

CHAPTER I

INTRODUCTION

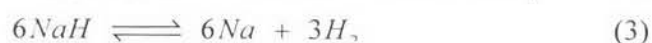
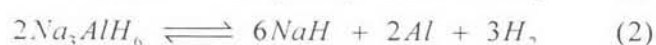
Pollution is threatening life on earth through accelerating climate change and by aggravating serious health problems. The primary source of pollution is emissions from a growing number of motor vehicles. Vehicles emissions contribute much of the nitrogen dioxide, sulphur dioxide, carbon monoxide and lead. The major environmental concern is the amounts of gases that are released to the atmosphere daily causing the green house effect. The combination of climate change and health concerns has led to increasing pressure on both car manufacturers and refining companies from government agencies and environmental groups to reduce the amount of pollutants created by vehicles. It is becoming clear that without alternatives to fossil fuels, life on the planet may become unsustainable. There are examples of alternative fuels: biodiesel, electricity, ethanol, liquid petroleum gas, natural gas and hydrogen [1]. But hydrogen is expected play an important role in developing sustainable transportation, because it may be produced in virtually unlimited quantities using renewable resources.

Hydrogen is one of the most abundant elements. It has a heating value three times higher than petroleum [2]. It is an odorless, colorless, tasteless and non-poisonous gas. It is a renewable resource. When burned in an internal combustion engine, it produces almost zero exhaust and the only by product is water. A key characteristic of hydrogen is that it is not a primary source of energy. Hydrogen must be produced through several methods using alternative energy sources, such as gasoline, natural gas, solar and wind. The supply is endless and depends on the production process. Therefore, hydrogen bears a manufacture cost, which made it cost 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 a given volume, by using as cost-effective method as possible. Obviously, any method for storage must have an acceptable means of reversibility. Currently, six reversible storage

cryogenic tanks, (iii) adsorbed hydrogen (hydrogen stored on the atomic surface of a material), (iv) absorbed hydrogen on interstitial sites (hydrogen stored in cells of a crystal lattice), (v) complex metal hydrides (i.e. alanates), (vi) metal and complexes together with water. While each of these methods have various strengths and weaknesses, storage in complex metal hydrides appears to be the most promising for many applications.

Alanate can be defined by the general formula $A_xAl_yH_z$, where A is an alkali earth metal, Al is aluminum, and H is hydrogen. In general, A is usually either Na or Li. Sodium alanate (sodium tetrahydroaluminate: $NaAlH_4$) has been known as a reducing agent in organic chemistry. It contains a large amount of hydrogen (7.4 wt%). The released hydrogen occurs in 3 step reactions. The hydrogen desorption of $NaAlH_4$ proceeds as follows [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 the 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 $NaAlH_4$ are the slow hydrogen desorption kinetics and it cannot reabsorb hydrogen in the cycling.

In 1997, Bogdanovic and Schwikardi modified $NaAlH_4$ by doping with a 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 a moderate condition (150°C, 60-150 bar). The reversible hydrogen capacity is 3.1-4.2 wt%. After this breakthrough, many works have been published on the transition metal-doped sodium alanate. Zidan *et al.* (1999) [6] reported that $Zr(OPr)_4$ affected catalytically the hydrogenation/dehydrogenation of $NaAlH_4$ on different reactions. $Zr(OPr)_4$ catalyzed the second reaction while $Ti(OBu)_4$ catalyzed the first reaction. $NaAlH_4$ stabilized with Ti/Zr

was reported to release hydrogen greater than 4wt%. Gross *et al.* [7] reported NaAlH₄ can reversibly desorb/absorb hydrogen under relatively mild conditions when NaAlH₄ was doped with a Ti-based catalyst. NaAlH₄ doped with TiCl₃ released 3wt% hydrogen.

Not only does a type of transition metal catalyze the kinetics, but also the preparation method. 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 [8]. In 2000, Bogdanovic and coworkers [9] introduced the homogenous Ti and/or Fe doped NaAlH₄. A synergistic effect was observed, resulting in materials that released hydrogen up to 4 wt% in the cyclic stability test (17 cycles) in the range of 140-170 °C and 104-170 bar. Moreover, they concluded that desorption/absorption of doped NaAlH₄ depended on type and amount of dopant, morphology and method of preparation.

