CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Hydrogen Storage*

Hydrogen is one of the lightest elements and has small molecule. In order to use hydrogen as fuel, it is necessary to store it in the proper way. The fundamental criteria for hydrogen storage in vehicles include the following issues:

- favorable for hydrogen uptake and release (temperature and pressure)
- safety under normal use and acceptable risk under unusual condition
- low cost
- light in weight and conservative in space
- high storage capacity
- quickly uptake and release hydrogen
- effective heat transfer
- long cycle lifetime

Storing hydrogen methods can be classified into 2 systems based on assemble conditions.

2.1.1 Physical Storage System

2.1.1.1 Compressed Hydrogen Gas

Because of its low density, hydrogen is compressed to store at 2000-2500 psi. This justifies requirement of large and heavy containers, which must be occasionally inspected to ensure their safety.

2.1.1.2 Cryogenic Liquid

The advantage of liquid hydrogen is its high energy to mass ratio which is 3 times higher than that of gasoline. However, the considerable energy consumption is still a main drawback.

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* This material was summarized from Kukkonen *et al.* (1993), Miller (1998), Hart (2000), and Becker (2001).

Practically, the energy is required for liquefaction processes and maintenance the suitable storage temperature in the tanks. This makes liquid hydrogen storage an incredibly expensive method compared to the others.

2.1.2 Solid-state Storage System

2.1.2.1 Gas- on- solid Technology

Hydrogen can be stored by being adsorbed onto the surface of activated carbon. This technology relies on the affinity of carbon and hydrogen atoms. Though it provides better volume density than compressed gas storage, it is effective only at low temperature. Accordingly, storing techniques at ambient temperature is under development.

2.1.2.2 Metal Hydrides Technology

A metal hydride is a chemical compound formed from metal and hydrogen. The hydrogen atoms entirely occupy the interstices of metal, such as lattice defects. It is the safest manner as no hydrogen will be released in unpredictable accident.

2.1 Metal Hydrides

There are two possible ways of hydriding a metal, direct dissociative chemisorption and electrochemical splitting of water, but only the former will be mentioned:

$$M + (x/2)H_2 \quad \leftrightarrow \quad MH_x \qquad (2.1)$$

where M represents the metal. Hydrides store only about 2% to 7% hydrogen by weight, but have higher volumetric storage densities than liquid or solid hydrogen.

H₂ GAS   INTERFACE   METAL
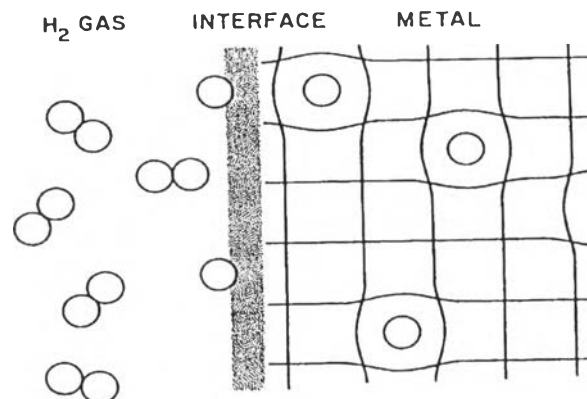
Figure 2.1 Schematic of hydrogen chemisorption on metal (Hottinen, 2001).

Chemisorption is a general mechanism for hydrogen doping. Beyond hydrogen atmosphere, hydrides absorb hydrogen and release heat. By reducing the pressure and supplying heat, hydrogen is released. The H_2 molecule firstly dissociates into individual hydrogen atoms at the surface, then enter the channels connected to interstices, and finally bounded strongly to the structure as H atoms, shown in Figure 2.1.

