

## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Hydrogen Storage

Hydrogen is one of the most abundant elements. It is an odorless, colorless, tasteless and non-poisonous gas. It is also a renewable resource. When it is burned in an internal combustion engine it produces almost zero exhaust and the only by product is water. Hydrogen can be produced by several methods using alternative energy sources, such as gasoline, natural gas, solar and wind. Eventhough it is not a natural source but a man made fuel, hydrogen has a heating value three times higher than petroleum. Therefore, hydrogen bears a manufacture cost, which made it costing three times higher than the petroleum products. For this reason, any method of storage is not allowed to considerably increase the cost of hydrogen fuel. Storage basically implies to reduce the enormous volume of the hydrogen gas. The goal of any hydrogen storage method is to pack as much hydrogen as possible in given volume, by using as cost-effective method as possible. The methods of interest include compression, liquefaction, physisorption, metallic hydrides, and complex hydrides, which are commented with respect to the technical state and the viability in future applications.

Methods for storing hydrogen can be classified into 2 systems based on assemble conditions.

##### 2.1.1 Physical Storage System

##### 2.1.1.1 *Compressed Hydrogen Gas*

It might be the simplest way to store hydrogen in a cylinder of pressure up to 20 MPa but the energy density is too low to satisfy the fuel demand of driving practice. About four times higher pressure is needed to meet the driving purpose, however, such industrial cylinders have not been commercially available. The hydrogen density is remarkably lower than the cryoadsorption method, and the high cost of compression

and the cylinder might hinder the method to be accepted commercially. Moreover, the cost of compressed hydrogen is much higher than the cost of liquid hydrogen. It seems, therefore, this method is not likely to be used in the future. Furthermore, the safety of pressurized cylinders is of big concern especially in the densely populated regions.

#### *2.1.1.2 Liquefaction*

This method faces two challenges: The efficiency of the liquefaction and the boil-off of the liquid. The theoretical work necessary to liquefy hydrogen gas of room temperature is 3.23 kW h/kg, but the technical work is about 15.2 kW h/kg, which is almost half of the lower heating value of hydrogen [2]. Gasification of liquid hydrogen inside the cryogenic (21.2K) vessel is an inevitable loss even with a perfect insulation technique. The exothermic reaction of the conversion from ortho- to para-hydrogen provides a heat source of the gasification. The heat of conversion is 519 kJ/kg at 77 K, and 523 kJ/kg at temperature lower than 77 K, which is greater than the latent heat of vaporization (451.9 kJ/kg) of normal hydrogen at the normal boiling point. The critical temperature of hydrogen is very low (33.2 K), above which liquid state cannot exist. Therefore, liquid hydrogen can only be stored in an open system otherwise the pressure in a closed system can be as high as 1000 MPa at room temperature. So, the boil-off of liquid means the emission of hydrogen into the atmosphere. The relatively large amount of energy necessary for liquefaction and the continuous boil-off of liquid limit this storage system to utilizations where the cost of hydrogen is not an important issue and the hydrogen is consumed in a rather short time.

#### 2.1.2 Solid-state Storage System

##### *2.1.2.1 Gas on solid technology*

Hydrogen can be stored onto the surface of a porous solid. The physisorption of supercritical gases follows two basic rules: monolayer adsorption mechanism, and the exponential decrease of adsorption with the increasing temperature. It follows that the adsorption capacity of hydrogen on a material depends on the specific surface area of the material and that higher temperatures will lower the adsorption capacity. The total

storage capacity in a porous solid is, however, not only the adsorption capacity, but also the sum of contributions due to adsorption on solid surface and that due to compression in the void space [2].

### 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. This method seems to be an alternative for onboard hydrogen storage.