However, none has met the DOE target for onboard hydrogen storage (>6.5 wt%). Moreover, the exact state of the transition metal dopants is suspicious. Some study has claimed that the catalyst species are located on the surface of the particles in form of a pure metal or alloys [10-11]. The formation of an alloy between Al and transition metal has been report to occur during ball milling or during the hydrogen desorption/absorption. The delocalizations of transition metal result in decreasing the effectiveness of catalyst in the reaction [12-15]. In addition, the available Al was reduced due to the formation of large Al crystallites, which may possibly be coated by NaAlH₄. These affect the loss of stability in cycling and incomplete in the hydrogen desorption/absorption [11].

Further improvement in the rates of the dehydriding and, more crucially, the rehydriding of NaAlH₄ are required in order for this material to achieve commercial viability. With this goal, we studied the reversible reaction of HfCl₄-doped NaAlH₄ at moderate temperature and pressure, as well as the stability in the hydrogen desorption/absorption.

Our approach is to use a chelating complex as a co-catalyst to reduce or prevent the formation of Hf/Al alloy and/or metals that deteriorates the performance of the system. The chelating complexes used in this work were H₂TPP (Meso-Tetraphenylporphyrin) and HfCl₂TPP ((Tetraphenylporphyrinato) hafnium (IV) chloride),

which is typically used as a catalyst for photosynthetic reaction and hydrogen transfer in organic reaction. Brandy *et al.* [16] studied the sunlight-catalytic effect of porphyrin-embedded periodic mesoporous organosilica (POM) materials to conversion of cyclic organic. Elza *et al.* [17] studied the reductive hydrogenation of polycyclic aromatic hydrocarbon which were catalyzed by Ni, Fe and Co porphyrins. Abdolreza *et al.* [18] investigated the catalytic system at high efficiency and relative stability of Mn-porphyrin catalyst towards oxidative degradation of benzyl alcohols. The advantages of this complex are i) not deteriorate the original system, ii) not decompose or degrade during their operation and iii) chelated with aluminium or hafnium.

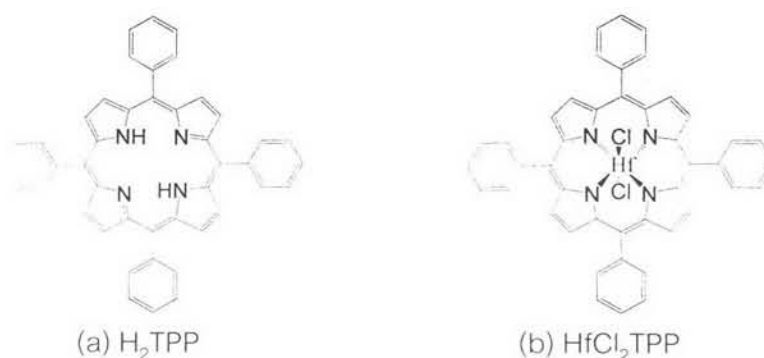


Figure 1 Chemical structure of (a) Tetraphenylporphyrin ($C_{44}H_{30}N_4$): H_2TPP and (b) (Tetraphenylporphyrinato)hafnium(IV)chloride ($HfCl_2C_{44}H_{28}N_4$): $HfCl_2TPP$

To further improve the hydrogen capacities, copper chromium oxide ($CuCrO_4$) (a dehydrogenation catalyst) and nickel metal (an active catalyst for hydrogen dissociation) were used as a co-catalyst to decrease the desorption temperature and improve the amount of released hydrogen of $HfCl_4-NaAlH_4$. The examples of the catalytic properties studying of copper chromium oxide are the dehydrogenation of methanol over copper-containing catalyst (copper chromite, copper hydroxysilicate and copper-zinc hydroxysilicate) by Minyukova *et al.* [19] and the hydrogenation/dehydrogenation reactions of isopropanol over copper chromite catalysts by Rioux *et al.* [20].