CHAPTER 1

INTRODUCTION

1.1 Background of Study

In search of alternative energy sources for the reduction of environmental impact by green house gas emissions, hydrogen emerged to be one of the most promising candidates. Alternative energy sources are needed not only because of the environmental concerns but also due to the increasing energy demands which causes the depletion of fossil fuels [1]. Hydrogen is attractive as an energy carrier because it exhibits the highest heating value per mass (39.4kWh/kg) among all the chemical fuels. Apart from that, hydrogen is also regenerative and environmental friendly. Since the hydrogen element can only be found in abundance in the form of water, it has to be produced [2]. Some of the methods used to produce hydrogen include water electrolysis, steam methane reforming (SMR), and also gasification of coal and biomass [1].

In order to utilize hydrogen as a replacement of fossil fuels, there are both technical and economic challenges that must be overcome. Hydrogen storage is one of the challenges apart from the real-time production and efficient combustion of hydrogen [2]. The separation and direct storage of hydrogen during its production at high-temperature may be able to save costs as the reactor system can be operated at lower temperatures [3]. Compressed gas and liquid storage are the conventional methods of storing hydrogen. Hydrogen may also be stored as physically bound hydrogen where hydrogen gas is physisorbed to a high surface area adsorbent. A material has to be safe, light, and cheap with a high hydrogen adsorption capacity to qualify as a potential hydrogen adsorbent [4].

Among the materials that have been investigated for application as a hydrogen storage adsorbent are metal hydrides [5], [6], carbon materials [7]-[9], zeolite [10] and metal organic frameworks (MOFs) [11]. However, these materials have shortcomings in the area of hydrogen storage [12]. Generally, all the reversible hydrides working around ambient temperature and atmospheric pressure consist of transition metals and this makes the gravimetric hydrogen density is limited to less than 3 wt% [2]. The high-temperature requirement for hydrogen removal, slow desorption kinetics as well as high reactivity towards air and oxygen are the disadvantages of using Mg-based metal hydrides [13] although they have high storage capacity (7.6wt%). Meanwhile, carbon materials such as activated carbon have low hydrogen adsorption capacity at room temperature [8] and the hydrogen storage by some carbon materials are not reversible [12]. In addition, the hydrogen storage at ambient temperature in metal organic frameworks also gives low hydrogen capacity of 1.0 to 1.5wt% (at 298K and 100bar) for bridged MOFs with hydrogen spillover, and this amount is three to five times higher than adsorption capacity of MOFs without bridging [11]. Furthermore for MOFs, the high-temperature hydrogen storage capacity was found to be small even at high pressure (0.17 wt% at 129bar and 350°C) [1].

Another material that can be investigated for the purpose of hydrogen storage application is hydrotalcite-like compounds (HTlcs). HTlcs are ionic and basic clays which are composed of brucite-like ($Mg(OH)_2$) structure with trivalent cations substituting for divalent cations resulting in a layer charge. This positive charge is counterbalanced by the anions in the interlayer [14]. The cations are located at the centers of octahedral sites of the hydroxide sheet. Meanwhile, the vertex of the hydroxide sheet contains hydroxide ions where each –OH group is shared by three octahedral cations and points to the interlayer regions [15].

The properties of HTlcs such as their layered structure and high anion exchanging abilities enable them to be used in various technical applications [16]. Their specific uses and applications are determined by the nature of their cations and anions [17]. HTlcs have been applied as catalysts in various chemical reactions [18]-[20] and they are also used as adsorbents for dyes, surfactants [21] and other compounds in wastewater treatments [22]. Additionally, HTlcs have also been utilized in adsorption of gases such as carbon dioxide [23], nitrogen oxides [24] and sulfur oxides [25].

Besides their anion exchange a property, another useful feature of HTlcs is that upon calcination at moderate temperatures (300°C-500°C), they form mixed oxides, which have the ability to recover the layered structure after rehydration or immersion in solutions containing anions [17], [19]. This feature is important as these mixed oxides will be utilized in this study to adsorb the hydrogen gas, since mixed oxides have been reported to possess quite a high hydrogen adsorption capacity [26]-[27]. A number of previous studies have also investigated hydrogen storage using metal oxides such as Ni/Ce oxides [28], sodium oxide, Na_2O (hydrogen capacity of 3wt% at 175-250°C and 1.8MPa) [29], NiO and MgO [30]. Therefore, it is worthwhile to synthesize a hydrotalcite-like compound which can be used, upon mild calcinations, to store hydrogen.