An ideal solid hydrogen-storage material (HSM) for practical applications in both economic and environmental reasons:

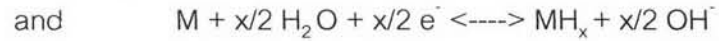
- 1) High storage capacity: minimum 6.5 wt% and at least 65 g L<sup>-1</sup> of hydrogen available from material
- 2) Temperature for desorption is between 60 – 120°C
- 3) Reversibility of the thermal desorption/absorption cycle: low temperature of hydrogen desorption and low pressure of hydrogen absorption
- 4) Low cost
- 5) Low-toxicity and possibly inert storage medium

## 2.2 Metal Hydrides

Metal Hydrides are composed of metal atoms that constitute of a host lattice and hydrogen atoms that are trapped in interstitial sites, such as lattice defects. The trap site can be a vacancy or a line defect. In the case of a line defect, a string of hydrogen atoms may accumulate along the defect. Such a string increases the lattice stress, especially if two adjacent atoms recombine to form molecular hydrogen. Since adsorption of hydrogen increases the size of lattices, the metal is usually ground to a powder in order to prevent the decrepitation of metal particles.

There are two possible ways of hydriding a metal, direct dissociative chemisorption and electrochemical splitting of water. These reactions are, respectively





Where M represents the metal. In electrochemical splitting there has to be a catalyst, such as palladium, to break down the water.

A schematic of hydrogen chemisorption is shown in Figure 2.1(b). The molecular hydrogen reaches a shallow potential minimum near the surface and the atomic hydrogen a deeper minimum almost at the surface. In the metal lattice hydrogen has periodic potential minimums in the interstitial sites of metal lattice. This behavior is explained below and is visualized in Figure 2.1(b).

As a hydrogen molecule approaches the metal surface, weak van Der Waal's forces begin to act upon it drawing it closer. The molecule reaches the potential well  $E_p$  at distance  $z_p$ , and very large forces would be required to force it any closer the surface in a molecular form. However, the dissociation energy of hydrogen molecule is exceeded by the chemisorption energy. Thus the hydrogen molecule dissociates and individual hydrogen atoms are attracted to the surface by chemisorptive forces and they reach the potential well  $E_{CH}$ . From this point sometimes even the ambient temperature's thermal energy is enough to increase the vibrational amplitude of hydrogen atoms which can thus reach and enter the metal surface.

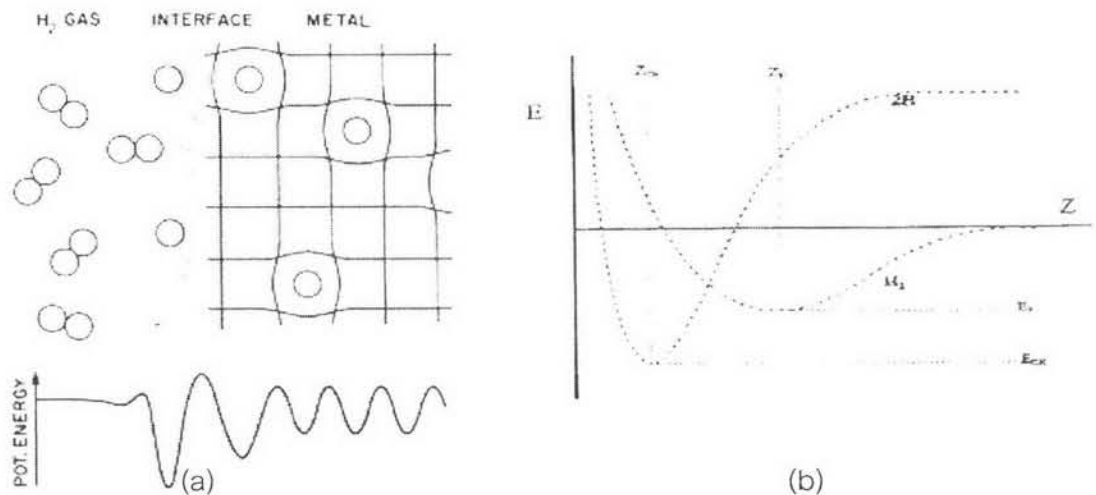


Figure 2.1 a) Schematic of hydrogen chemisorption on metal, b) Potential wells of molecular and atomic hydrogen.

A schematic of phase transition is presented in Figure 2.2. When charging, hydrogen diffuses from the surface of the particle through the  $\beta$ -phase to the phase-transition interface and forms additional diffuses  $\beta$ -phase hydride. When discharging, hydrogen from the phase-transition interface diffuses through the  $\alpha$ -phase to the surface of the particle where it is recombined into the form of molecular hydrogen.