By applying the nucleation and growth model, the absorption and desorption mechanisms of the metal hydrides were discussed through the $\alpha-\beta$ interface diffusion as illustrated in Figure 2.2(a) and 2.2(b), respectively (Asakuma *et al.*, 2003). First, for the absorption reaction, the α-solid solution is formed while the hydrogen dissolution proceeds. Second, the nucleation of the β-phase begins and then the β-phase starts to deposit from the supersaturated α-solid solution and forms the layer. Finally, it encloses gradually on the domain of neighbors as its growth proceeds. Similarly, the desorption reaction is supposed to backward reaction against the absorption.
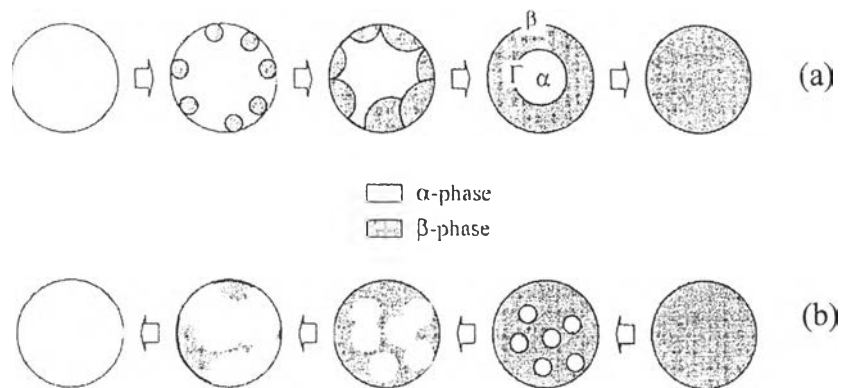
Figure 2.2 Hydrogen (a) absorption (b) desorption (Asakuma *et al.*, 2003).

The hydrogen sorption behavior of metal hydride is characterized using equilibrium Pressure-Concentration-Temperature (PCT) data as shown in Figure 2.3. These data are determined by keeping an alloy sample at constant temperature while precisely measuring the quantity of sorbed hydrogen and the pressure at which sorption occurs. The hydrogen concentration is usually expressed in term of alloy composition, either as atomic ratio of hydrogen atoms to the number of atoms in the base metal alloy (H/M), or as the capaciy of hydrogen in the alloy on a weight percent basis. The PCT diagram illustrates the formation of solid solution (α-phase) at low H-pressure and atomic ratio, pressure plateau where there is a continuing transformation from the solid solution α–phase to the metal hydride β–phase at constant temperature, and the growth of the β-phase with increasing hydrogen pressure (Asakuma *et al.*, 2003).
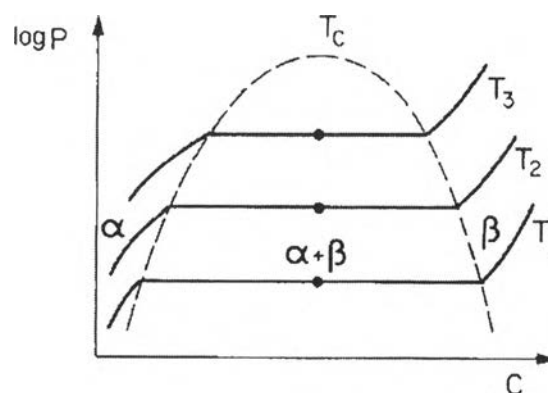
Figure 2.3 Theoretical PCT diagram of a metal hydride (Hottinen, 2001).

The formation of a hydride can take place simultaneously at several different places in the metal, especially in the case of vacancies, dislocations, grain boundaries etc., which are preliminary present at interfaces among composite metals. The growth of a hydride increases the size of lattices which are directly affected the kinetics because their continuous films can block further hydrogen uptake. To ensure that the large volume is able to be stored, it is essential to use small granule of the base material to make a large surface area.