Mg-(Ni)-Al hydrotalcite-like compound was chosen as the research material in this study. Although the hydrogen adsorption on as-synthesized Mg-Al-$Fe(CN)_6$ HTlc have been reported to be insignificant [31], the partial replacement of Mg with Ni can induce reducibility and subsequent hydrogen adsorption. The mixed oxide (MgO-NiO) produced after calcination is expected to be reduced when exposed to hydrogen and then form nickel magnesium hydride (Ni-MgH_2) when it reacts further with hydrogen. This method was selected since this hydride has the highest hydrogen storage capacity (7.6wt%) compared to other metal hydrides. Meanwhile, the addition of Al into the MgH_2 system was found to improve the kinetics of hydrogen adsorption in previous investigations [13], [32]. Furthermore, the alumina (Al_2O_3) which is also produced during the calcination has been known to have thermal endurance making suitable for use in high-temperature adsorption processes [33]. Additionally, magnesium and aluminum is cheaper than most other metals which makes their use economical [34].

1.2 Problem Statement

One of the obstacles that must be overcome in order to utilize hydrogen as replacement of fossil fuels is the hydrogen storage technology. The conventional hydrogen storage via gas cylinders and liquid hydrogen in cryogenic tanks has limitations such as use of high pressure and high energy requirement for the liquefaction process [2].

The direct storage of hydrogen and/or carbon dioxide during steam reforming process can save costs as the reactor can be operated at lower temperatures [3], [35]. A method of storing hydrogen that can be used for this purpose is via physisorption on solid adsorbents [2].

Many potential hydrogen storage adsorbents have been investigated such as metal hydrides, carbon materials, zeolites and metal organic frameworks (MOFs). However, each material has its own shortcomings when applied for hydrogen storage purpose. For instance, metal hydride requires high desorption temperature, the hydrogen storage capacity of carbon materials are inconsistent [36], MOFs give low hydrogen storage capacity even at high temperature and pressure [4], [13], [37], [11]. These drawbacks make the search of alternative hydrogen storage materials essential.

Meanwhile, studies on mixed oxides as hydrogen adsorbents have shown promising results in terms of hydrogen adsorption capacity [27]. A potential source of mixed oxides that may be used as hydrogen storage adsorbent is hydrotalcite-like compounds or HTlcs. However no research works have been known to involve in the investigation of the hydrogen storage properties of hydrotalcite-derived mixed oxides. This basic and layered compound can form mixed oxides upon calcination at temperatures between 300°C and 500°C. Additionally, calcined HTlcs have also been used as adsorbents for many polar and non-polar gases in previous researches [25], [38].

1.3 Objectives of Study

The objectives of this study are:

1. To synthesize and characterize the (Ni)-Mg-Al HTlcs and the derived mixed oxides.
2. To investigate the hydrogen storage capabilities of (Ni)-Mg-Al HTlcs-derived mixed oxides.
3. To study the effects of temperature and composition of the materials on its hydrogen adsorption-desorption characteristics.

1.4 Scopes of Study

The research involves the study of the performance in terms of equilibrium and kinetics of hydrogen adsorption by the synthesized materials. In this study, only the coprecipitation method is used to prepare the hydrotalcites. The composition of the hydrotalcites is also limited to (Mg + Ni)/Al molar ratio of 0.5 to 4 with Ni/Mg ratio of 0:1, 1:2 and 2:1. The type of HTlcs that is used in this study is (Ni-)Mg-Al HTlcs. There are two approaches that are utilized for the study of hydrogen adsorption. The first is a volumetric method called temperature programmed reduction (TPR). In this technique the HTlc is calcined to produce a mixture of NiO, MgO and Al_2O_3 or their solid solution. The mixed oxides are subsequently subjected to reduction under hydrogen flow (5% H_2 in N_2) to obtain the corresponding metal ((Ni-) Mg) which are then used to adsorb hydrogen and form metal hydride. The second approach for hydrogen adsorption study is by thermogravimetric analysis (TGA). In this technique, the amount of hydrogen adsorption on reduced mixed oxides is determined by measuring the mass change of the adsorbent as it is exposed to hydrogen flow under a controlled temperature programme. The conventional static volumetric (pressure-volume adsorption isotherm) is not used in this study.

1.5 Significance of Study

Although mixed oxides have been studied for hydrogen storage abilities, the hydrogen adsorption using mixed oxides derived from (Ni)-Mg-Al HTlcs have never been discussed in previous literature. Therefore this study is a novel attempt to use hydrotalcite-like compounds as an alternative source for the hydrogen storage materials.

1.6 Thesis Outline

Chapter two presents the literature review for this study. The sources for the literature review include related journal articles, books and other published work. This chapter is divided into subsections such as theory of adsorption, potential hydrogen adsorbents, and hydrotalcite-like compounds. Additionally, related characterization of the materials and hydrogen adsorption techniques are also discussed. Chapter three provides the methodology of this study. The methods that are presented here include material synthesis, material characterization and hydrogen adsorption. Details of the experimental setup and equipments used in this study are also mentioned in this chapter. Chapter four presents the results and discussions of the material characterizations and hydrogen adsorption experiments. The discussions are also based on the results and information obtained from literature for similar works. Chapter five provides the conclusions and recommendations of the study. This section highlights the main findings and outcomes of the research. Recommendations and suggestions for future work are also presented here.