CHAPTER III

EXPERIMENTAL

3.1 Sample Preparation

Sodium aluminum hydride ($NaAlH_4$) from Aldrich Chemical Inc. (technical grade, 90%) was used in this work. $TiCl_3$ (99.9%), $ZrCl_4$ (99.5%), and $HfCl_4$ (99.95%) were obtained from Aldrich Chemical Inc. Hydrogen gas (99.99%) used in sorption kinetics and helium gas (99.99%) used as the inert gas to determine the volumes of a manifold and sample holder. THF (99.5%) and n-pentane (98%) were also obtained from Aldrich Chemical Inc.

Twenty-five g of commercial $NaAlH_4$ in 250 cm^3 of THF (solubility of $NaAlH_4$ in THF: 162 g/l at 20 °C) was stirred for 3 hr and precipitated by a centrifuge. The clearance was concentrated under vacuum to the volume of 50 cm^3, whereby $NaAlH_4$ started to separate from the solution. Under rigorous stirring, 200 cm^3 of pentane was added to the THF solution causing $NaAlH_4$ to clearly separate from the solution as a fine precipitate. The suspension was stirred for an hour, filtered and washed with 40 cm^3 of pentane twice. After drying in high vacuum overnight (10^{-3} torr at room temperature), 13.5 g (54%) of $NaAlH_4$ was obtained as colorless powder. One g of the purified $NaAlH_4$ was used for each experiment. To prepare metal-loaded $NaAlH_4$, one of the three metals (Zr, Ti, Hf) was added to the freshly re-crystallized $NaAlH_4$ under nitrogen atmosphere. The metal was simply mixed with $NaAlH_4$ using mortar and pestle for 15 min and this method is known as dry doping (Jensen *et al.*, 1999). Various amounts of $ZrCl_4$ (2, 4, 6, 9 mol%) and 4 mol% of $TiCl_3$ or $HfCl_4$ were used.

3.2 Experimental Set-up

The thermovolumetric apparatus was used to study the gas-solid interaction between hydrogen and $NaAlH_4$. The schematic diagram of the experimental set-up and the actual set-up are shown in Figure 3.1 and Figure 3.2, respectively. The pressure regulator with 4000 psig maximum limit purchased from Tescom Co., Ltd.

was installed to control a gas flow rate into the whole system. The set-up consisted of a high pressure stainless steel vessel (20 cm^3), which was used to hold the sample, and part of stainless steel tube as a gas reservoir (5 cm^3). The pressure transducer used in this system was purchased from Setra Co., Ltd. (Model 206) capable for measuring in the range of 0-3000 psig with 0.13% global error. Its output signal was a voltage 0.1-5.1 V, and recorded by a data acquisition system. The data acquisition software (Labview 7 express) was purchased from National Instruments, shown in Figure 3.3. It displayed and managed real-time information as shown in Figure 3.4. The pressure gauge was a module from Ashcroft, measuring in the range of 0-3000 psig. The sample holder contained a thermo well that had a K-type thermocouple inside. The entire reactor was wrapped by a heating tape, which was directly connected with a PID digital temperature controller. The controller was able to control with a high precision (approximately $\pm$ 2 °C) and program sample temperature in the range of 25-270 °C.

