

CHAPTER III

EXPERIMENTAL

3.1 Materials

NaAlH_4 (>90 %), HfCl_4 (>98 %) and Ni metal were obtained from Aldrich chemical.

3.1.1 Porphyrin synthesis

Meso-Tetraphenylporphyrin, $\text{C}_{44}\text{H}_{30}\text{N}_4$ (H_2TPP) was synthesized by heating 40 ml of propanoic acid. Once the propanoic acid begins to reflux vigorously, add a mixture of 1.65 ml of benzaldehyde and 1.0 ml of pyrrole by slowly pouring this solution down the reflux condenser. Rinse the pyrrole and benzaldehyde down the condenser with 10ml of propanoic acid. Reflux the solution for 30 min and allow the flask cool for a few minutes. Filter the dark brown mixture through a medium porosity frit. Rinse the mixture with methanol until the washings are clear and purple. Crystals remain on the frit. Allow the crystals to dry.

Synthesis of (Tetraphenylporphyrinato)hafnium(IV)chloride, $\text{HfCl}_2\text{C}_{44}\text{H}_{28}\text{N}_4$ (HfCl_2TPP) by added 20 ml of N,N-dimethylformamide (DMF) into 0.1 g of H_2TPP and stirred the mixture for few minutes until H_2TPP dissolved. Then 0.26 g of HfCl_4 was added to dark purple solution. Reflux the solution for 30 minutes. Cool the solution to room temperature in an ice bath, add 50 ml of distilled water and return to the ice bath again for 5-10 minutes to precipitate the product. Filter the reaction mixture through a medium porosity frit and wash the precipitate with distilled water. Allow the crystals to air-dry [12].

3.1.2 Copper-chromium oxide synthesis

Copper-chromium oxide was prepared from Ammonium copper chromate by a method similar to that describe by Adkins and Connor [32]. Coprecipitating of ammonium copper chromate from a solution containing the required amounts of copper(II) nitrate and ammonium dichromate with aqueous ammonia at room temperature, at pH of 7-7.2. The resulting precipitate was filtered and washed with

distilled water until it was free from nitrate ions. The filtrate was dried in an air-oven at 80-100°C for 24hr. The dried precipitate was heated at 300-320°C for 30 min. Then cooled it and the black dusty powder was used for the dehydrogenation without further purification.

3.2 Sample Preparation

All preparations were carried out under argon atmosphere. *Method A*: about 1 g NaAlH₄ was mixed with 4 mol% HfCl₄ (S2) and the different amount of co-catalyst (H₂TPP or HfCl₂TPP) as follow: 0.1 mol% H₂TPP - HfCl₄ - NaAlH₄ (S4), 0.1 mol% HfCl₂TPP - HfCl₄-NaAlH₄ (S6), 1 mol% H₂TPP - HfCl₄ - NaAlH₄ (S3), and 1 mol% HfCl₂TPP - HfCl₄ - NaAlH₄ (S5). The mixture was milled by using centrifugal ball mill for 15 min. In addition, a mortar and pestle were also used as a means of mixing for 10-15 min. *Method B*: about 1 g NaAlH₄ was mixed with 4 mol% HfCl₄ by using centrifugal ball mill for 10 min and added 0.1 mol% H₂TPP then mill for further 5 min (S7). (S8) is 0.1 mol% H₂TPP - HfCl₄ - NaAlH₄ prepared by method B. Moreover, 4mol% CuCrO₄ - NaAlH₄ (S9), 0.1 mol% CuCrO₄ - HfCl₄ - NaAlH₄ (S10) and 4 mol% Ni - HfCl₄ - NaAlH₄ (S12) were prepared by method A. (S11) is 0.1 mol% CuCrO₄- HfCl₄ - NaAlH₄ prepared by method B.

