CHAPTER II
LITERATURE SURVEY

2.1 Hydrogen storage and its target

Hydrogen storage is an important topic to the conversion the world to a hydrogen economy, particularly storing hydrogen for vehicular application or the fuel cell driven car. The requirement of hydrogen-storage system for practical applications in both economic and environmental reasons (Grochala and Edwards, 2004) includes:

1) High storage capacity in both gravimetric and volumetric density

2) Operating temperature is in the range of 60 – 100°C, which is suitable for PEM (proton exchange membrane) fuel cell applications.

3) Quick charging and recharging hydrogen

4) Low cost

5) Safe and reasonable cost

The hydrogen storage targets, which are fixed by U.S. department of energy (DOE) for driving a car more than 500 km, are shown in Table 2.1.

Table 2.1 U.S. DOE hydrogen storage system targets (Satyapal *et al.*, 2007)

Storage parameter	units	2007	2010
System gravimetric capacity	$H_2 \ kg^{-1}$ system	0.045	0.06
System volumetric capacity	$H_2 \ L^{-1}$ system	0.036	0.045
Storage system cost	$ $kg^{-1} \ H_2$	200	133
Cycle life	Cycles	500	1000
Operating temperature	°C	< 100	< 85

The current and developing methods, which approach for storing hydrogen, include compressed hydrogen gas, liquid hydrogen storage, nanostructured materials, and metal hydrides (Schlapbach and Züttel, 2001; Schapbach 2002).

2.1.1 Compressed hydrogen gas

Hydrogen is compressed in classical high-pressure tanks that are made of fairly cheap steel. Its advantages include simplicity of design and room temperature compressed gas storage. The drawbacks are high volume, high pressure, low density, and difficult to control pressure. Novel high-pressure tanks made of carbon-fiber-reinforced composite material are being developed. The carbon-fiber-reinforced composite tank for 350 bar and 700 bar have already been used in the prototype hydrogen powered vehicles. However, at 700 bar, hydrogen can be stored in the tank about 3.1 kg of hydrogen and driving a car for 270 km, which still does not reach the DOE target. Moreover, the cost and safety of system are key challenges for compressed hydrogen tanks (Satyapal *et al.*, 2007).

2.1.2 Liquid hydrogen storage (LH$_2$)

Hydrogen is condensed into liquid by liquefaction and stored in a cryogenic tank. This system can store more hydrogen in a given volume than compressed tanks since the volumetric of liquid hydrogen is 70.8 kg m^{-3}. However, the drawbacks are high cost for liquefaction process (condensation temperature of hydrogen at 0.1 MPa is -252°C) and heat transfer through the container leads to hydrogen loss (Satyapal *et al.*, 2007).

2.1.3 Solid stage hydrogen storage

Hydrogen is stored in or on the materials by absorption or adsorption while the material can release hydrogen when it is heated. This system has been considered as the alternative method for on-board hydrogen storage. Major alternative solid state storage technologies are based on the use of metal hydrides (more specifically alanates) and nanostructured materials (Orimo *et al.*, 2007).

2.1.3.1 Nanostructured materials

Nanostructured materials are a new class of materials with unique properties that stem from their reduced length scale (1 < d < 100 nm). The nanostructured types, which are in consideration for storing hydrogen, include carbon nanostructure (carbon nanotubes, carbon nanofiber, and graphite nanofiber) and metal organic framework (MOF). Hydrogen is stored by adsorbing

(physisorption) on surface of material. Since physisorption is a non-activated process, fast kinetics, and reversibility can be expected (general rule). There are the main favorable characteristics of physical adsorbents. However, the major drawback is a very weak bond between hydrogen and adsorbent so hydrogen adsorption can take place only in cryogenic temperature. Moreover, a real value of hydrogen capacity by these materials is still contradicted, particularly for carbon nanotubes (http://www.sc.doe.gov/bes/hydrogen.pdf).