Evacuation the manifold and sample holder were accomplished with a Vacuubrand vacuum pump, model type RZ2 and monitoring with an Edwards vacuum pressure sensor (Model AGD 101L).
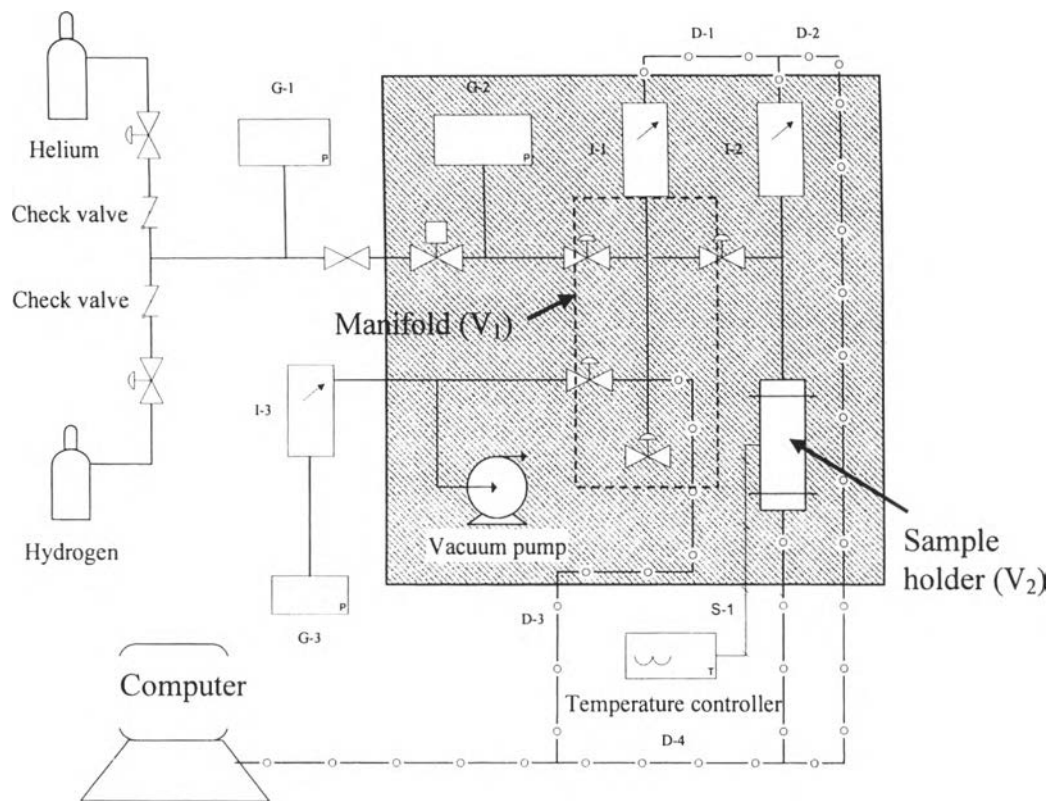
Figure 3.1 Schematic diagram of the experimental set-up.

