CHAPTER III
EXPERIMENT

3.1 Materials

In this study, mixtures of lithium amide (95% $LiNH_2$) and lithium hydride (95% LiH) mixtures of $LiNH_2$ and lithium aluminium hydrides (95% $LiAlH_4$) were investigated. The $LiNH_2$ was purchased from Acros Organics and LiH and $LiAlH_4$ were purchased from Fluka. Nickel (Ni) and titanium (II) oxide (TiO_2) were from Searle Company and Degüssa. Zirconium (IV) chloride (99.5% $ZrCl_4$), and vanadium (III) chloride (>99% VCl_3), were obtained from Aldrich Chemical and MERCK, respectively. Iron powder was synthesized following the preparation procedure in Section 3.1.1. In order to mix starting materials and the catalysts homogeneously, ball milling (Pulverisette 6) and mortar with a diameter of 10 cm were used. Hydrogen gas (>99.999%) was used in the absorption. Water in hydrogen was removed by using a series of traps. All the material handlings (including weighing and loading) were performed in a glove-box filled with purified nitrogen to keep a low water vapor concentration, a low oxygen concentration during operation using a gas recycling purification system (MP-P60W, Miwa MFG Co., Ltd.), and without exposing the samples to air.

3.1.1 Preparation of Nanoscale Iron Particle

Synthesis of nanoscale iron particles was achieved by adding a 1:1 volume ratio of 0.25 M sodium borohydride (97% $NaBH_4$) into 0.045 M iron (III) chloride hexahydrate (99% $FeCl_3 \cdot 6H_2O$) (Lien and Zhang, 2001). The solution was mixed vigorously under room temperature (25±1°C) for 5 min. Ferric iron was reduced by borohydride according to the following reaction:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2 \qquad (3.1)$$

Excessive borohydrate was the key factor for rapid and uniform growth of iron crystals. The metal particles formed from the above reaction were then washed with large volume of milli-Q water for at least three times. Air-dried particles from the above procedures have sizes generally <0.1 μm (mostly between 10 and 100 nm).

3.2 Sample Preparation

Firstly, we studied the effect of transition metals, Fe, Ni, $ZrCl_4$ and TiO_2 on hydrogen desorption/absorption of Li-N-H system. Approximately, one g of the mixture of $LiNH_2$, LiH, and additives and 15 pieces of agate balls with diameter of 20 mm were placed into an agate pot, made of SiO_2, and milled with 400 rpm for 120 min. In this part, the mixture of $LiNH_2$ and LiH were studied for the effect of mixing process, mortar and ball milling, agate pot. In the second part, we studied the reversibility of Li-Al-N-H system, consists of $LiAlH_4$ and $LiNH_2$. The hydrogen desorption/absorption of $LiNH_2$ and $LiAlH_4$ with different mol ratios (1:1, 1:3, and 1:5) doped with catalysts such as $ZrCl_4$, TiO_2, and VCl_3 and the effect of packing sample in the reactor were studied. In this part, the samples were mixed by ball milling with 400 rpm for 60 min. Immediately after milling in each experiment, approximately one g of the sample was placed into the thermo-volumetric apparatus.

3.3 Experimental Set-up

The thermo-volumetric apparatus was used to study the gas-solid interaction (Li-N-H system). The schematic diagram of the experimental set-up and the actual set-up are shown in Figures 3.1 and 3.2, respectively. The high pressure stainless steel reactor was heated from room temperature to 200°C with the heating rate of 2°C min^{-1} via a furnace controlled by a PID temperature controller. The K-type thermocouple was placed inside the reactor to measure the temperature. The pressure regulator with 4,000 psig maximum limit purchased from Concoa (Model BU-2581-AQ) was installed to control a gas flow rate into the whole system. The set-up

consisted of a high pressure stainless reactor (SS316, ~25 cm^3), which was used to hold the sample and part of stainless steel tube as a gas reservoir (~31 cm^3). The pressure transducer used to measure pressure of the system was purchased from Cole-Parmer (Model 68073-68074) capable for measuring in the range of 0 – 3,000 psig with 0.13% global error.

