



CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Materials

1. Lithium amide (LiNH_2), (95% from Aldrich Chemical)
2. Lithium aluminum hydride (LiAlH_4), (95% from Aldrich Chemical)
3. Magnesium hydride (MgH_2), (90% from Aldrich Chemical)
4. TiO_2 (from JJ-Degussa-Hüls)
5. TiCl_3 (from Aldrich Chemical)
6. Ti-metallic (from Aldrich Chemical)
7. Hydrogen (UHP from TIG)
8. Argon (UHP from TIG)

3.1.2 Equipment

1. High-energy ball-milling
2. Thermo-volumetric apparatus
3. X-ray diffraction (XRD) measurement
4. TPDRO 1100 (ThermoFinnigan) directly connected to an MS
5. Glove-box filled with nitrogen

3.2 Experimental Procedures

3.2.1 Sample preparation

In this study, different mixtures of LiNH_2 , LiAlH_4 , and MgH_2 (Table 3.1) were prepared using a centrifugal ball mill (Retsch ball mill model S100, stainless steel vial size 250 ml, stainless balls with 1 cm diameters) for 2 h with a speed of 300 rpm. In addition, 5 mol% of Ti-compounds including TiO_2 (Degussa P25), TiCl_3 (Aldrich Chemical), and Ti-metallic (Aldrich Chemical) were doped into the ternary hydride mixtures as a catalyst by the milling process.

Table 3.1 The molar ratio of the hydrides used in the experiment.

Sample	Materials	Molar ratio
1	LiNH ₂ /LiAlH ₄	2:1
2	LiNH ₂ /MgH ₂	2:1
3	LiNH ₂ /LiAlH ₄ /MgH ₂	2:1:1
4	5 mol%TiO ₂ -LiNH ₂ /LiAlH ₄ /MgH ₂	2:1:1
5	5 mol%TiCl ₃ -LiNH ₂ /LiAlH ₄ /MgH ₂	2:1:1
6	5 mol%Ti-LiNH ₂ /LiAlH ₄ /MgH ₂	2:1:1
7	5 wt%Carbon nanotube + LiNH ₂ /LiAlH ₄ /MgH ₂	2:1:1
8	10 wt%Carbon nanotube + LiNH ₂ /LiAlH ₄ /MgH ₂	2:1:1

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

3.2.2 Experimental set up

The thermo-volumetric apparatus was used to study the gas-solid interaction (LiNH₂/LiAlH₄/MgH₂). The schematic diagram of the experimental set-up is shown in Figures 3.1.

- The set-up consisted of a high pressure stainless reactor, which hold the sample and part of stainless steel tube as a gas reservoir.
- The pressure transducer was used to measure pressure of the system for measuring in the 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 into the whole system.

- Inside the reactor, the K-type thermocouple was placed to measure the temperature.
- The high pressure stainless steel reactor was heated from room temperature to 300°C with the heating rate of 2°C min⁻¹ via a furnace controlled by a PID temperature controller.