According to Figure 3.1, the parts within the shaded boundary were placed in the lab hood for safety reason. G-1 and G-2 refer to the pressure gauges. G-3 is the vacuum gauge. I-1 and I-2 refer to the pressure transducers. I-3 is the vacuum sensor. D-1 and D-2 are the analog data transferred from the pressure sensor. D-3 and D-4 are the analog data transferred from the thermocouple for ambient temperature and the sample temperature measurements, respectively.
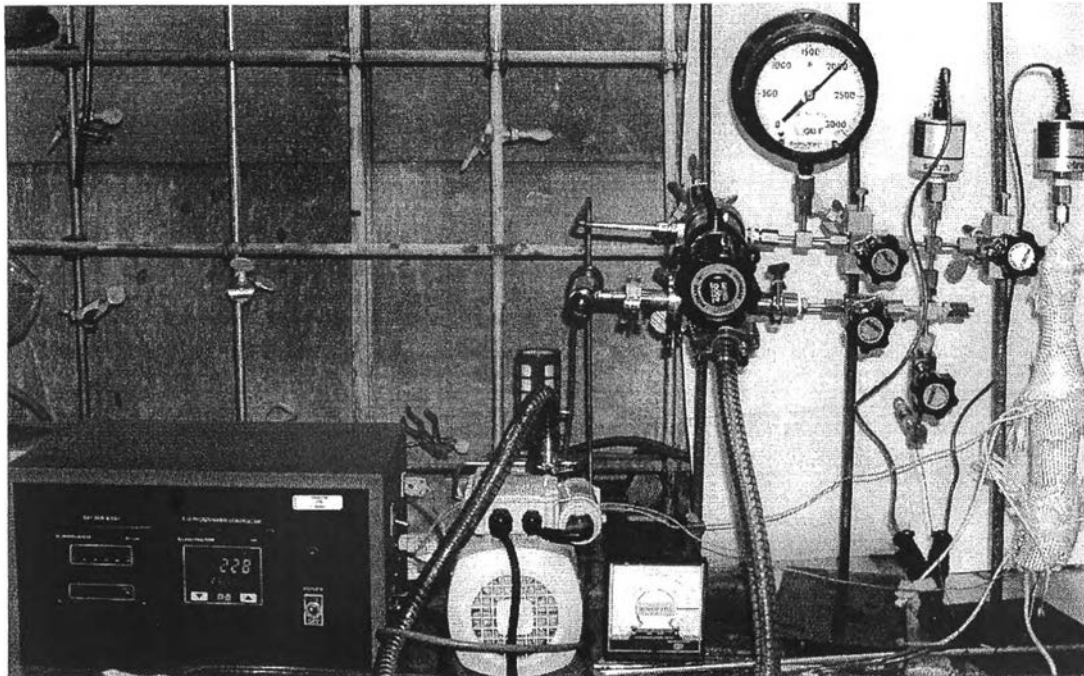
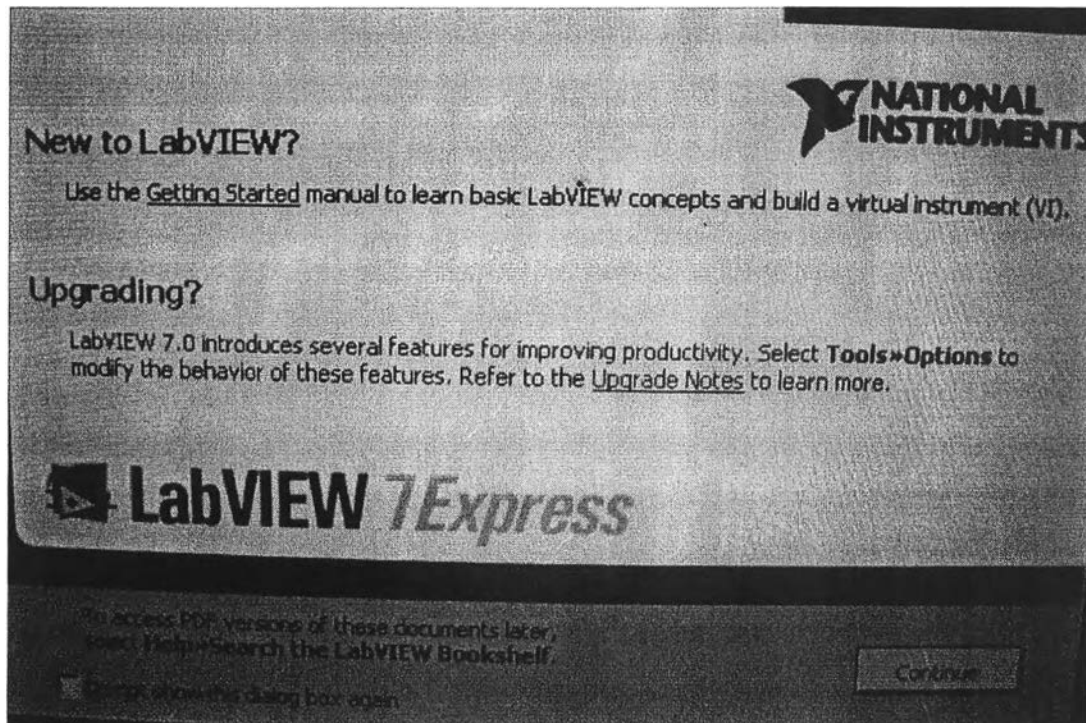**Figure 3.2** Photograph showing the experimental set-up.