The thermodynamic reaction equilibrium is defined in Equation (2.2) with the equilibrium constant (K) at specified temperature (T);

$$RT \ln K = \Delta H - T\Delta S \tag{2.2}$$

where ΔH is the reaction enthalpy and ΔS is the reaction entropy. R signifies an ideal gas constant. For a solid-gas reaction, the equilibrium constant reduces the pressure of the gas. Thus, the Van't Hoff equation is obtained;

$$\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{2.3}$$

Plotting the equilibrium (P, T)-values on a ln P versus 1/T scale can be called that Van't Hoff plot. The reaction enthalpy can be derived from the angular coefficient of the plot with the help of Equation (2.3) and the plot exhibits the suitability of P – T behavior of a hydride for practical applications. The theoretical Van't Hoff plot usually describes very well the real properties of metal hydrides. A schematic drawing of a typical Van't Hoff plot is given in Figure 2.4.
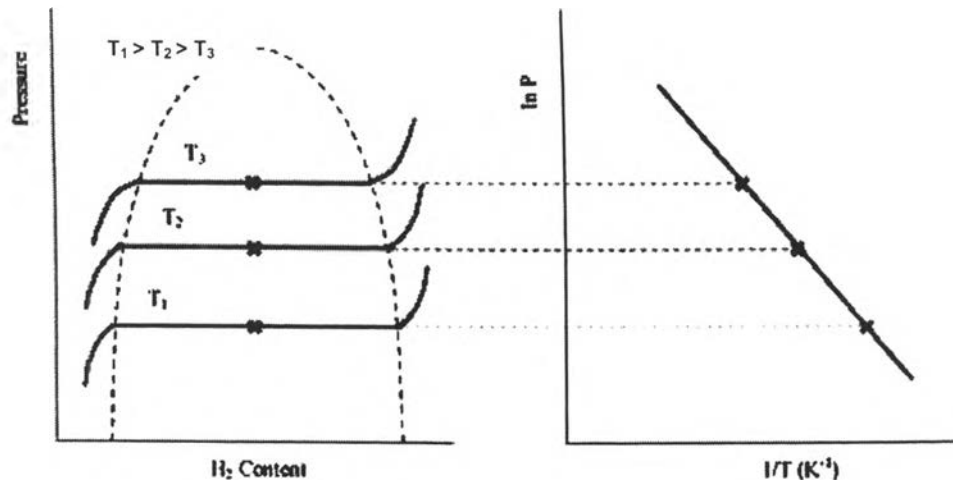
Figure 2.4 Relationship between PCT diagram and Van't Hoff plot (www.mb.luth.se/EEIGM/eeigmprojpres/ presentationprojet.ppt).

In real metal hydrides, the PCT diagram shows some hysteresis during adsorption and desorption, and the plateaus have some slope in it. These occur if strain fields that are accumulated in the hydrides during hydride formations are relaxed by plastic deformation. These properties are shown and defined in Figure 2.5, where the subscripts a and d refer to adsorption and desorption, respectively.
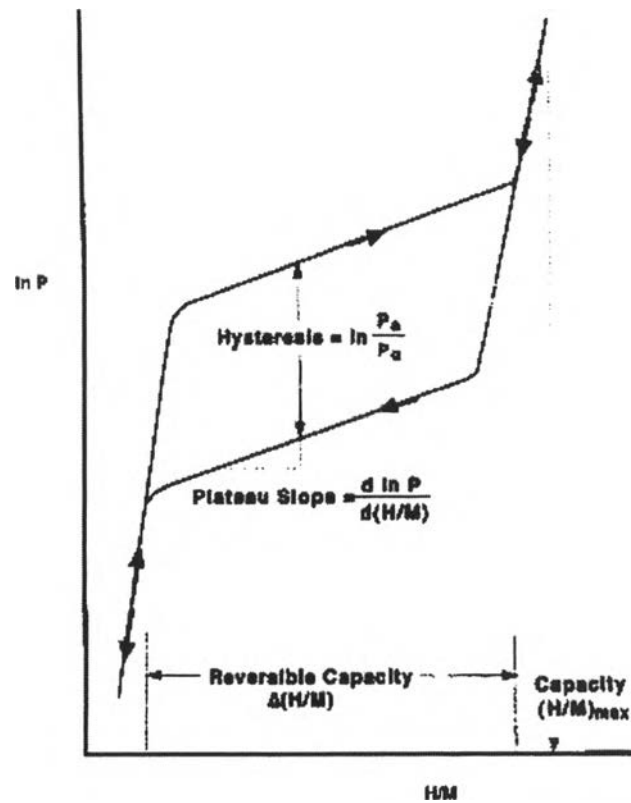
Figure 2.5 Schematic drawing of real PCT diagram (Hottinen, 2001).