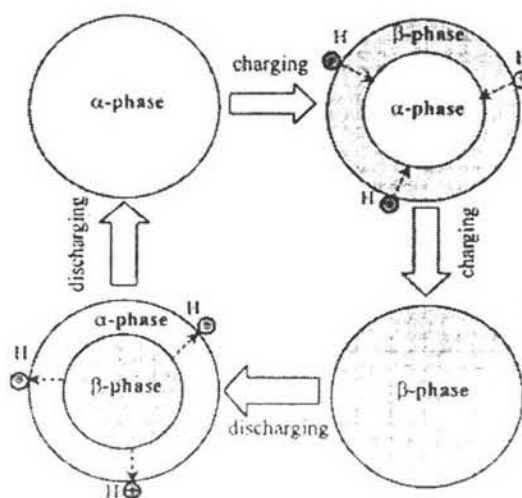


Figure 2.2 Schematic of phase transition in metal hydride.

Some studies suggest that the  $\alpha$ -phase diffusion is not influenced by the hydrogen concentration but is more like a random walk of a single atom known as the Einstein's diffusion. Either way, the studies show that the diffusion coefficient in  $\beta$ -phase is an order of magnitude lower than in  $\alpha$ -phase, i.e. the diffusion of hydrogen is much slower in  $\beta$ -phase. This can easily lead to imperfect charging especially with larger particles. A study of nano-scaled particles shows that when the metal grains are in the range of 5 to 50 nm, the kinetics of both absorption and desorption is improved by an order of magnitude because of improved thermal conductivity.

The kinetics can also be improved with a catalyst. These catalysts can be in liquid or solid form, but because the catalyst does not affect the overall reaction, its amount should be kept as low as possible in order to keep the storage capacity sufficient.

The most common characterization method of a metal hydride is the PCT (pressure-concentration-temperature) curve in a form of P-C isotherms. A theoretical P-C isotherm with  $\alpha$ - and  $\beta$ -phase is shown in figure 2.3.

The concentration, i.e. the hydrogen capacity, is usually defined as hydrogen atoms per metal molecule  $H/M$ . In order to characterize the metal hydride it is convenient to use the maximum hydrogen capacity  $(H/M)_{\max}$ . The reversible capacity  $\Delta(H/M)$ , defined as the plateau width (see Figure 2.3), is also a useful tool when considering the engineering capacities of metal hydrides. The concentration can also be expressed as mass per cent from the total mass, especially for the energy density comparison.

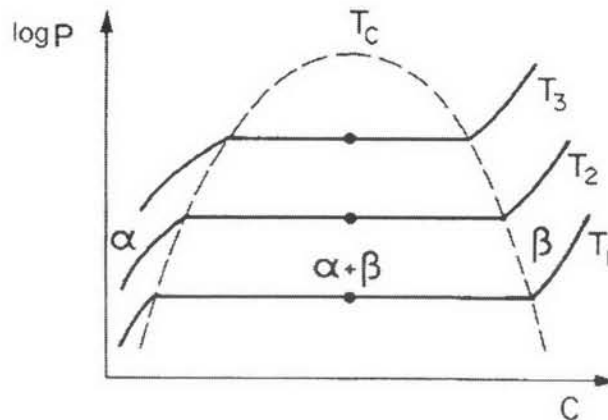


Figure 2.3 Theoretical P-C isotherm of a metal hydride

In real metal hydrides, the P-C isotherms show some hysteresis between adsorption and desorption. Also the plateau has some slope in it. These properties are shown and defined in Figure 2.4 where the subscripts *ads* and *des* refer to adsorption and desorption, respectively.