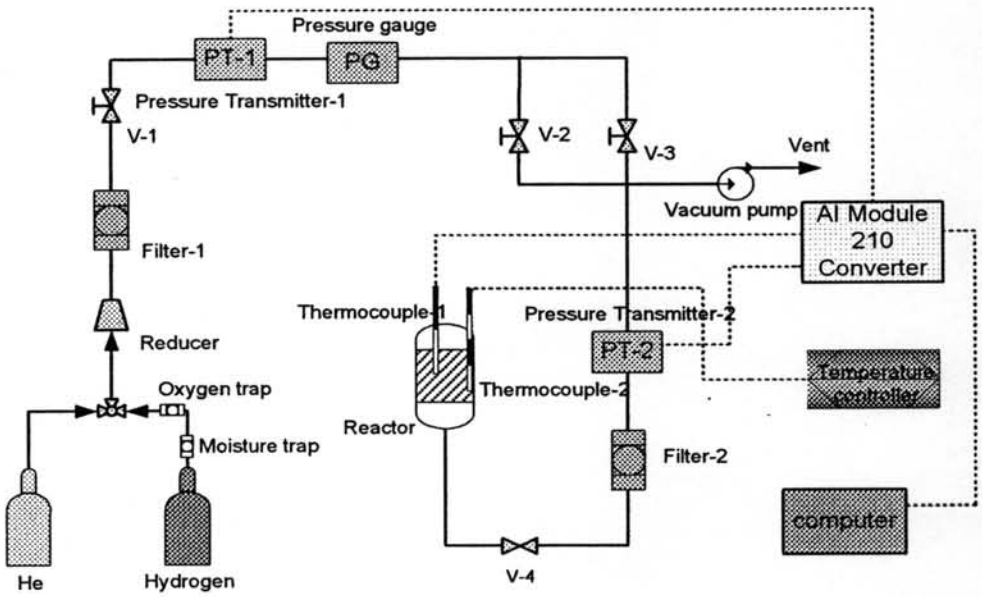

Figure 3.1 Schematic diagram of the experimental set-up.

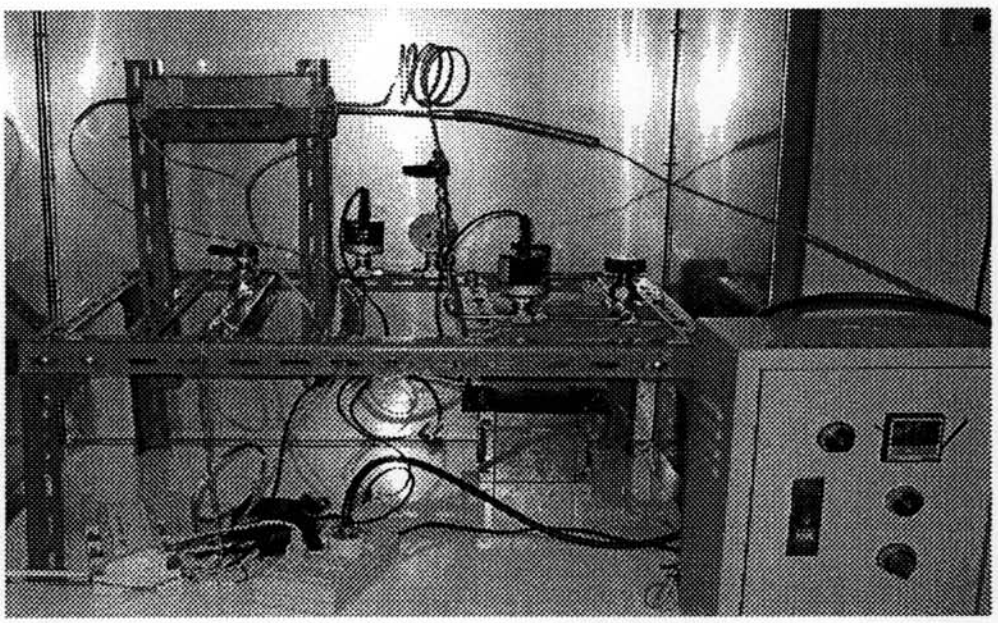

Figure 3.2 Schematic diagram of the actual set-up.

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. After the doping procedure, the amount of $LiNH_2$ and LiH used in each experiment was about one gram depending on the molecular weight of a loading metal. A sample was then placed into the sample holder and volume of the sample holder, V_s, was determined. The degassing procedure at about 10^{-3} torr and 25°C was conducted to remove the remaining gas for at least an hour. Later, the temperature of the sample holder was controlled to achieve desired desorption temperature (200°C) by stepwise increasing of the heating rate of 2°C min^{-1}. 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:

The hydrogen capacities were estimated by the equation of state as stated in Eq. (3.2) and (3.3). The compressibility factor (Z) used in this relation was given in Table 3.1.

$$P_H V_s = Z n_H R T_H \tag{3.2}$$

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 cm^3 atm mol^{-1} K^{-1}

T_H = temperature of the sample, K

Table 3.1 Compressibility factors at different temperature ranges

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

$$Hydrogen\ capacity, wt\% = \frac{Released\ hydrogen \times 100}{Amount\ of\ sample} \tag{3.3}$$

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.

3.4.2 Absorption

Hydrogen was fed into the sample holder until the pressure reached approximately 1500 psig. The sample was heated with the 2°C min^{-1} heating until the

desired absorption temperature, 180°C was reached. Hereafter, the hydrogen uptake began and further extended for the next 12 h. The pressure values were recorded every minute.