In order to characterize the metal hydrides, it is convenient to use the maximum hydrogen capacity $(H/M)_{max}$. H/M stands for hydrogen atoms per metal molecule. The reversible capacity $\Delta(H/M)$, defined as the plateau width, is also a useful tool when considering the engineering capacities of metal hydrides. The concentrations can also be expressed as mass percents from the total masses, especially for the energy density comparison.

Most applications of the hydrides, indicated in Figure 2.6, are in ambient temperature, or at least in the range of 0 – 100 °C.
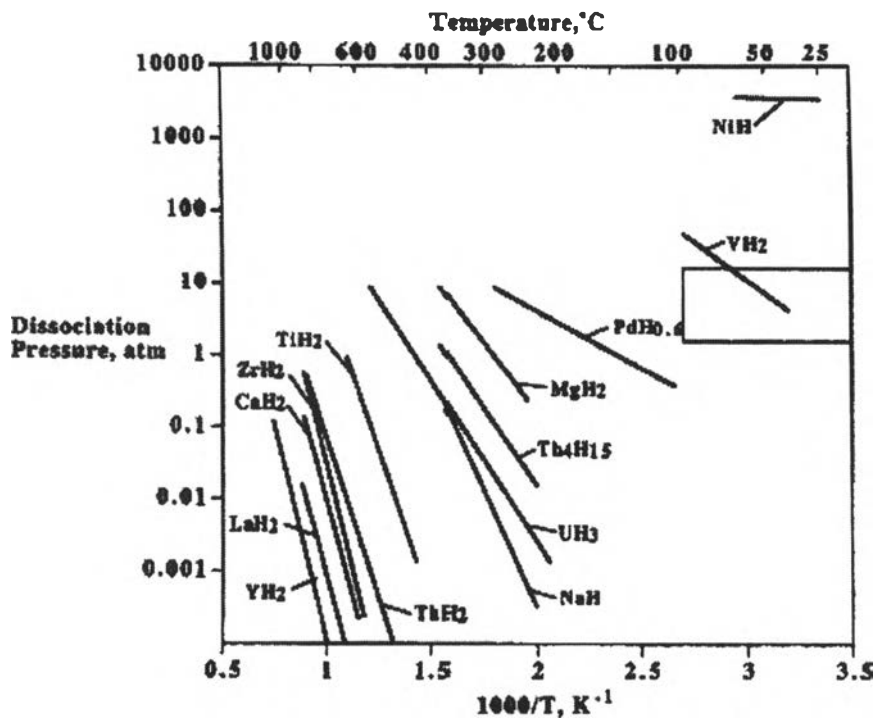
Figure 2.6 Van't Hoff plots for some natural elements (Hottinen, 2001).

There are several types of metal hydride i.e., intermetallic compounds contained different amounts of A and B elements, compounds that are more like solid solutions, and hydride complexes that are formed with transition metals.

2.2.1 Intermetallic Compounds

In general, these alloys are combinations of A metals which have ability to absorb H_2 independently (rare earth metal such as La,Ti, Zr, Mg, Ca) with B metals which can not absorb H_2 (Fe, Ni, Mn, Co) (Hottinen, 2000).

