CHAPTER I

INTRODUCTION

Hydrogen has been expected to be the most promising energy source as it has higher energy per mass than conventional fossil fuels, and it is also environmentally friendly (Fakioglu *et al.*, 2004). It can be used in proton exchange membrane (PEM) fuel cells for transportation but it has lower energy per volume because of its gaseous form at the room temperature (Züttel, 2004). To be able to provide hydrogen for PEM fuel cells for on-board applications efficiently and safely, appropriate hydrogen storage methods are needed.

Four main storage technologies are being considered, namely high-pressure hydrogen, liquid hydrogen, and solid hydrogen (including carbon and other high surface area materials, H_2O-reactive chemical hydrides, thermal chemical hydrides, and rechargeable metal hydrides) (Riis, 2006). The first two methods have already reached on-board applications but each of them has some drawbacks. The high-pressure hydrogen storage has both low gravimetric and volumetric energy density and also low hydrogen storage capacity, while the liquid hydrogen storage, which has over 800 times higher density than its gaseous form, is unable to avoid heat transfer through a super-insulating container that leads to loss of hydrogen due to boil-off (Fujii and Ichikawa, 2006). The last two methods are still under development.

The solid-state hydride storage including metal hydrides, complex hydrides, and intermetallic compounds exhibits a great gravimetric, volumetric hydrogen density, safety, and reversibility. However, some of them must be activated at an elevated temperature or pressure. Porous solids or carbon nanostructures such as activated carbon, single-walled carbon nanotubes (SWNTs), multiple-walled carbon nanotubes (MWNTs), graphite, and metal-organic frameworks (MOFs) can only adsorb a small amount of hydrogen at the ambient temperature and pressure but they can promote cycle stability (Luo *et al.*, 2007).

The US Development of Energy (DOE)'s target for hydrogen storage capacity is specified to be greater than 5.5 wt% in 2015, equivalent to 300 miles driving distance and 65 g l^{-1} available hydrogen, at a decomposition temperature

between 60 and 120°C for commercial uses. Moreover, cost, safety, and cycle life times (> 500 times) are also the key challenges (www.eere.energy.gov).

One of the most promising materials for PEM fuel cells, which operates at a temperature about 90°C, is sodium alanate, $NaAlH_4$. Its theoretical reversible storage capacity is about 5.5 wt%. Hydrogen starts to decompose in a temperature range of 200-400°C and absorbs in a pressure range of 10-40 MPa hydrogen. It can be seen that the practical applications seem out of reach because its thermodynamics and kinetics are too stable. However, Bogdanovic´ and Schwickardi (1997) reported that if $NaAlH_4$ was doped with a small amount of a metal catalyst (such as Ti), the system could be rehydrogenated under much milder conditions (temperature slightly above 100°C and pressure around 10 MPa hydrogen). But the hydrogen capacity is still lower than that of the practical usage.

To achieve the target of 6.5 wt%, other materials, which have a higher hydrogen storage capacity such as lithium borohydride, $LiBH_4$, have emerged as potential candidates. $LiBH_4$ is considered to be one of the materials for hydrogen storage because it has the highest theoretical hydrogen capacity of 18.4 wt%. However, it releases hydrogen at a temperature above 400°C (Züttel et al., 2003a). Although it seems to be too stable for on-broad applications, the addition of magnesium hydride, MgH_2, to $LiBH_4$ can decrease the desorption temperature to 315-400°C and release 11.4 wt% hydrogen (Vajo et al., 2005). Furthermore, the addition of a catalyst can improve cycle stability and hydrogen desorption temperature (Miyaoka et al., 2006).

This research focused on the destabilization of the mixture of $LiBH_4$ and MgH_2 and pristine MgH_2 by adding a transition metal catalyst or its derivatives (such as Ti, TiO_2, $TiCl_3$, $ZrCl_4$, and $HfCl_4$). In addition, effects of an amount of a catalyst, ball-milling time, and hydrogen desorption/absorption conditions were studied. The hydrogen desorption temperature, amounts of released hydrogen, cycle stability, phase transformation, and reaction kinetics were used to evaluate the possibility of using the mixture as a hydrogen storage material.