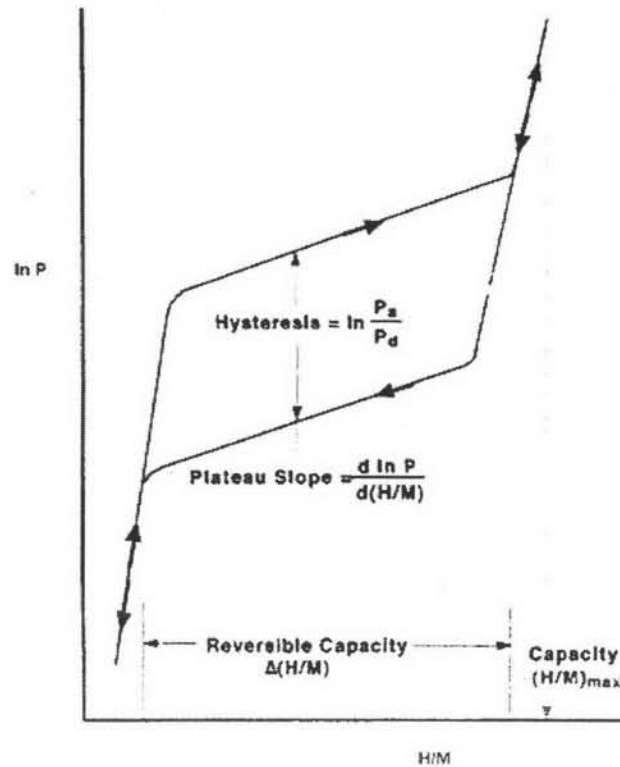


Figure 2.4 Schematic of real P-C isotherm.

The thermodynamic reaction equilibrium is defined with the equilibrium  $K$

$$RT \ln K = \Delta H - T\Delta S \quad (a)$$

Where  $\Delta H$  is the reaction enthalpy and  $\Delta S$  the reaction entropy. For a solid-gas reaction the equilibrium constant reduces to the pressure of the gas. Thus the Van't Hoff equation is obtained:

$$\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (b)$$

Plotting the equilibrium  $(P, T)$  values on a  $\ln P$  versus  $1/T$  scale gives the so-called Van't Hoff plot. The reaction enthalpy can be derived from the angular coefficient of the plot with the help of equation (b) and the plot tells 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 of a typical Van't Hoff plot is in Figure 2.5.

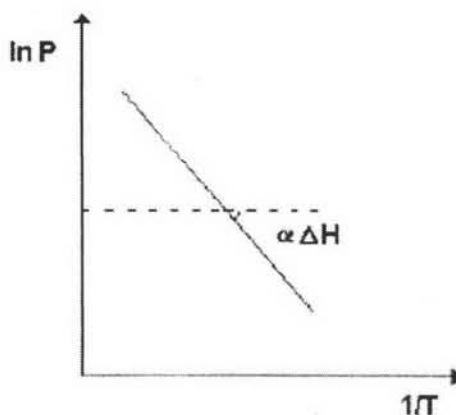


Figure 2.5 Schematic of Van't Hoff plot

The reaction enthalpy of hydride formation is an important quality. It is usually negative so the reaction is exothermic and thus the hydride formation release energy. Therefore the dehydration needs energy to be able to take place. Since most of the applications are used in ambient temperature, or at least in the range of 0-100°C, the reaction enthalpy should be quite small so that the hydride could take heat from the surroundings when releasing hydrogen. In some fuel cell systems the hydride can take heat directly from the fuel cell. According to equation (b), the reaction enthalpy also effects directly the stability of a hydride since the gas pressure is exponentially proportional to it..

There are two classes of hydrides: metallic hydrides and complex hydrides. The main difference between them is the transition of metals to ionic or covalent compounds for the complex hydrides upon absorbing hydrogen. Some of the metallic hydrides of interest for the storage purpose are listed in table 2.1. The prototype metallic hydrides are composed of two elements. The A element is usually a rare earth or an alkaline earth metal and tends to form a stable hydride. The B element is often a transition metal and forms only unstable hydrides. Ni is often used as B element since it is an excellent catalyst for the hydrogen dissociation.