Table 2.1 Assorted conformations of intermetallic compounds*

	AB$_5$	AB$_2$	AB
A	Mm, Ca, Y, Zr	Ti, Zr or a lanthanide (atomic number 57 – 71)	Ti
B	Al, Mn, Si, Zn, Cr, Fe, Cu, and Co	V, Cr, Mn, and Fe	Fe, Mn and Ni
advantage	not form protective oxide layers, good tolerance against small amounts of O$_2$ and H$_2$O impurities in H$_2$	lower cost than AB$_5$ alloys	quite low cost
disadvantage	maximum capacity 1.9 wt%(extremely low), quite high cost	maximum capacities usually 1.5–2 wt%	instability of the upper plateau, easily formed oxide films which decreases the sensitivity to impurities in hydrogen
example	LaNi$_5$	ZrMn$_2$	Ti-Fe based alloys

* The material in this table was summarized from Cuevas *et al.* (2001).

2.2.2 Solid Solution Alloys

A solid solution alloy means a primary element into which minor elements are dissolved. The minor elements can be present in a disordered substitutional or interstitial distribution. Solid solution alloys with good PCT properties are the Pd-based alloys. Unfortunately, these usually have a very low hydrogen capacity seldom exceeding 1 wt%. One promising, but quite expensive group is alloys based on vanadium. Especially, a combination of V-Ti-Fe is an attractive alternative. For example, $(V_{0.9}Ti_{0.1})_{0.95}Fe_{0.05}$ has a maximum hydrogen capacity of 3.7 wt% and a reversible hydrogen capacity of 1.8 wt% and still with good PCT properties (Hottinen, 2001).

2.2.3 Complex Hydrides

Some certain transition metals form a hydride with some elements from the periodic table groups IA and IIA when hydrogen is present. Others form hydrides with non-transition metals, such as $NaAlH_4$. The kinetics of hydride complexes tends to be slower compared to the traditional interstitial hydrides since their formation and decomposition requires some metal atoms for diffusion. Hydrogen desorption also needs usually quite high temperature (over 150 °C). In spite of these disadvantages, the high hydrogen capacity makes these materials potential for hydrogen storage (Hottinen, 2001). The theoretical hydrogen contents of some complex hydrides are given in Table 2.2.

Table 2.2 Hydrogen storage capacities of complex hydrides (Sandrock 1999)

| Hydride	Hydrogen (wt%)
$NaAlH_4$	7.5
$LiAlH_4$	10.6
$Mg(AlH_4)$	9.3

2.3 Metal Hydride Developments

The key factors in developing practical, economic hydride systems for vehicular applications are:

1. Weight
2. Operating temperature
3. Capacity and amount of usable hydrogen
4. Rate of absorption/desorption
5. Cyclic stability
6. Cost and availability

Many scientific and engineering studies have been carried out on the absorption/desorption of hydrogen in metals and development of such storage devices. A prototype car fueled by hydrogen where the storage tank was a chunk of FeTi alloy is called Daimler-Benz but the hydride is 20 times heavier than equivalent gasoline tank.

2.4 NaAlH₄

A priori, sodium aluminum hydride, NaAlH₄, would seem to be a viable candidate for practical on-board hydrogen storage material. It has high weight percent available hydrogen content (5.6%), low cost ($50 /kg) and is readily available in bulk. Unlike the interstitial intermetallic hydrides, these compounds release hydrogen through a series of decomposition/recombination reactions e.g.:

$$NaAlH_4 \rightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2 \rightarrow NaH + Al + \frac{3}{2}H_2 \qquad (2.4)$$
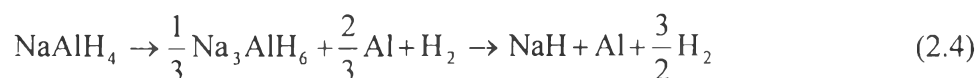
However, these reactions are irreversible and could not serve as the basis for a rechargeable hydrogen storage system. Thermally activated evolution of hydrogen from NaAlH₄ occurs at appreciable rates well above its melting point of 183 °C. Additionally, this process can be reversed only under severe conditions. Thus, until

