CHAPTER III
EXPERIMENTAL

3.1 Starting Materials

3.1.1 Metal Hydrides

- Lithuim borohydride ($LiBH_4$, 95%, Arcos)
- Magnesium chloride ($MgCl_2$, 98%, Sigma-Aldrich)

3.1.2 Catalysts

- Niobium (V) oxide (Nb_2O_5,Sigma-Aldrich)
- Niobium (V) chloride ($NbCl_5$, 99.99%, Sigma-Aldrich)
- Titanium powder (Ti, 99.99%, Sigma-Aldrich)
- Titanium (IV) oxide (TiO_2, Degüssa)
- Titanium (III) chloride ($TiCl_3$, as-prepared)

$TiCl_3$ powder was obtained from drying 12% $TiCl_3$ in hydrochloride solution (Riedel-de Haën). About 30 ml $TiCl_3$ solution was stirred in an enclosed glassware bottle, which was connected with a high vacuum pump. The solution became $TiCl_3$ powder (violet powder), and it was left under vacuum overnight.

3.2 Sample Preparation

For the mixture of $LiBH_4$ and $MgCl_2$, the sample was prepared with a 2:1 molar ratio and mixed with and without a transition metal. A transition metal catalyst - Nb_2O_5, $NbCl_5$, Ti, TiO_2, and $TiCl_3$, - was included. The mixing was achieved by a ball-milling technique (Retsch ball mill model S100, 250 ml stainless steel vial, stainless steel ball with 1 cm diameter under nitrogen atmosphere with a ball to powder ratio of 60:1 and a rotation speed of 300 rpm) at 2 and 5 h. For mixed samples, 16 wt% of Nb_2O_5, $NbCl_5$, Ti, TiO_2, and $TiCl_3$ were added to the sample and milled for 2 h. The milling process with the same condition was used. All material handlings (including weighing and loading) were performed in a glove

box filled with nitrogen to keep a low water vapor concentration and avoid exposing the samples to air.

3.3 Experimental Set-up

The thermo-volumetric apparatus was used to study the gas-solid interaction. The schematic diagram 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. The high pressure stainless steel reactor was heated from room temperature to 450°C for the $LiBH_4$ and $MgCl_2$ mixture with a heating rate of 2°C/min via a furnace controlled by a PID temperature controller. Inside the reactor, a K-type thermocouple was placed to measure the temperature. The pressure regulator with 3,000 psig maximum limit was installed to control the gas flow rate into the whole system. 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.

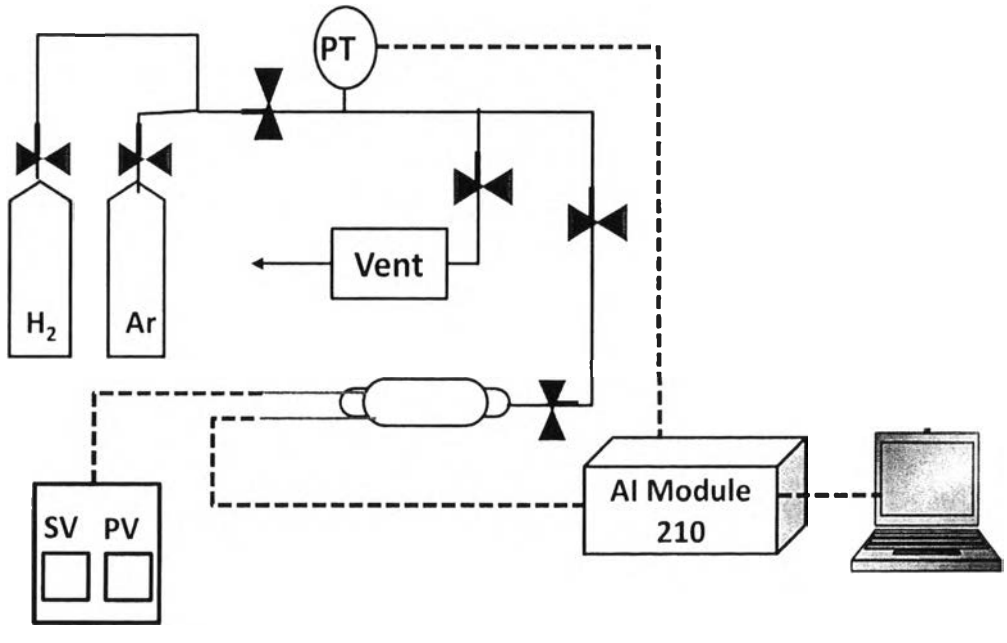

Figure 3.1 Schematic diagram of the experimental set-up.