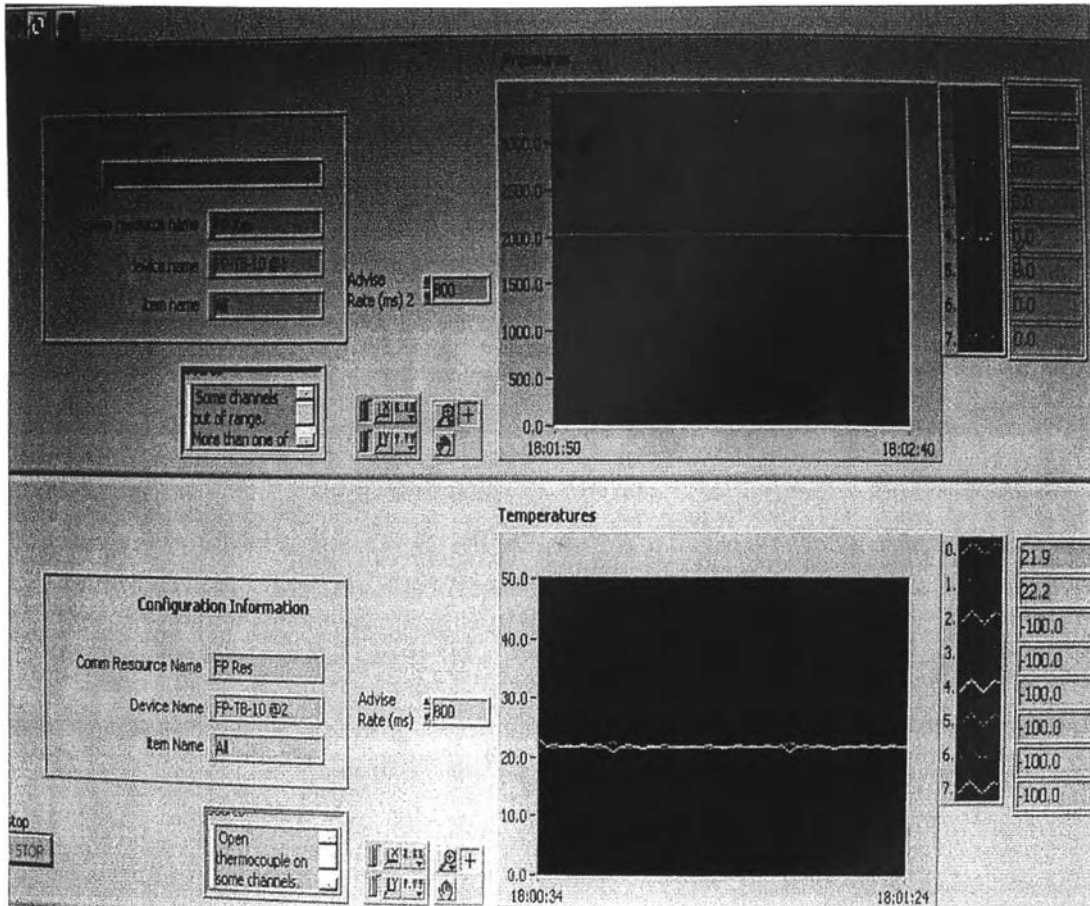**Figure 3.3** Picture of data acquisition program.

Figure 3.4 Photograph of display of hydrogen absorption program (Labview 7).

3.3 Experimental Set-up Calibration

3.3.1 Blank Test

Blank test was employed to check the reliable of the experimental set-up and any leakage of the system. When there was no specimen in the sample holder, the blank test was started with pressurizing the system to 2000 psig with helium and left it for at least 12 hr. The pressure difference between 12 hr was used to indicate any leakage.

3.3.2 Calibration of Volume Space

3.3.2.1 Volume of Manifold (V_1)

Volume of the manifold was estimated by means of water displacement. A graduated cylinder was used by placing it in the upside down position into a bucket of water. The cylinder had one end connected to the hose to the sample holder while the other end of the hose was hooked to the bottom of the graduated cylinder. The manifold was pressurized with helium gas in the range of 100-2000 psig. Once the pressure was equilibrated, the valve to the hose was opened and the pressurized gas would displace the water in the graduated cylinder. The amount of the displaced water was recorded for each pressure and then the volume was calculated by using Equation (3.1).

$$P_m V_1 = Z_w P_w V_w \tag{3.1}$$

where,

P_m = pressure of helium at the equilibrium state

P_w = atmospheric pressure

V_w = volume of displaced water

Z_w = Correction factor equals to 0.889 for water vapor at standard temperature and pressure.