Table 2.1 Most important families of hydrides forming in compounds

Intermetallic compound	A	B	Advantage	Disadvantage	Example
AB	Ti	Fe, Mn, Ni	Low cost	Instability of the upper plateau, easily form oxide films which decreases the sensitivity to impurities in hydrogen	Ti-Fe based alloys
AB <sub>2</sub>	Ti, Zr or a lanthanide (atomic number 57-71)	V, Cr, Mn, Fe	Low cost than AB <sub>5</sub>	Maximum capacity usually 1.5-2 wt%	ZrMn <sub>2</sub>
AB <sub>5</sub>	Mm, Ca, Y, Zr	Al, Mn, Si, Zn, Cr, Fe, Cu and Co	Not form protective oxide layers, good tolerance against small amounts of O <sub>2</sub> and H <sub>2</sub> O impurities in H <sub>2</sub>	Maximum capacity 1.9 wt% (extremely low), quite high cost	LaNi <sub>5</sub>

### 2.2.1 Intermetallic compound

In general, these alloys are combinations of A metals which have ability to absorb H<sub>2</sub> independently (rare earth metal such as La, Ti, Zr, Mg, Ca) with B metals which cannot absorb H<sub>2</sub> (Fe, Ni, Mn, Co) [22].

### 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 [22].

### 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. The theoretical hydrogen contents of some complex hydrides are given in Table 2.2.

Table 2.2 Hydrogen storage capacities of complex hydrides (Sandrock 1992) [26]

Hydrides	Hydrogen (wt%)
$NaAlH_4$	7.5
$LiAlH_4$	10.6
$Mg(AlH_4)_2$	9.3

## 2.3 Metal Hydride Developments

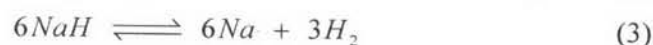
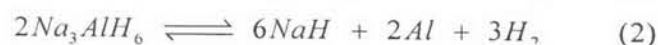
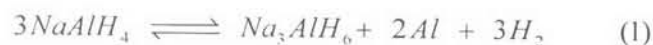
The key factors in developing practical, economic hydride systems for vehicular applications are:

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 NaAlH<sub>4</sub>

Sodium alanate (sodium tetrahydroaluminate: NaAlH<sub>4</sub>) has been known as reducing agent in organic chemistry. It contains large amount of hydrogen (7.4 wt%). The released hydrogen occurs in 3 step reactions. The hydrogen desorption of NaAlH<sub>4</sub> proceeds as follow [3-4]



The first reaction releases 3.7 wt% of hydrogen and starts at a temperature between 185 °C and 230 °C. The second reaction occurs at about 260 °C with a further desorption of 1.8 wt% of hydrogen (relative to the starting material) [5]. Finally the third reaction, NaH decomposes at a very higher temperature with 1.9 wt% of hydrogen. Only the first two

reactions with total hydrogen release of 5.5 wt% are considered for onboard hydrogen storage because of the moderate desorption temperature for practical storage systems. However, the disadvantages of  $\text{NaAlH}_4$  are the slow hydrogen desorption kinetics and it cannot reabsorb hydrogen in the cycling. Until in year 1997, Bogdanovic and Schwikardi have modified  $\text{NaAlH}_4$  by doping with transition metal (Ti and Fe) [5]. It was found that the transition metal doping reduces the temperature of hydrogen desorption and made the reversible reaction under moderate condition (150 °C, 60-150 bar).

It is surprising that both titanium and zirconium have catalytic effects on different reactions in decomposition of  $\text{NaAlH}_4$ ,  $\text{Ti}(\text{OBu})_4$  for the first step and  $\text{Zr}(\text{OPr})_4$  for the second step. In the addition, the dry doping method (homogenization) is more effective than the wet doping method [6,8].

Another work on the absorption/desorption kinetics of mechanical grinding was done by Zaluska and coworkers (2000) [15]. 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 ( $\text{Na}_3\text{AlH}_6$ ,  $(\text{Li-Na})_5\text{AlH}_6$  and  $(\text{Li-Na-B})_3\text{AlH}_3$ ) prepared by ball milling were able to release hydrogen reversibly and had more rapidly kinetics than previously reported catalyzed system, supported the notion that reduced particle size play an important role in improving kinetics. Remarkably, with carbon as an additive of the hydrides enhanced desorption kinetic at low temperature and rehydrogenated without catalysts.

