

CHAPTER III METHODOLOGY

3.1 Starting Materials

3.1.1 Metal Hydrides

- Lithium borohydride (LiBH₄, 95%, Arcos)
- Magnesium hydride (MgH₂, 90%, mainly Mg, 10%, Fluka)

3.1.2 Catalysts

- Zirconium (IV) oxide (ZrO₂, 98.5%, Riedel-de Haën)
- Zirconium (IV) chloride (ZrCl₄, 99.5%, Sigma-Aldrich)
- Vanadium (III) chloride (VCl₃, >99%, MERCK)
- Hafnium (IV) chloride (HfCl₄, 99.9%, Sigma-Aldrich)
- Titanium powder (Ti, 99.99%, Sigma-Aldrich)
- Titanium (IV) oxide (TiO₂, Degussa)
- Titanium (III) chloride (TiCl₃, as-prepared)

TiCl₃ powder was obtained from drying 12% TiCl₃ in hydrochloride solution (Riedel-de Haën). TiCl₃ solution of 30 ml was stirred in an enclosed glassware bottle, which was connected with a high-vacuum pump. The solution became TiCl₃ powder (violet powder), and it was left under vacuum overnight.

3.1.3 Gases

- Hydrogen gas (H₂, 99.9999%, Prexair)
- Argon gas (Ar, >99.9%, TIG)

3.2 Sample Preparation

For the mixture of LiBH₄ and MgH₂, the sample was prepared with a 2:1 molar ratio and mixed with and without transition metals. A transition metal catalyst

(1 to 7 mol%) - Ti, TiO₂, TiCl₃, ZrCl₄, HfCl₄, and VCl₃ - were included. The mixing was achieved by a ball-milling technique (Retsch ball mill, model S100) at a different period of time (1, 5, and 10 h). The starting materials were used as-received. In the milling process, the sample was milled using a centrifugal ball mill (Retsch ball mill model S100, 250 ml stainless steel vial, stainless steel ball with 1 cm diameter) under nitrogen atmosphere and a rotation speed of 300 rpm. All the 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 high pressure stainless steel reactor was heated from the room temperature to 450 or 500°C with a heating rate of 2°C min⁻¹ 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 4,000 psig maximum limit was installed to control the gas flow rate into the whole system. 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 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.

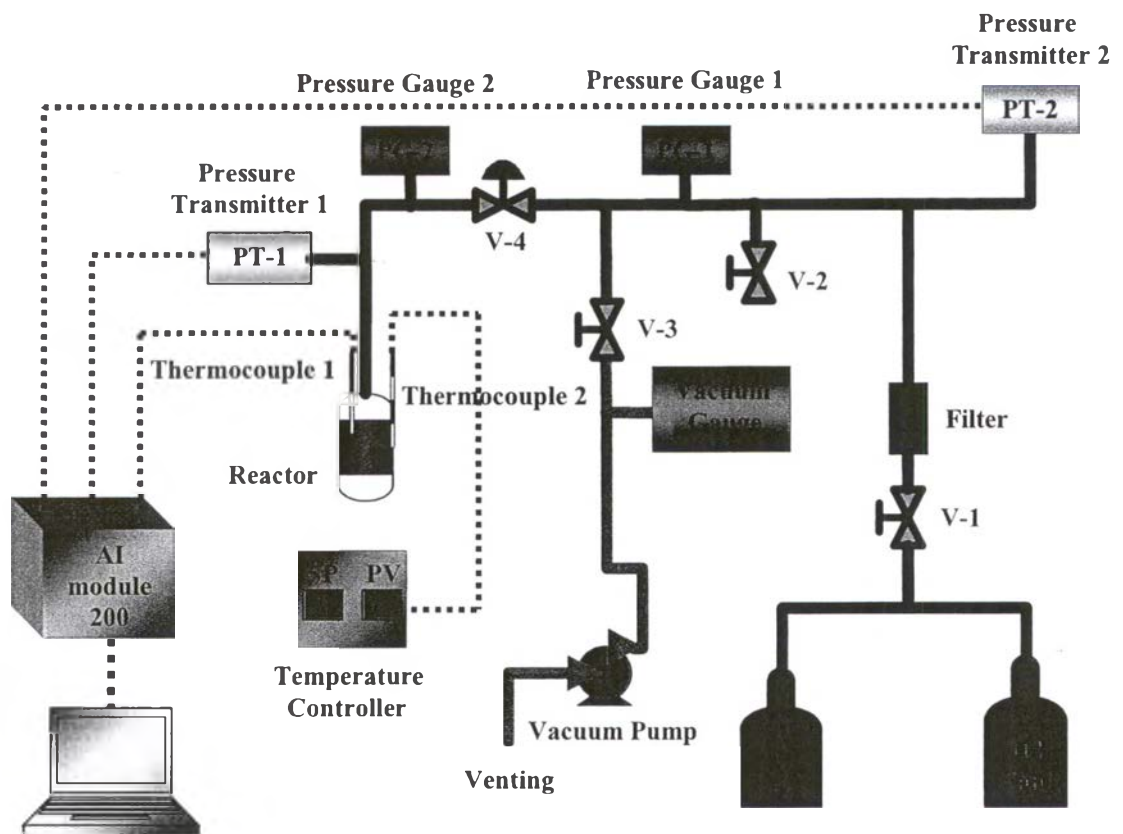


Figure 3.1 Schematic diagram of the experimental set-up.