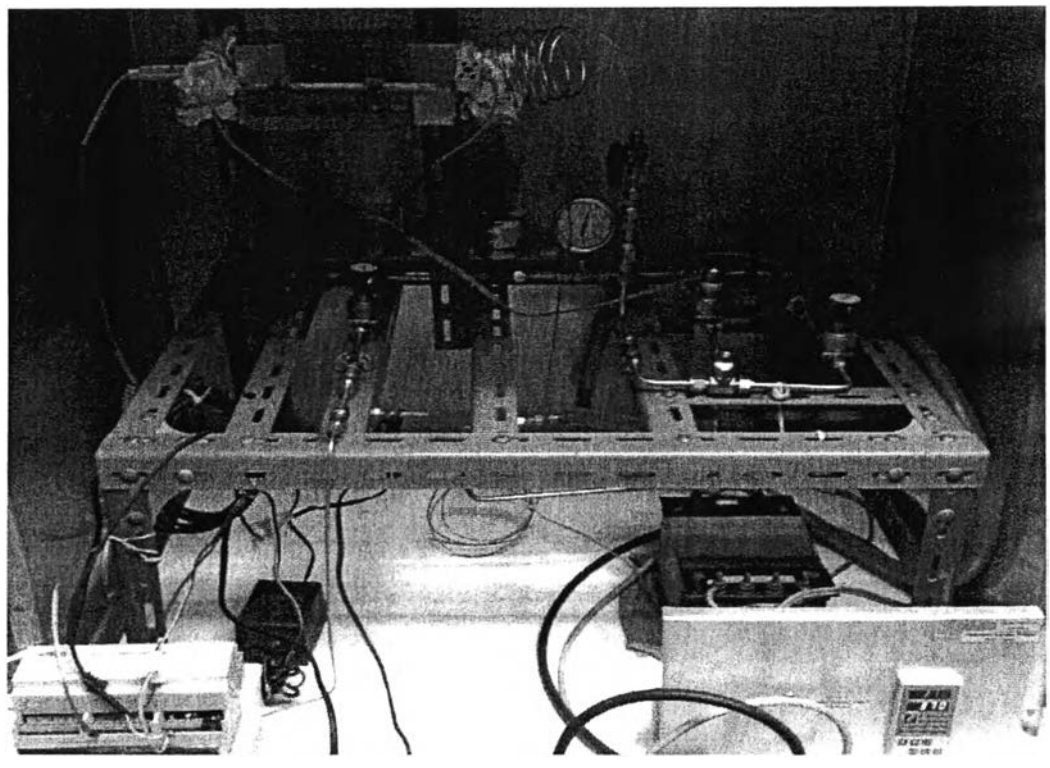

Figure 3.2 Photograph of the experimental set-up.

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. The amount of sample used in each experiment was about 0.3 gram. A sample was placed into the sample holder, and the sample holder volume 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. The sample holder was initially pressurized with helium gas at 30 psig. Hence, the valve between the manifold and the sample holder was closed. After that, hydrogen desorption was performed from 25 °C to the set point (450 °C for the $LiBH_4$ and $MgCl_2$ mixture) by a stepwise increase with a heating rate of 2 °C/min. A sample was held at 450 °C until no further hydrogen desorption was observed. While the above processes were continuing, the pressure values were recorded every 1 min until the

pressure in the sample holder was rather constant. The released pressure was cooled down to room temperature to avoid the gas expansion by heat before evaluating the hydrogen capacity. The observed pressure values were treated by the deduction method and the hydrogen capacity can be estimated from equations (3.1) – (3.3).

$$\text{Hydrogen pressure} = \text{Observed pressure} - \text{Initial pressure} \tag{3.1}$$

The hydrogen capacity was estimated by the equation of state:

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

$$\text{Hydrogen capacity (wt\%)} = \frac{n_H \times MW_H \times 100}{\text{Amount of sample}} \tag{3.3}$$

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 (evaluated from Table 3.1)

n_H = mole of desorbed hydrogen, mol

R = 82.06 cm^3 atm/mol·K T_H = temperature of the sample, K

MW_H = molecular weight of hydrogen, 2.016 g/mol

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

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 helps in the regeneration of the substrate.

3.4.2 Absorption

After completing hydrogen desorption, the sample was compressed under 9.5 MPa hydrogen (99.9999%) at a constant temperature of 350 °C for 12 h for hydrogen adsorption. After that, both hydrogen desorption and absorption were repeated in order to investigate the reversibility.

3.5 Characterization

In order to identify phase transformation during hydrogen desorption of the samples, X-ray diffraction (XRD, Rigaku) 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, phase transformation temperature, and temperature that reactions occured were measured by a differential scanning calorimeter (DSC 822, Mettler Toledo) from 30 °C to 450 °C. IR spectra of B-H bond were measured with the Thermo Nicolet/Nexus 670 FTIR instrument. The spectrometer collected 64 spectra in the range of 400-4000 cm^{-1} with the resolution of 4 cm^{-1}.