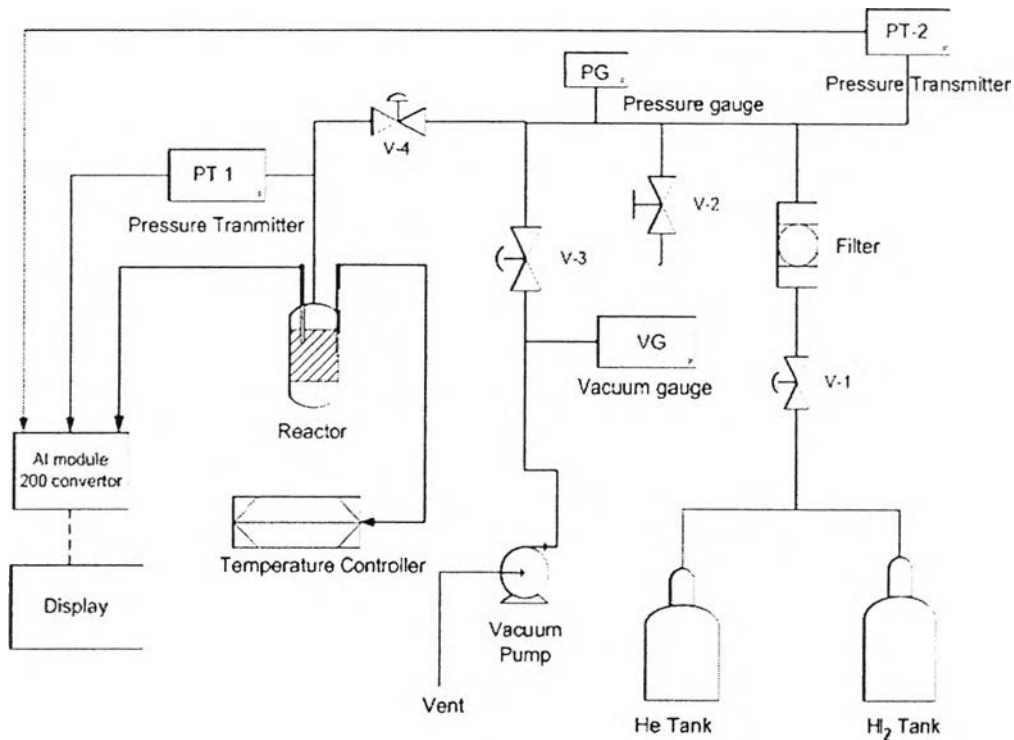


Figure 3.1 Schematic diagram of the experimental set-up.

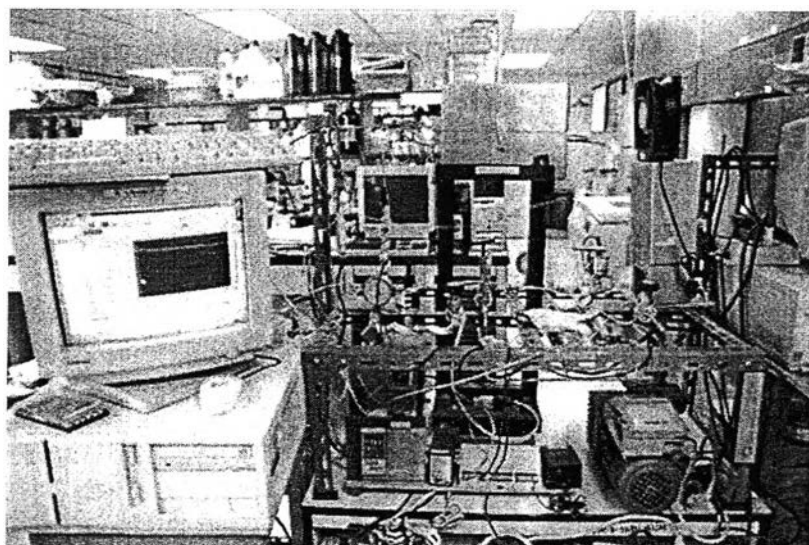


Figure 3.2 Actual set-up.

3.3 Hydrogen Desorption/Absorption and Characterization

3.3.1 Hydrogen desorption

The pressure transducers must be calibrated for each desorption experiment. Atmospheric pressure, 14.7 psi, was used as the reference pressure.

- The amount of LiNH_2 , LiAlH_4 , and MgH_2 used in each experiment was about 500 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 helium gas at 30 psig. Hence, the valve between the manifold and the sample holder was closed.
- The dehydrogenation was performed by increasing of the heating rate of 2°C min^{-1} from room temperature to 300°C via a furnace controlled by a PID temperature controller. A sample was held at this condition until no further desorption is observed.
- During the experiment, the pressure values of PID 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 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

n_H = mole of desorbed hydrogen, mol

R = 82.06 cm³·atm/mol·K

T_H = temperature of the sample, K

Table 3.2 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

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

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 Hydrogen absorption

Hydrogen was fed into the sample holder until the pressure reached approximately 1000 psig. The sample was heated with the rate of $2^{\circ}\text{C min}^{-1}$ 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.

3.3.3 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.

3.3.4 Temperature-programmed desorption mass spectroscopy (TPDMS)

The decomposition of LiNH_2 , $\text{LiNH}_2/\text{LiAlH}_4$, $\text{LiNH}_2/\text{MgH}_2$, and $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$ was observed for NH_3 formation by using TPDRO 1100 (ThermoFinnigan) directly connected to an MS with heating rate of $5^{\circ}\text{C min}^{-1}$ from 40-450°C.