the break-through discovery in 1997, Bogdanović and Schwickardi used wet doping technique with selected titanium compounds (β–$TiCl_3$ and $Ti(OBu)_4$) on alkali metal aluminum hydride (Bogdanović et al., 1997). The volumetric analysis showed that Ti dopant catalyzes the thermal dissociation to gain a higher storage capacity, and better cyclic stability than the undoped hydride. The PCT diagram reveals that the catalyzed $NaAlH_4$ could be made to reversibly release and absorb approximately 4 wt% hydrogen under moderate condition (150 °C for second step).

It is surprising that both titanium and zirconium have catalytic effects on different reactions in decomposition of $NaAlH_4$, $Ti(OBu)_4$ for the first step and $Zr(OPr)_4$ for the second step. In addition, the dry doping method, homogenization, is more effective than the wet doping method (Jensen et al., 1999, Zidan et al., 1999).

Another work on the absorption/desorption kinetics of mechanical grinding was done by Zaluska and coworkers (2000). By conducting in the volumetric system operated over the temperature range from room temperature to 500 °C and measuring pressure-concentration isotherms, they found that lithium and sodium aluminum hydrides (Na_3AlH_6, $(Li-Na)_5AlH_6$, and $(Li-Na-B)_3AlH_3$)) prepared by ball milling were able to release hydrogen reversibly and had more rapidly kinetics than previously reported catalyzed systems, supported the notion that reduced particle size plays an important role in improving kinetics. Remarkably, with carbon as an additive of the hydrides enhanced desorption kinetic at low temperature and re-hydrogenated without catalysts.

Like titanium and zirconium, doping the hydride with $Ti(OBu)_4$ and $Fe(OEt)_2$ also produces a synergistic effect, resulting in materials that can be rehydrided to 4 wt% at 104 °C and 87 atm of hydrogen. The improved kinetics allowed researchers to carry out constant-temperature, equilibrium-pressure studies of $NaAlH_4$ that extended to temperatures well below the melting point of the hydride (Bogdanović et al., 2001). Moreover, they concluded that desorption/absorption of solid doped $NaAlH_4$ depends on type and amount of the dopants, morphology and size of $NaAlH_4$ particles, and doping procedure (kind of solvent). Furthermore, a high catalytic activity was exerted by either Ti, Zr, or V.

After that, phase transitions and crystal structure modifications were

observed during the thermal-desorption decomposition of the $NaAlH_4$ by Gross and coworkers (2000). Using in-situ X-ray powder diffraction (XRD) provided a real-time representation of the decomposition reactions and suggested long-range transport of a metal species in solid state process. The result of Thomas and his colleagues (2002) showed that a clear understanding of solid state mechanism in the presence of liquid Ti/Zr catalyst was observed through scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

Sandrock *et al.* (2002a) studied various practical engineering considerations on hydrogen storage. Properties measured were cyclic capacity, charging and discharging rates, thermal effects, gaseous impurities, volume changes, low temperature plateau pressures and detailed isothermal desorption kinetics over the temperature range 23–180 °C. They concluded that the alkoxide-catalyzed materials have low reversible capacities and release significant levels of hydrocarbon impurities during H_2 discharge. These problems were virtually eliminated with the inorganic catalyst precursor like $TiCl_3$. According to these findings, measuring absorption and desorption kinetics were surprisingly good and 3–4.5 wt% H_2 can be stored and recovered in reasonable times at 125 °C. So, it may be ultimately possible to use the $NaAlH_4$ decomposition reaction to provide 3 wt% H_2 at room temperature for low-rate applications.