2.1.3.2 Metal hydrides

Metal hydrides are chemical compound of hydrogen and metal (chemisorption). Metal hydrides can store and retain hydrogen under specific temperature and pressure condition and release hydrogen under different conditions (increase temperature, decrease pressure). Hydrogen is both located in the form of atom on interstitial sites of the host metal lattice (transition metal hydride) or bond the ionic-covalent bond with metal (light weight metal hydride). So they have quite high capacity to store hydrogen, particularly light metal hydride such as LiH 12.7 wt%, MgH_2 7.6 wt%, $LiBH_4$ 8.6 wt%, $NaAlH_4$ 7.4 wt%. Thus, these materials are widely researched as a medium for hydrogen storage. However, the key issues of these materials are irreversibility, low kinetics, and too stable, which corresponds to high temperature for hydrogen desorption (Orimo *et al.*, 2007).

2.2 Metal hydrides

Metal hydrides can be divided into two types: transition metal hydrides and light weight metal hydrides.

2.2.1 Transition metal hydrides (Dantzer, 2002)

Transition metal hydrides are compound of hydrogen atom with a transition metal such as VH_2, $PdH_{0.6}$, TiH_2 or the formation of hydrogen with alloy metals (intermetallic compound) consisting of **A** metals (rare earth such as La, Ti, Zr, Mg, Ca), which form stable hydrides, and **B** metals (such as Al, Mn, Cr, Ni, Cu, Co), some of which cannot form hydrides but can perform several additional functions: (1) it can play a catalytic role in enhancing the hydriding-dehydriding kinetic

characteristic, (2) it can alter the equilibrium pressure of the hydrogen absorption-desorption process to a desired level, and (3) it can also increase the stability of the alloy and preventing dissolution or formation of a compact oxide layer of component A (Kleperis *et al.*, 2001). Some intermetallic compounds and their properties are shown in Table 2.2. This type of hydride can dissociate hydrogen at their surface as hydrogen atom, and then located on interstitial sites of the host metal lattice like a sponge. As shown in Figure 2.1, the host metal dissolves some hydrogen as a Sieverts type solid solution (α-phase). As the hydrogen pressure leading to the concentration of hydrogen in the metal matrix is increased, interaction between hydrogen atom becomes locally important, and can start to see nucleation and growth of the hydrides (β) phase.

The advantageous of intermetallic hydride are the hydrogen reversibility and high hydrogen volumetric density but their gravimetric density is very low. So their property is too far from as a medium for onboard hydrogen storage.

Table 2.2 Examples of intermetallic compound and their properties (Sandrock *et al.*, 2002)

Type	Metal	Hydride	wt %	$P_{eq}(bar)$, $T(K)$
AB_5	$LaNi_5$	$LaNi_5H_6$	1.37	0.02, 298
AB_2	ZrV_2	$ZrV_2H_{5.5}$	3.01	10^{-8}, 323
AB	FeTi	$FeTiH_2$	1.89	5, 303
A_2B	Mg_2Ni	Mg_2NiH_4	3.59	1, 555
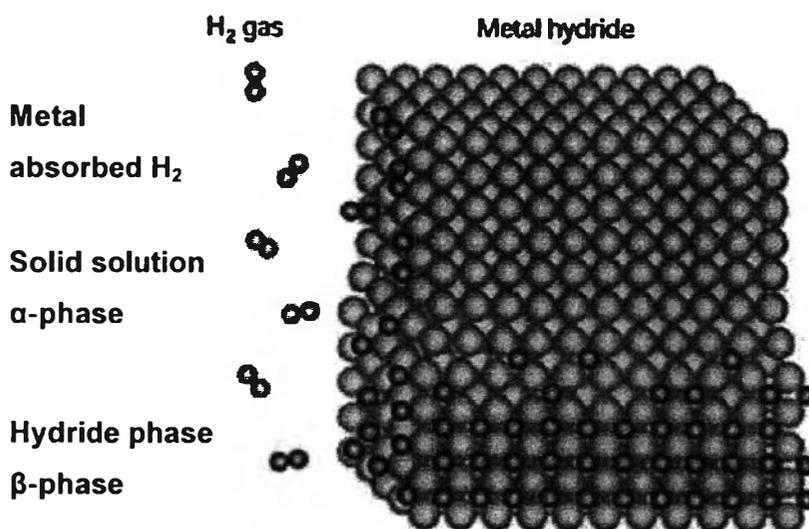
Figure 2.1 Schematic model of metal structure with hydrogen atom in the interstices between the metal atoms and hydrogen molecules at the surface (www.bnl.gov/est/erd/hydrogenstorage).

