

CHAPTER III

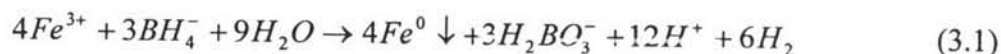
EXPERIMENT

3.1 Materials

The adsorbent used in this research was graphite. Pure graphite (>99.99%, average size 40 μm) powder was obtained from S.M. Chemical Supplies Co., Ltd. as a starting material. The transition metals, zirconium tetrachloride (99.5% ZrCl_4), and vanadium trichloride (>99% VCl_3), were obtained from Aldrich Chemical and MERCK, respectively. Anhydrous potassium carbonate (K_2CO_3) with 98% purity was supplied by Fluka. Titanium dioxide (commercial grade TiO_2) was obtained from Degussa. And iron powder was synthesized following the preparation procedure in section 3.1.1. These metals were selected for mixing with graphite by mechanical ball milling. Hydrogen gas (>99.999%) was used in the adsorption. Water in hydrogen was removed by using a series of traps. Helium gas (99.99%) and Argon (>99.999%) were used as inert gases. All samples were handled in a glove-box filled with argon to minimize oxidation and water adsorption.

3.1.1 Preparation of Nanoscale Iron Particle

Synthesis of nanoscale iron particles was achieved by adding 1:1 volume ratio of NaBH_4 (0.25 M) into $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.045 M) (Lien and Zhang, 2001). The solution was mixed vigorously under room temperature ($25 \pm 1^\circ\text{C}$) for 5 min. Ferric iron was reduced by borohydride according to the following reaction:



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 $<0.1 \mu\text{m}$ (mostly between 10 and 100 nm).

3.2 Sample Preparation

Firstly, we studied the effect of mechanical ball milling. Approximately, one g of graphite and 50 pieces of steel balls with diameter of 10 mm were placed into a steel pot, and milled with 400 rpm for 30, 60, 90, 120, 180, 300, 600, and 1920 min. The second part, graphite was combined with one of the metals ($ZrCl_4$, VCl_3 , TiO_2 , K_2CO_3 , and Fe powder) at 6 wt% and milled with 400 rpm for 120 min. The third part, we studied the effect of metal loading with different amounts (0, 3, 6, 9 wt%) for only $ZrCl_4$ -doped graphite, which was carried out with 400 rpm for 120 min. Immediately after milling in each experiment, approximately one g of a sample was placed into the thermovolumetric apparatus.

3.3 Experimental Set-up

Determination of the hydrogen adsorption/desorption values was done volumetrically in a Sievert-type installation. The schematic diagram of the experimental set-up and the actual set-up were shown in Figures 3.1 and 3.2, respectively. The pressure regulator with 4,000 psig maximum limit purchased from Concoa (Model BU-2581-AQ) was installed to control the gas flow rate into the whole system. The moisture and oxygen traps from Ligand Scientific Co., Ltd. were installed for the hydrogen gas for all experiments. Water and oxygen in the hydrogen gas were removed until the amounts of water and oxygen were less than 1 ppm and 1 ppb, respectively. The set-up consisted of a high pressure stainless reactor ($\sim 25 \text{ cm}^3$), which was used to hold the sample and part of stainless steel tube as a gas reservoir ($\sim 28 \text{ cm}^3$). 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.