Gross *et al.* (2002a) pointed to develop new non-alkoxide based catalysts and doping methods to increase the capacity and reduce the level of hydrocarbon impurities found in the desorbed hydrogen. β-$TiCl_3$ doped $NaAlH_4$ with homogenization technique is an alternative. Using XRD discovered that β-$TiCl_3$ decomposes 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 pressure of 1 bar from catalyzed $NaAlH_4$ is 33 °C. Hydrocarbon impurities such as, H_2O, CO, and CO_2 examined by RGA (Residual Gas Analysis) and GC (Gas Chromatography). EDS supported the long-range transport of metal species theory. Moreover, most catalyst remained at the material surface, was demonstrated by Augar spectroscopy analysis.

The experiment performed by Sun *et al.* (2002) illustrates the XRD patterns and lattice parameters that the catalyst quantity impacts on low hydrogen capacities of $NaAlH_4$ doped with either titanium or zirconium. They explained that the lattice undergoes significant expansion as the doping level increases by using the model that entailed substitution of sodium cations by variable valence transition metal cations and the creation of Na^+ vacancies in the bulk hydride lattice.

Later, the effect of Ti-catalyst content on the reversibly hydrogen storage properties of the sodium aluminum hydride was done by Sandrock *et al.* (2002b). Performing isothermal Arrhenius analysis over a wide temperature range (20-225 °C) for dry-doped material varied from 0.9-9 mol% $TiCl_3$ led to conclude that the more Ti concentration, the more dehydriding and hydriding rates while the H-capacity reduces substantially. In addition, the finite ambient temperature decomposition of catalyzed $NaAlH_4$ phase was reconfirmed.

The view that the highly purified sodium aluminum hydride requires high temperature to decompose and long duration time to hydride to Na_3AlH_6 was proposed by Meisner and collogues (2002). They also established that ball milling with the diamond powder, mixing with Pt powder, and doping with Ti organometallic compound can reduce the decomposition temperature and facilitate hydriding.

In order to understand the process of hydrogen discharging and recharging of Ti-doped $NaAlH_4$, the investigation via XRD and NMR spectroscopy was published by Bogdanović *et al.* (2003). Both methods showed that large Al particle formation during dehydrogenation causes mass transfer problem which affects the low capacity in rehydrogenation.

Gross *et al.* (2003) introduced TiH_2 and pre-reacting $TiCl_2$ with LiH as a catalyst precursor. Though they could avoid the formation of inactive byproduct (Na-halide and Na-oxide), the slightly satisfied hydriding rate was achieved after 10 cycles. Besides, they supported the suggestion that Ti-substitution in the $NaAlH_4$ lattice is responsible for advancing kinetics.

$NaAlH_4$ can also be rehydrogenated at low temperature (25-125 °C) under

titanium-doped state for 12 hours (Sun *et al.*, 2003). Approximately 2-2.5 wt% hydrogen capacity was reported.

Majzoub and Gross (2003) observed that doping NaH and Al with $TiCl_3$, TiF_3, and $TiBr_4$ by mechanical milling effectively improved sorption kinetics. Arrhenius data obviously indicated that these catalyst precursors behave in the identical fashion. Many sodium halides, causing a reduction in the overall reversible hydrogen capacity of the material, were found in the doping process. In contrast, the presence of $TiAl_3$ peaks in XRD during the absorption is on the basis of participation to enhance the kinetics.

The discovery by Anton (2003) explained why different types of catalyst result in different hydrogen desorption rates. He disclosed that the valence electron of metal (catalyst) is not a driving factor, but ionic radius is more prominent for the catalyst activity. He assumed that anions do not play a role in $NaAlH_4$ catalysis so he paid an attention on cations which have ionic radius in the range of 0.73-0.8 Å as highest possible dopants to enhance the hydrogen discharge rate.

Recently, Sun *et al.* (2004) focused on hydrogen absorption and cycling studies of $NaAlH_4$. At given temperature, the rate of hydrogen absorption is speed up as the hydrogen pressure rises up. With the increase in the temperature, the declining in the absorption rate was noticed. Lastly, they concluded that the optimum temperature and pressure for absorption are 120 °C and 12 MPa, respectively.