After that the sample was added with 0.1 mol% H₂TPP and milled further 5 min. After mixing procedure, approximately 0.5 g of a sample was placed into the thermovolumetric apparatus. The high pressure stainless steel reactor (316SS) was heated from room temperature to 280 °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. A pressure transducer (Cole Parmer, model 68073-68074) was used to measure the pressure change, which resulted from hydrogen desorption from the sample. For the absorption experiments, hydrogen (99.99%) was used to pressurize the high pressure vessel in a step-wise manner. The sample was re-absorbed at 120 °C and 10 MPa for 12 h. Once the pressure reading was constant over a period of time, the data was used to calculate the amount of hydrogen absorbed into the sample. Amount of the released hydrogen shown in the results (H/M) was calculated regarding to the amount of NaAlH₄ in the sample. The same

procedure was repeated to investigate the sample reversibility. A schematic of the experimental set-up is shown in Fig. 3.1.

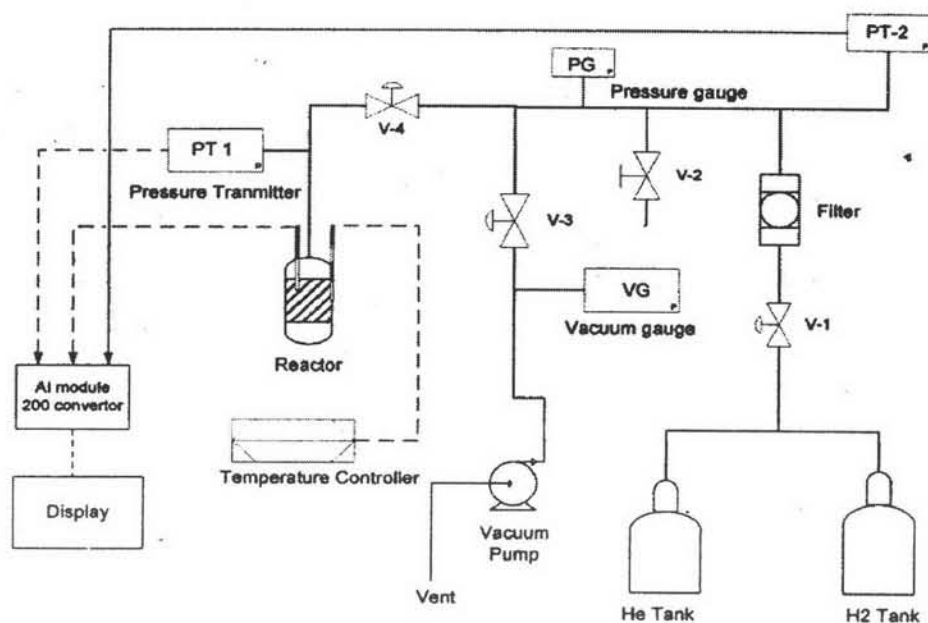


Figure 3.1 Schematic diagram of the experimental set up.

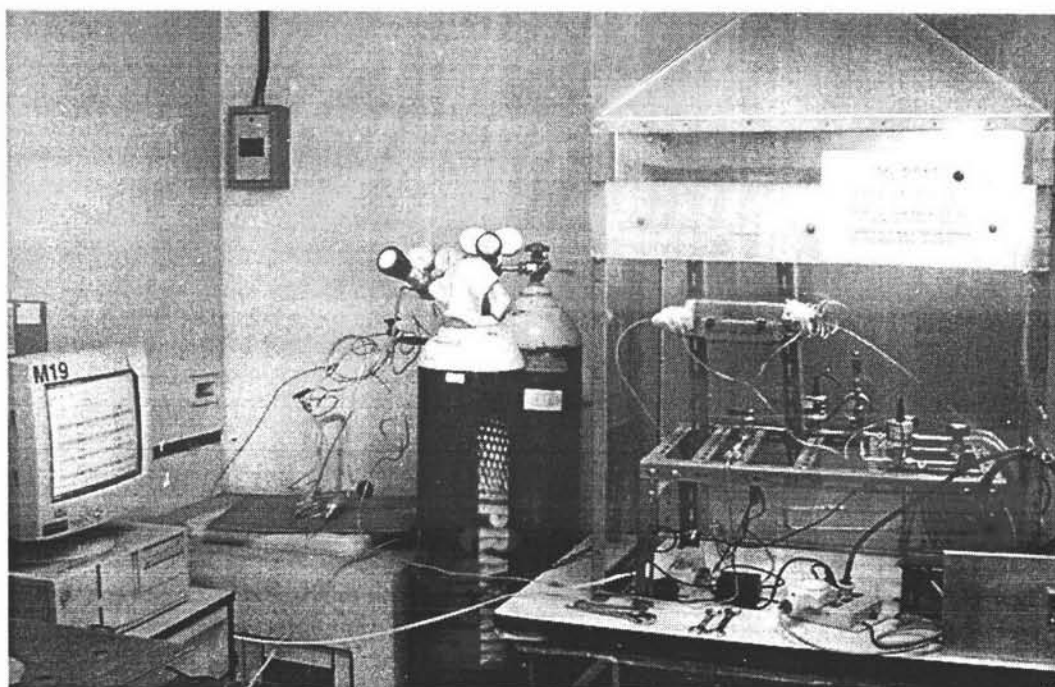


Figure 3.2 Photograph showing the experimental set up.

3.3 Experimental Set-up Calibration

3.3.1 Blank test

Blank test was employed to check the reliability 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 argon 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).

$$P_m V_1 = Z_w P_w V_w \quad (3.1)$$

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 hydrogen 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 steady. During both steps, pressure and temperature of the system were real-time collected via the computer program (Wisco Online Datalogger; ODO4)

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.

$$\text{Total mole of gas at the initial state} = \text{Total mole of gas at the final state} \quad (3.2)$$

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

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

where,

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

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

V_2 = volume of the sample holder, m^3

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

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

P_2 = pressure of gas inside the sample holder at the 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

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

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

$$Z = 0.9991 + 0.0004P \quad (3.5)$$

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 psig 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 0.5-1.0 g depending on the molecular weight of 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 calculated 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;

$$\text{Hydrogen pressure} = \text{observed pressure data} - \text{helium pressure} \quad (3.6)$$

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.

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

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

$$\text{Hydrogen capacity, wt\%} = \frac{\text{Released hydrogen}}{\text{Amount of sample}} \times 100 \quad (3.7)$$

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
25-44	$0.00004P + 0.9991$
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	$0.00003P + 1$

3.4.2 Absorption

Hydrogen was fed into the sample holder until the pressure reached approximately 1,600 psig (11MPa). The sample was heated at the $7\text{ }^{\circ}\text{C min}^{-1}$ heating rate until the desired absorption temperature ($125\text{ }^{\circ}\text{C}$) was reached. Hereafter, the hydrogen uptake began and further extended for the next 12 h. The pressure values were recorded every 1 min.

3.5 Characterization

3.5.1 X-ray Diffraction

The most widespread use of X-ray powder diffraction, and the one we focus on here, is for identification of crystalline compounds by their diffraction pattern. Characterized by an X-ray diffractometer at room temperature over a range of diffraction angle from $2\theta = 20^\circ - 80^\circ$ with CuK-alpha radiation ($\lambda=1.54\text{\AA}$, 40 kV, 30 mA). Sample preparation is statistically infinite amount of randomly oriented powder with crystallite size less than 10 μm , mounted in a manner in which there is no preferred orientation. Due to the powder samples are the air sensitive substances, before the X-ray diffraction analysis, they were covered with Kapton tape. Interaction of X-rays with sample creates secondary "diffracted" beams of X-rays relating to interplanar spacings in the crystalline powder according to a mathematical relation called "Bragg's Law"

$$n\lambda = 2d \sin \theta$$

Phase identification is accomplished by comparing the data from our specimen with data from a very large set of "standard" data provided by the International Center for Diffraction Data (ICDD). In our lab we use Jade (from Materials Data, Inc., a.k.a. MDI) facilitate the access to this massive database. Jade includes an automated search-match function that compares the sample pattern with the ICDD database.