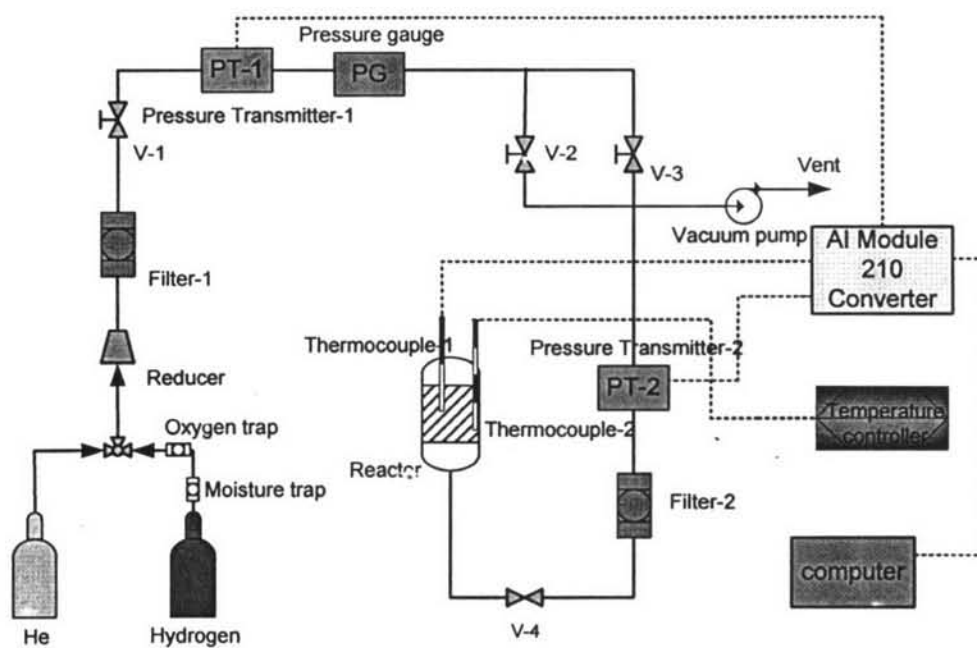


Figure 3.1 Schematic diagram of the experimental set-up.

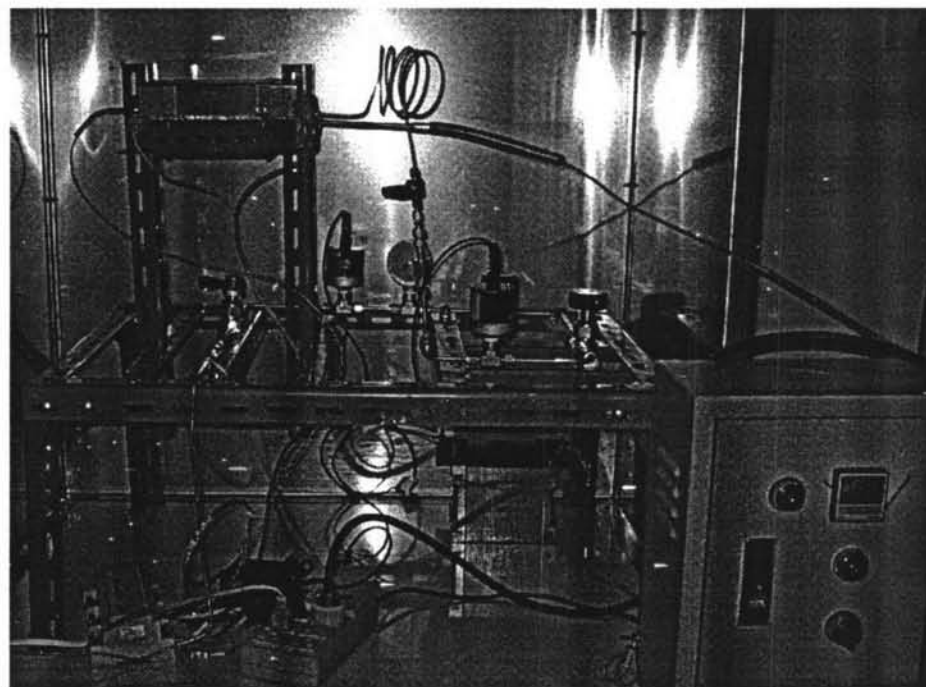


Figure 3.2 Experimental set-up.