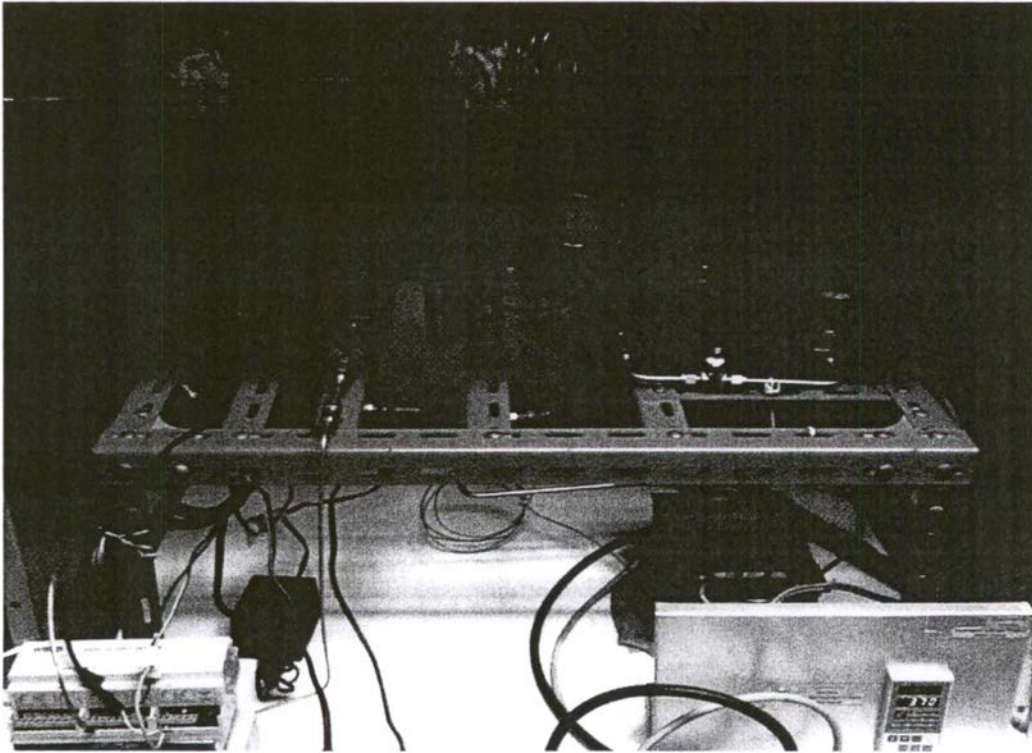


Figure 3.2 Photograph of the experimental set-up.

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 or set it to 14.7 psi. After the doping procedure, the amount of sample used in each experiment was about 0.3-0.5 gram. A sample was then placed in 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 at a ramped temperature from 25 to the set point (450 or 500°C) by a stepwise increase with a heating rate of $2^{\circ}\text{C min}^{-1}$. A sample was held at temperature 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 the 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 obtained from Eqs. (3.1)-(3.3).

$$\text{Hydrogen pressure} = \text{Observed pressure} - \text{Initial pressure} \quad (3.1)$$

The mole of released hydrogen is estimated by the equation of state:

$$P_H V_s = Z n_H R T_H \quad (3.2)$$

The hydrogen capacity is determined from:

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

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

T_H = temperature of the sample, K

M_H = molecular weight of hydrogen, 2.016 g mol^{-1}

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 the 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 finish hydrogen desorption, the sample was compressed under 10 MPa hydrogen (99.9999%) at a constant temperature of 350°C for 12 h for hydrogen adsorption.

After that, both of hydrogen desorption and absorption were repeated in order to investigate the reversibility.

3.4.3 Characterization

3.4.3.1 *X-ray diffractometer (Rigaku, CuK α radiation, 40 kV, 30 mA)*

The X-ray diffractometer was used to identify phase transformations and crystal structures at various conditions. It was operated at room temperature over the range of diffraction angles from 20° to 80°.

3.4.3.2 *Temperature program desorption/reduction/oxidation connected to an MS (TPDRO 1100, Thermo Finnigan)*

The temperature program desorption/reduction/oxidation was operated in the temperature program desorption mode in order to examine the starting hydrogen desorption temperature of the sample. The sample temperature was ramped from 50 to 500°C with the heating rate of 5°C min⁻¹.

3.4.3.3 *Differential scanning calorimetry (DSC 822, Mettler Toledo)*

The differential scanning calorimetry was used for thermal analysis. The sample was examined over a temperature range of 50 to 500°C with a heating rate of 5°C min⁻¹ in a nitrogen flow of 40 ml min⁻¹.