Like titanium and zirconium, doping the hydride with  $\text{Ti}(\text{OBu})_4$  and  $\text{Fe}(\text{OEt})_2$  also produces a synergistic effect, resulting in materials that can be rehydrided to 4 wt% at 104 °C and 87 atm of hydrogens. The improved kinetics allowed researchers to carry out constant -temperature, equilibrium-pressure studies of  $\text{NaAlH}_4$  that extended to temperature well below the melting point of the hydride [9]. Moreover, they conclude that desorption/absorption of solid doped  $\text{NaAlH}_4$  depends on type and amount of the dopants, morphology and size of  $\text{NaAlH}_4$  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  $\text{NaAlH}_4$  by Gross and coworkers (2002) [7]. Using in-situ X-ray powder diffraction (XRD) (see Fig.2.6) 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) [23] showed that a clear understanding of solid state mechanism in the presence of liquid Ti/Zr catalyst was observed through scanning electron microscope (SEM) (see Fig. 2.7) and energy dispersive spectroscopy (EDS).

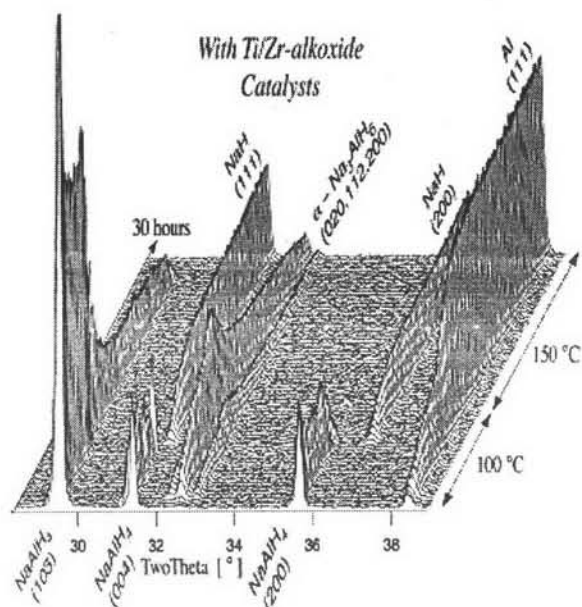
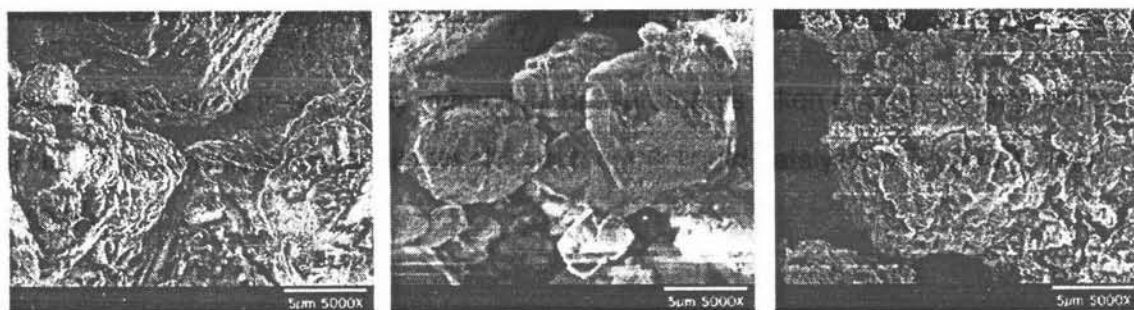


Figure 2.6 Dynamic in-situ X-ray diffraction measurements taken during decomposition of  $\text{NaAlH}_4$  mechanical mixed with 2mol% each of the liquid catalysts of  $\text{Ti}(\text{OBU}^n)_4$  and  $\text{Zr}(\text{OPr}^i)_n$ .



a)  $\text{NaAlH}_4 \rightleftharpoons$  b)  $\frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3}\text{Al} + \text{H}_2 \rightleftharpoons$  c)  $\text{NaH} + \text{Al} + \frac{3}{2}\text{H}_2$

Figure 2.7 SEM images showing changes in morphology that occur during the decomposition of  $\text{NaAlH}_4$  doped with 2 mol% each of the liquid catalysts of  $\text{Ti}(\text{OBU}^n)_4$  and  $\text{Zr}(\text{OPr}^i)_4$ .