In hydrogen adsorption, the temperature was set at room temperature ($25\pm 3^\circ\text{C}$) and hydrogen pressure at 1,600 psig. A data logger program was utilized to record temperature and pressure. The amount of hydrogen was calculated by the constant volumetric method.

3.4 Experiment Set-up Calibration

3.4.1 Blank Test

The blank test was employed to check the reliability of the experimental set-up and any leakage from the system. When there was no specimen in the sample holder, the blank test was started with pressurizing the system to 1,600 psig with hydrogen and left it for at least 12 h. The pressure difference during the first ten hours was used to indicate any leakage.

3.4.2 Calibration of Volume Space

3.4.2.1 *Volume of Manifold (V_m)*

Volume of the manifold was estimated by hydrogen expansion. The known volume (V_k) was pressurized to 1,500 psig and held for 2 min. Then, the gas was fed into the manifold part 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 (Data logger).

3.4.2.2 *Volume of Sample Holder (V_s)*

Before each experiment, an 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 1,500 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.

The volume of the manifold (V_m) and the sample cylinder (V_s) were determined from hydrogen expansion at the pressure of 1,500 psig.

To determine V_m , the following steps were required:

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

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

$$\frac{P_k V_k}{ZRT_k} = \frac{P'_k V'_k}{ZRT'_k} + \frac{P'_m V'_m}{ZRT'_m}$$

$$[\text{mole in } V_m + \text{mole in } V_s]_{\text{initial state}} = [\text{mole in } V_m + \text{mole in } V_s]_{\text{final state}} \quad (3.4)$$

$$\frac{P_m V_m}{ZRT_m} = \frac{P'_m V'_m}{ZRT'_m} + \frac{P'_s V'_s}{ZRT'_s}$$

where,

V_k = volume of the known volume at initial state, cm^3

V'_k = volume of the known volume at final state, cm^3

V_m = volume of the manifold at initial state, cm^3

V'_m = volume of the manifold at final state, cm^3

V'_s = volume of the sample holder, cm^3

P_k = pressure of gas inside the known volume at initial state, atm

P'_k = pressure of gas inside the known volume at final state, atm

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

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

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

T_k = temperature inside the known volume at initial state, K

T'_k = temperature inside the known volume at final state, K

T_m = temperature inside the manifold at initial state, K

T'_m = temperature inside the manifold at final state, K

T'_s = 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 Eq. (3.5).

$$Z = 0.00004P + 0.9991 \quad (3.5)$$

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

3.5 Hydrogen Sorption Data Collection

3.5.1 Adsorption

After the sample preparation, the amount of graphite used in each experiment was about one g. A sample was then placed into the sample holder and V_s was determined. The degassing procedure at about 10^{-3} torr and room temperature was conducted to remove the remaining gas for at least 12 h. The pressure transducers must be calibrated for each adsorption 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. Subsequently, hydrogen was fed into the sample holder until the pressure reached approximately 1,600 psig. The sample was adsorbed at room temperature ($\sim 25^\circ\text{C}$). Hereafter, the hydrogen uptake began and further extended for the next 12 h. The pressure values were recorded every minute.

3.5.2 Desorption

The hydrogen gas in the sample holder was purged out to the ventilation system. Afterwards, the valve between the manifold and the sample holder was closed. The temperature of the sample holder (T_s) was controlled to achieve the desired desorption temperature (450°C) by stepwise increasing of the heating rate of $7.5^\circ\text{C min}^{-1}$. 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 minute until the pressure in the sample holder was rather constant

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

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

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

$$\text{Hydrogen capacity, wt\%} = \frac{\text{Released hydrogen}}{\text{Amount of sample}} \times 100 \quad (3.8)$$

Subsequently, the sample holder is cooled down at room temperature and the desorbed gas in the sample holder is purged out to the ventilation system

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
90-114	0.00004P+0.99995
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