2.2.2 Light weight metal hydrides

Light weight metal hydrides or alkali metal hydrides are divided into two parts: simple metal hydrides such as NaH, CaH_2, and LiH, and complex metal hydrides are group I and II salts of $[AlH_4]^-$, $[NH_2]^-$, and $[BH_4]^-$ (alanates, amides, and borohydrides) such as $NaAlH_4$, $LiAlH_4$, and $LiBH_4$. Hydrogen is covalently bonded to the central atoms in complex anions (in contrast to interstitial hydrides).

The releasing hydrogen from complex metal hydride can take place into two ways by a hydrolysis reaction method and by heat decomposition (hydrogen desorption). The former method is not complex and can take place at ambient temperature but the regeneration process of product is very complex and cannot take place at the on-board applications. The example of the hydrolysis reaction of complex metal hydride is shown in Table 2.3. Although the complex metal hydrides have high hydrogen capacity, most of them are too stable, which lead to the hydrogen desorption at high temperature, low kinetics, or some of them is irreversibility. From the problem, the developments of complex hydride properties are needed to improve their property to approach to the property of materials for hydrogen storage. And one of complex metal hydrides that shows a noticeable

property is sodium aluminum hydride or sodium alanate. Some alkali metal hydrides and their properties are shown in Table 2.4.

Table 2.3 Hydrolysis reaction of light weight metal hydrides (Schüth *et al.*, 2004)

Hydrolysis reaction	wt% H_2
$LiH + H_2O \rightarrow LiOH + H_2$	7.7
$LiBH_4 + 4H_2O \rightarrow LiOH + H_3BO_3 + 4H_2$	8.6
$NaBH_4 + 4H_2O \rightarrow NaOH + H_3BO_3 + 4H_2$	7.3
$NaAlH_4 + 4H_2O \rightarrow NaOH + Al(OH)_3 + 4H_2$	6.4

Table 2.4 Examples of alkali metal hydrides and their properties (Annemieke *et al.*, 2008)

Materials	Max. wt% H_2	$T_{decomposition}$, °C	Note
$LiBH_4 + MgH_2$	11.4	400	Low kinetics
$NaBH_4$	13	400	Too stable, low kinetics
$LiBH_4$	19.6	380	Irreversible
$LiAlH_4$	10.54	190	Irreversible
$NaAlH_4$	7.4	180	Reversible with adding Ti

2.3 Sodium aluminum hydride or sodium alanate ($NaAlH_4$)

Sodium alanate or sodium aluminum hydride shows very some promising properties for on-board hydrogen storage. It has high weight percent available hydrogen content (7.4 wt%), low cost (50$ kg^{-1}) and is readily available in bulk. The

hydrogen desorption of NaAlH$_4$ takes place in three steps. The first reaction, Eq. (2.1), releases 3.7 wt% hydrogen and starts at temperature between 185°C (melting temperature of NaAlH$_4$ = 178°C) and 230°C. The second reaction, Eq. (2.2), occurs at about 260°C, further releasing 1.85 wt% hydrogen. The third step takes place at temperature higher than 500°C, Eq. (2.3). As the third step, decomposes at very high temperature, only the first and second steps are practical for hydrogen storage (Zaluska *et al.*, 2000).