3.3.2.2 Volume of Sample Holder (V_2)

Before each experiment, unknown volume of a sample was loaded. The dead volume of the sample holder was then determined from the helium expansion. The manifold was pressurized to 2000 psig and held for 2 min. Then, the gas was fed into the sample holder and left until the pressure in the manifold and sample holder was nearly the same. During both steps, pressure and temperature of the system were real-time collected via the computer program (hydrogen absorption Labview version 7.0).

The mole balance was performed for the first and second states of the expansion. The first state was the initial state, before the expansion, where helium gas was only present in the manifold volume and no gas was present in the sample holder. The second state was after the expansion, where gas was present

in both manifold and the sample holder. Two thermocouples, which were inserted into both volumes, were used for actually temperature measurements.

Total mole of gas at the initial state =   Total mole of gas at the final state   (3.2)

[mole in V_1 + mole in V_2]$_{initial\ state}$ = [mole in V_1 + mole inV_2]$_{final\ state}$ (3.3)

$$\frac{P_1 V_1}{ZRT_1} = \frac{P_1' V_1'}{ZRT_1'} + \frac{P_2 V_2}{ZRT_2} \qquad (3.4)$$

where,

V_1 = volume of the manifold at initial state, m^3

V_1' = volume of the manifold at final state, m^3

V_2 = volume of the sample holder, m^3

P_1 = pressure of gas inside the manifold at initial state, atm

P_1' = pressure of gas inside the manifold at final state, atm

P_2' = pressure of gas inside the sample holder at final state, atm

T_1 = temperature inside the manifold at initial state, K

T_1' = temperature inside the manifold at final state, K

T_2 = temperature inside the sample holder at final state, K

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

The calculated Z is equivalent to compressibility factor at 20-30 °C as given in Equation (3.5).

$$Z = 0.9999 + 0.0004P \qquad (3.5)$$

The sample holder was continuously pressurized in the same manner for at least 10 times to obtain the precise volume.

3.4 Hydrogen Sorption Data Collection

3.4.1 Desorption

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

set the zero span on the transducer to vacuum or set it to 14.7 psig. After doping procedure as mentioned before, the standard amount of $NaAlH_4$ used in each experiment was about 1-1.5 g depending on the molecular weight of a loading metal. A sample was then placed into the sample holder and V_2 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 50 psig. Hence, the valve between the manifold and the sample holder was closed. Later, the temperature of the sample holder (T_2) was controlled to achieve desired desorption temperature (250 °C) by stepwise increasing of the heating rate of 5 °C/min. A sample was held at this condition until no further desorption was observed. While all of the above processes were continuing, the pressure values were recorded every 2 sec until the pressure in the sample holder was rather constant. The observed pressure values were treated by deduction method as followed;

$$\text{hydrogen pressure } = \text{ observed pressure data } - \text{ helium pressure} \qquad (3.6)$$

The hydrogen capacities were estimated by the equation of state as stated in Equation (3.7). The compressibility factor (Z) used in this relation was given in Table 3.1.

$$P_H V_2 = Z n_H R T_H \qquad (3.7)$$

where,

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

n_H = mole of desorbed hydrogen, mol

T_H = temperature of the sample, K

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 an hour. The use of the high vacuum pressure helped in the regeneration of the substrate.

Table 3.1 Compressibility factors at different temperature ranges

Temperature (°C)	Z
25-49	1+ 0.0006P
50-99	1+ 0.0005P
100-149	1+ 0.0005P
150-199	1+ 0.0004P
200-249	0.9999 + 0.0004P

3.4.2 Absorption

Hydrogen was fed into the sample holder until the pressure reached approximately 2000 psig. The sample was heated with the 20 °C/min heating rate until desired absorption temperature (125 °C) was reached. Hereafter, the hydrogen uptake began and further extended for the next 12 hr. The pressure values were recorded every 2 sec.