3.6 Adsorbent Characterization

3.6.1 Surface Area Measurement (BET)

The surface areas of all adsorbents were measured by the five-point BET method using a Sorptomatic 1990. Before the measurement, an adsorbent sample was outgassed by heating at 300°C for at least 12 h under vacuum to eliminate volatile adsorbates on the surface. BET surface areas were determined by measuring the quantity of gas adsorbed onto or desorbed from a solid surface at equilibrium vapor pressure (P/P_0) value by the static volumetric method. The data were obtained by admitting or removing a known adsorbate gas, nitrogen, into or out of a sample cell containing the solid adsorbent maintained at a constant temperature below critical temperature of the adsorbate, that is -196°C for nitrogen.

The adsorption data were calculated using the Brunauer-Emmett-Teller (BET) equation as shown in Eqs. (3.9) and (3.10):

$$\frac{1}{W\left(\frac{P_0}{P}-1\right)} = \frac{1}{W_m C} + \left(\frac{C-1}{W_m C}\right)\left(\frac{P}{P_0}\right) \quad (3.9)$$

- where W = weight of gas adsorbed at relative pressure P_0 ;
 W_m = weight of adsorbate constituting a monolayer of surface coverage;
 C = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area can be obtained from the following equation.

$$\text{Surface area of sample} = \frac{W_m A_{\text{nitrogen}} (6.02 \times 10^{23})}{M_{w,\text{nitrogen}}} \quad (3.10)$$

- where A_{nitrogen} = cross-sectional area of one molecule nitrogen
 = 0.162 nm² (at -196°C)
 $M_{w,\text{nitrogen}}$ = molecular weight of nitrogen (28)

3.6.2 X-ray Diffractometer (XRD)

The x-ray diffraction technique is a qualitative and quantitative analysis of crystallographic phase from of the adsorbent. The qualitative analysis is based on the fact that the x-ray diffraction pattern is unique for each crystallite phase. If the observed diffraction pattern of the samples can be matched to that of the reference substance, they are the same crystallite phase. For the individual substance, which has the same diffraction pattern, the intensity of crystallite indicates its content. The higher intensity, the higher content it is.

The Rigaku X-ray diffractometer (XRD) system equipped with RINT 2000 wide angle goniometer and a Cu tube for generating a $\text{CuK}\alpha$ 1 radiation ($\lambda = 1.54 \text{ \AA}$) was used to obtain the x-ray diffraction patterns at a generator voltage of 40 kV and a generator current of 30 mA. Nickel filter was used as the K_β filter. The goniometer parameters were divergence slit = 1° (2θ); scattering slit = 1° (2θ); and receiving slit = 0.3 nm. The adsorbent samples were, firmly pressed on a glass slide by another glass slide. A scan speed of 5° (2θ) min^{-1} with a scan step of 0.02° (2θ) was used during a continuous run in the 5 to 90° (2θ) range.

The Scherrer equation, which relates the mean crystallite diameter and the broadening of the x-ray diffraction lined per the expression, can be written as

$$d_b = K\lambda / B_d \cos\theta \quad (3.11)$$

where λ = Wave length of the monochromatic x-ray diffraction, \AA ;

K = Scherrer constant whose value depends on the shape of the particle

B_d = Angular width of the peak in the terms of $\Delta(2\theta)$, radian;

θ = Glancing angle, degree;

d_b = Mean crystallite diameter, \AA .

3.6.3 Scanning Electron Microscope (SEM)

The scanning electron micrograph (JEOL 5200-2AE) was used to identify the microstructure of the sample. The SEM used the electrons that are back-

scattered or emitted from the specimen surface. The powder sample (graphite and milled graphite) was placed on stub and sputtered with Au metal to render the surface conductive. The specimen was scanned with a narrow beam of electrons. The quantity of electrons scattered or emitted as the primary beam bombards each successive point of the metallic specimen surface was measured by an electron detector and used to modulate the intensity of a second electron beam and forms an image on a television screen.