$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2 \tag{2.1}$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + \frac{3}{2}H_2 \tag{2.2}$$

$$2NaH \rightarrow Na + H_2 \tag{2.3}$$
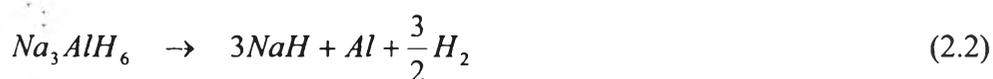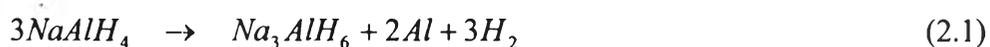
Although NaAlH$_4$ has quite high hydrogen capacity, it requires high temperature for hydrogen desorption, slow kinetics and an important point is irreversibility.

Bogdanovic and Schwickardi (1997) found that doping Ti compound can improve the reversibility and decrease the desorption temperature of NaAlH$_4$. This discovery ignites the development in this material as a medium for hydrogen storage.

Zidan *et al.* (1999) reported that Zr(OPr)$_4$ affected catalytically the hydrogenation/dehydrogenation of NaAlH$_4$ on different reactions. It was found that Zr(OPr)$_4$ catalyzed the second reaction while Ti(OBu)$_4$ catalyzed the first reaction. XRD results showed that some physical properties and mechanisms of enhanced hydrogen sorption kinetics of NaAlH$_4$ doped with Ti or Zr (Thomas *et al.*, 1999). Not only does a type of transition metal catalyze the kinetics but also the preparation method of alanate and doping catalysts. Mechanical technique for doping the catalysts and preparation of metal complex (Li$_3$AlH$_6$, Na$_3$AlH$_6$, (Li-Na)$_3$AlH$_6$ and (Li-Na-B)$_3$AlH$_6$) exhibited very good reactivity in hydriding/dehydriding with hydrogen capacity 3-4.5 wt% between 120-250°C. (Zaluski *et al.*, 1999; Zaluska *et al.*, 2000).

Comparison results of dry and wet doping methods revealed that the former was much more effective for the generation of catalytically active titanium sites than the latter (Jensen *et al.*, 1999).

Huot et al. (1999) directly synthesized Na_3AlH_6 and Na_2LiAlH_6 by energetic mechanical alloying (ball milling) of stoichiometric mixtures of NaH, LiH, and $NaAlH_4$ and ball milling time correlated with the particle size of $NaAlH_4$ that influenced to the kinetic improvement.

In 2000, Bogdanovic and coworkers introduced the homogeneous Ti and/or Fe doped $NaAlH_4$. A synergistic effect was observed, resulting in materials that released hydrogen up to 4 wt% in cyclic stability test (17 cycles) in the range of 140-170°C and 10.4-17 MPa. Moreover, they concluded that the desorption/absorption of doped $NaAlH_4$ depended on type and amount of dopant, morphology and method of preparation.

After that, Jensen *et al.* (2001) discovered new catalysts for rehydriding of NaH and Al to $NaAlH_4$. The kinetics of this process in the presence of this catalyst was improved by a factor of 5 over that of Ti/Zr doped hydrides. Thus, the required rehydriding time was reduced from 10 to 2 h. They also found that the problem of hydrocarbon contamination of the hydrogen evolved from catalytically enhanced $NaAlH_4$ can be eliminated by doping the hydride with $TiCl_4$ in place of $Ti(OBu)_4$. Moreover, partial substitution of sodium cation by potassium resulted in a lower plateau pressure associated with the dehydriding of X_3AlH_6 to XH and Al as X represented sodium and potassium.

Sandrock *et al.* (2002) studied the effect of Ti-content on $NaAlH_4$ by a dry preparation technique consisting of the ball milling of $NaAlH_4$ with (0-9 mol%) $TiCl_3$. It was believed that the solid state introduction of metallic Ti by the reduction of $TiCl_3$ led to the formation of NaCl. The amount of Ti content affected the hydriding/dehydriding rate and reversibility of hydrogen storage. Although Ti-content improved kinetic rate, the hydrogen capacity of $NaAlH_4$ decreased. 4% Ti was the optimum loading giving a good charging/discharging rate at 125°C, fast enough for practical applications. Isothermal kinetic study was carried out in the temperature range of 20-225°C and treated by Arrhenius analysis. The study revealed

that the first small addition of Ti-catalyst significantly and discontinuously lowered the thermal activation energies for both decomposition steps.

Gross *et al.* (2002) focused on the development of new-alkoxide based catalysts and doping methods to increase the capacity and reduce the level of hydrocarbon impurities in the desorbed hydrogen. β-TiCl$_3$ was doped to NaAlH$_4$ with the homogenization technique. XRD results discovered that β-TiCl$_3$ decomposed during the mechanical milling process to form NaCl and a dispersed titanium-based catalyst. The Van't Hoff analysis showed that the temperature required for equilibrium desorption at 1 bar from catalyzed NaAlH$_4$ is 33°C.

Anton (2003) described that different types of dopant resulted in different dehydrogenation rates due to the ionic size of each dopant. He discovered that cation having a radius in the range of 0.73-0.80 °A should hold the highest potential for enhanced hydrogen dehydrogenation rate. In addition, anion species have no effect on the dehydriding rate.

The enthalpy of activation and kinetic rate of the dehydrogenation of Ti doped NaAlH$_4$, Zr doped NaAlH$_4$, and Zr doped Na$_3$AlH$_6$ on the basis of Eyring theory is 100, 135, and 135 kJ mol^{-1}, respectively. Moreover, the dehydrogenation rate for both NaAlH$_4$ and Na$_3$AlH$_6$ was nearly the same when doped with Ti. These results imply that the dehydrogenation reaction pathways were highly sensitive to the nature and distribution of the dopant but not to differences in the Al-H bonding reaction in [AlH$_4$]$^-$ and [AlH$_6$]$^{3-}$ (Kiyobayashi *et al.*, 2003).

Investigation of stability of complex hydrides, AMH$_4$ and A$_3$MH$_6$ (A=Li, Na, K ; M=B, Al, Ga), by using ab-initio ultrasoft pseudo potential method. From the calculated heats of formation, some guidelines were extracted to explain and modify the stability of complex hydrides. It was possible to combine other components to substitute on Na and Al in order to modify the stability, i.e. Li substitution for Na reduced the hydrogen affinity of these materials while K increased the affinity and substitution on the Al site by B or Ga reduced the stability of the intermediate Na$_3$AlH$_6$ compound (Arroyo and Ceder, 2004).

NaAlH$_4$ containing Ti was characterized by synchrotron X-ray and neutron diffraction. It was found that, after ball milling, there were no signs of any Ti containing phase and no unit cell of all sodium aluminiumhydride. An addition of

TiF$_3$ by ball milling displayed different phases compared to TiCl$_3$/TiCl$_4$ (Brinks *et al.*, 2004).

Von Colbe *et al.* (2004) developed a simple method to monitor hydrogen evolution during ball milling of NaAlH$_4$ and titanium halides. Ball milling parameters such as milling time, size and weight of milling ball, amount of the added and oxidation state of dopant were the key factors for the dopant catalytic activity. They found that NaAlH$_4$ doped with 2 mol% TiCl$_3$ by ball milling showed the best dehydrogenation and proposed the stoichiometry of the chemical reaction between NaAlH$_4$ and TiCl$_3$:

$$xNaAlH_4 \; + \; \frac{1}{3}TiCl_3 \; \rightarrow \; (x-4)NaAlH_4 \; + \; Ti \; + \; \frac{4}{3}Al \; + \; 4NaCl \; + \; 8H_2 \quad (2.4)$$
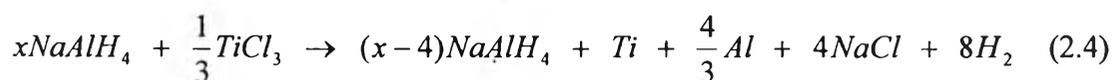
There are a number of proposed mechanisms for the role of Ti on the hydrogen absorption of NaAlH$_4$. Sun *et al.* (2002) suggested that Ti dopant might catalyze the hydrogen desorption/absorption of NaAlH$_4$. The substitution of dopant in the lattice of NaAlH$_4$ affected the activation and involved the lattice distortions. In the mechanism, Ti was thought to substitute Na$^+$ and form Ti^{4+} with Ti(OBu^n)$_4$ doped less than 2 mol% resulting in lattice distortions and vacancy formation and enhancement of hydrogen desorption kinetics. However, the proposed mechanisms by Graetz *et al.* (2004) using Ti K-edge x-ray absorption near-edge spectroscopy showed that Ti did not substitute in the bulk lattice nor form Ti metal, but it was present on the surface in the form of amorphous TiAl$_3$.

Wang *et al.* (2006) studied the effects of SWNTs, MWNTs, activated carbon, C$_{60}$, and graphite used as a cocatalyst with TiCl$_3$ on the hydrogen desorption/absorption of NaAlH$_4$. It was found that all five carbons exhibited significant, sustaining, and synergistic catalytic effects on the hydrogen desorption/absorption kinetics of Ti-doped NaAlH$_4$. These persisted through charge and discharge cycling. SWNTs were the best cocatalyst, graphite was the worst cocatalyst, and all five carbons were inactive as a catalyst unless Ti was present. They suggested that carbon might be playing a dual role by serving as a mixing agent manifested through lubrication phenomena and as a microgrinding agent manifested

through the formation carbide species, both during the high energy ball milling. Moreover, carbon most likely was imparting an electronic contribution through the interaction of its facile π-electrons with Ti through a hydrogen spillover mechanism, which explained why one carbon was better than another one in terms of optimal aromatic character, out-of-plane exposure of π-electrons, and interaction of π-bonds with neighboring sheets.

2.4 Carbon nanotubes and their hydrogen storage capacity

Carbon nanotubes (CNTs) are allotropes of carbon with a nanostructure that can have a length-to-diameter ratio greater than 1,000,000. These cylindrical carbon molecules have novel properties that make them potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat. Recently, they have been suggested that CNTs can be a promising medium for on-board hydrogen storage with high surface area and hollow space inside, which could provide the needed capacity for hydrogen storage (Dillon *et al.*, 2001; Cheng *et al.*, 2001).

Ye *et al.* (1999) measured the hydrogen capacity of single walled carbon nanotubes (SWNTs) using seivert's apparatus. They reported that the maximum hydrogen capacity of SWNTs exceed 8 wt% at 80 K and hydrogen pressure > 80 bar. They proposed that hydrogen was first adsorbed on the outer surfaces of the crystalline rope and diffused into the inside of SWNTs. Moreover, in the same year, multi-walled carbon nanotubes (MWNTs) were reported to have a hydrogen uptake of up to 14 wt% at room temperature and ambient pressure when doped with an alkaline metal (Chen *et al.*, 1999).

Since the first publication was reported with the high hydrogen storage capacity of CNTs, extensive research activity in this material has been carried out. However, the experimental data in each research are controversy and can not reproduce the data of the high hydrogen capacity.

In a later work by Yang (2000), it was revealed that the high hydrogen capacity of the alkaline metal-doped MWNTs was actually caused by moisture in the

hydrogen gas, and that the alkaline-doped MWNTs could only adsorb ~ 2 wt% hydrogen.

