraction measurement (Rigaku,

model: D/max-2200) was used at room temperature over a range of diffraction angles from 15 to 85° with CuK- $\alpha$  radiation (40 kV, 30 mA).