The experiment performed by Sun *et al* (2002) [24] illustrates the XRD patterns and lattice parameters (see Fig. 2.8) that the catalyst quantity impacts on low hydrogen capacities of  $\text{NaAlH}_4$  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  $\text{Na}^+$  vacancies in the bulk hydride lattice (see Fig 2.9).

Table 1  
Comparison of lattice parameters before and after doping

Samples	Lattice parameters, Å		Cell volume, Å <sup>3</sup>
	<i>a</i>	<i>c</i>	
Undoped $\text{NaAlH}_4$	5.02667(19)	11.35631(57)	286.945(21)
<i>Ti-doped NaAlH<sub>4</sub></i>			
2 mol.%	5.01639(16)	11.35389(46)	286.449(17)
5 mol.%	5.03880(20)	11.39259(54)	289.252(21)
6.4 mol.%	5.03062(20)	11.37088(55)	287.764(20)
8 mol.%	5.03064(18)	11.37090(48)	287.768(23)
10 mol.%	5.03018(19)	11.36622(55)	287.596(20)
<i>Zr-doped NaAlH<sub>4</sub></i>			
2 mol.%	5.01971(29)	11.34423(88)	285.846(32)
5 mol.%	5.03016(27)	11.36768(81)	287.630(30)
10 mol.%	5.03168(34)	11.37080(100)	287.884(37)

Figures in brackets are estimated standard deviation.

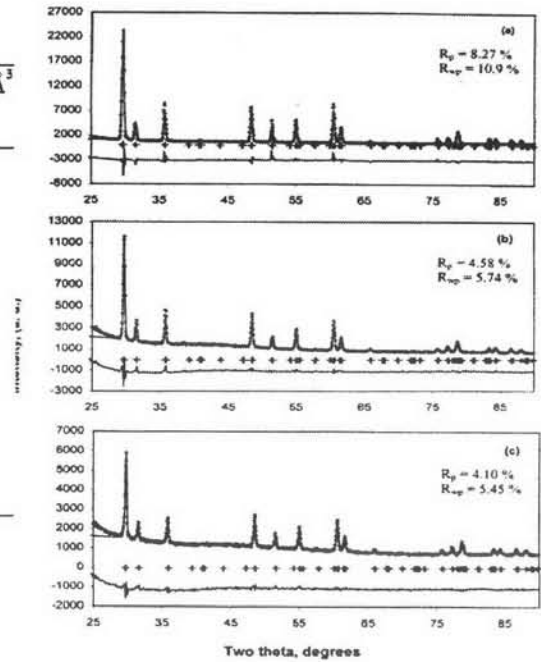


Figure 2.8 (a) Table of lattice parameter before and after Ti or Zr doping, (b) Rietveld refinement profile of Ti and Zr doped  $\text{NaAlH}_4$ .

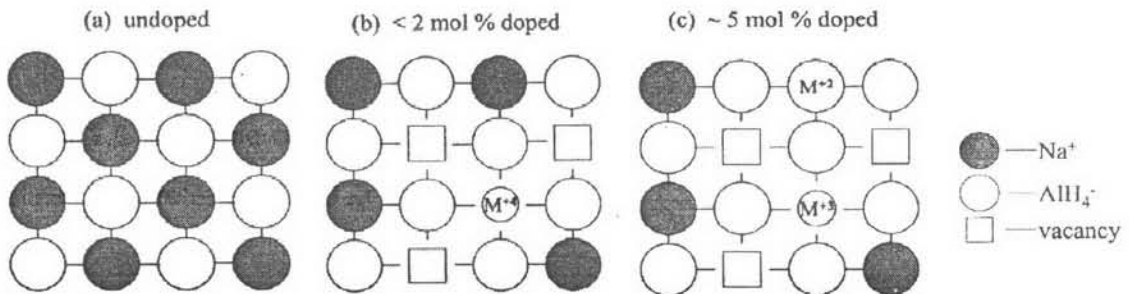


Figure 2.9 Schematic illustration of the changes in  $\text{NaAlH}_4$  lattice upon increased level of doping.

The process of hydrogen desorption and absorption of Ti-doped  $\text{NaAlH}_4$ , the investigating via XRD and NMR spectroscopy was reported by bogdanovic *et. al.* [11]. Both methods showed that large Al particle formation during dehydrogenation causes mass transfer problem which affects the low capacity in rehydrogenation.