Hirscher *et al.* (2003) studied the possibility of the hydrogen storage capacity of CNTs. They confirmed that no hydrogen can adsorb on the surface of carbon at the ambient temperature and the hydrogen capacity of CNTs compared with other experimental value is shown in Figure 2.2.
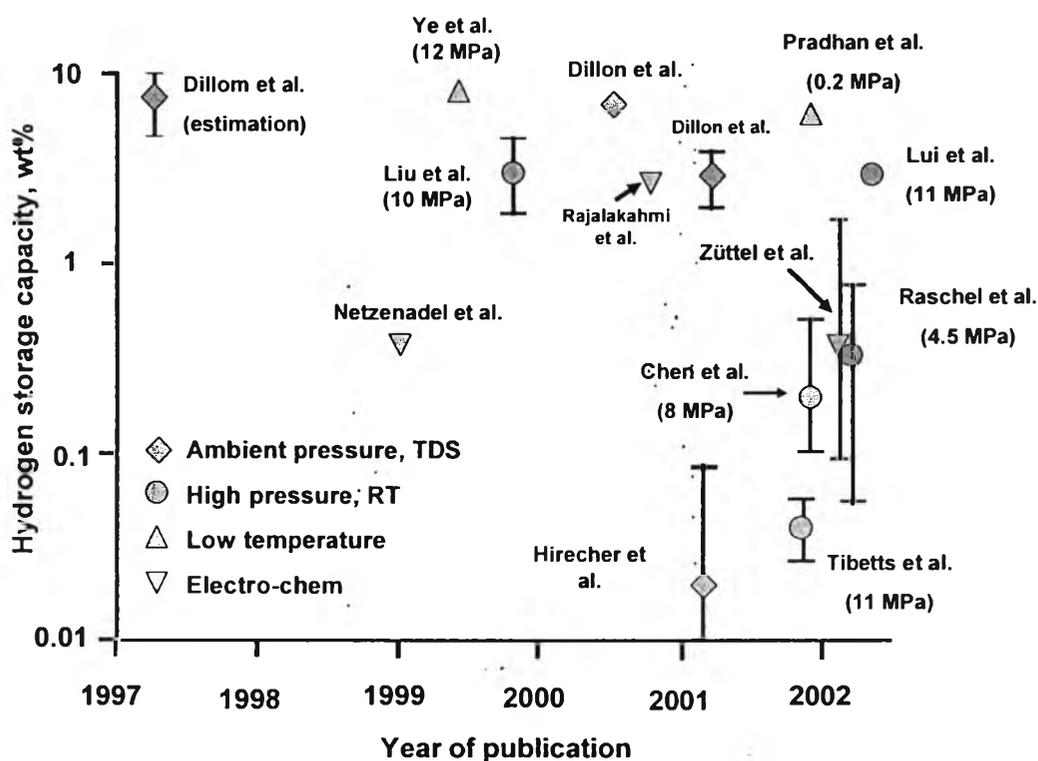
Figure 2.2 Experimental data for hydrogen storage capacity in carbon nanotubes versus publication year for different methods, pressure and temperature regimes (Hirscher *et al.*, 2003).

Different hydrogen storage capacity, using CNTs was reported to depend upon preparation methods, conditions in experiments, purity of CNTs, adsorption conditions, and errors from the measurements (Atkinson *et al.*, 2001). However, in practice, a small amount of hydrogen can be stored by pristine CNTs. Many research groups have attempted to improve the hydrogen adsorption capacity of CNTs by

modification of the relatively inert surface, which could be the cause of the difficulties encountered for hydrogen adsorption (Xu *et al.,* 2007).

Recently, using activated carbon decorated by metal nanoparticles, such as Pt and Pd, seems to be a promising method to improve hydrogen adsorption onto carbon materials. Such metals are known to play a role in the dissociation of hydrogen, followed by atomic hydrogen spillover and finally adsorption onto the support (Yang *et al.,* 2002; Anthony *et al.,* 2005; Li *et al.,* 2006). Moreover, Yildirim and Ciraci (2005) reported a first-principle computational study on the interaction between hydrogen molecules and Ti or V atoms adsorbed on CNTs (SWNTs). They found that a single Ti atom adsorbed on SWNTs can strongly bind up to four hydrogen molecules. In other words, SWNTs decorated with Ti can strongly adsorb up to 8 wt% hydrogen.