Majzoub and Gross (2003) [25] observed that doping NaH and Al with  $\text{TiCl}_3$ ,  $\text{TiF}_3$  and  $\text{TiBr}_3$  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  $\text{TiAl}_3$  peaks in XRD (see Fig. 2.10) during the absorption is on the basis of participation to enhance the kinetics.

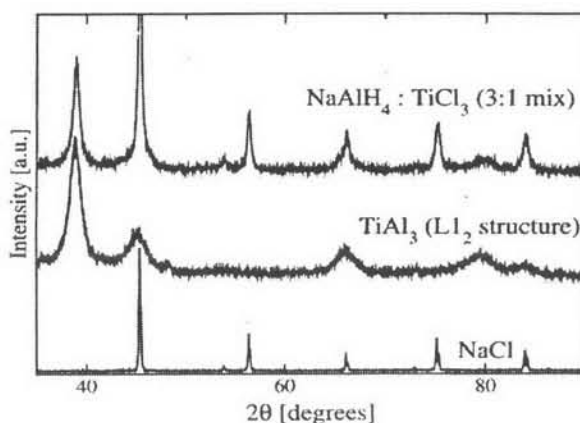


Figure 2.10 X-ray diffraction indicating that  $\text{TiAl}_3$  production in the  $\text{NaAlH}_4$  system when mechanically milled in 3:1 ratio with  $\text{TiCl}_3$ .

## 2.5 Porphyrins

Porphyrins are macrocyclic tetrapyrrole systems with conjugated double bonds and various groups attached to the perimeter (see scheme. 1). The extensive conjugated system makes the compound chromatic, hence the name porphyrin, from a Greek word for purple. The macrocycle has 22 pi electrons, 18 of which are active in the conjugated system. As they follow Hückel's rule, porphyrins have aromatic properties. A porphyrin can lose two protons to become a 2- anion. It is the anionic form of the porphyrin that complexes with metal ions to form metalloporphyrin complex.

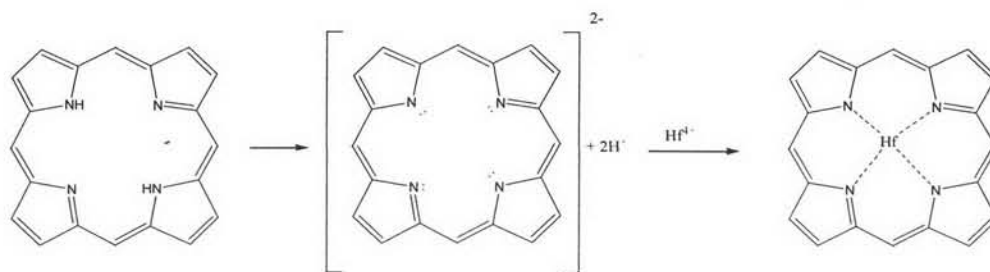


Figure 2.11 A general reaction showing the formation of a metalloporphyrin

### 2.5.1 Type of porphyrins and related molecules

Porphyrins combine readily with metals, coordinating with them in the central cavity. Iron- (heme), magnesium- (chlorophyll), zinc-, copper-, nickel-, and cobalt- containing porphyrins are known, and many other metals can be inserted. A porphyrin in which no metal is inserted in its cavity is called a free base. The general reaction shows the formation of a metalloporphyrin in Figure 2.11. It is typically used as catalyst in organic chemistry [21].

### 2.6 Copper-chromium oxide

The "copper-chromium oxide" hydrogenation catalyst, effective for some types of organic compounds is normally prepared by decomposing a copper ammonium chromate at low temperature to give a material reported as copper-chromium oxide, copper chromite, copper oxide-chromite, etc. Of the descriptive names for the catalyst "copper-chromium oxide" appears to be the most generally accepted and will be used to designate the normal catalyst. The decomposition of copper ammonium chromate occurs in four stages. The decomposition in the first stage is exothermic and occurs in the temperature range 200°-290°C. The probable reactions occurring in this stage are as follows:

