# Surface Effect of Magnesium-Aluminium And Lithium-Aluminium Hydrotalcite Based Adsorbent In Hydrogen Adsorption

by

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15611

Dissertation submitted in partial fulfillment of
the requiremenst for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

____________________
(Dr. Md Abdus Salam)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
September 2015

# CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NOR HIRLIN BINTI TAHIR

# ABSTRACT

The project entitled surface effect of Magnesium-Aluminium and Lithium-Aluminium hydrotalcite based adsorbent in hydrogen adsorption which aims to determine the surface effect of modified adsorbent. The adsorbent were synthesized using coprecipitation method while surface modification performed by impregnation method. The adsorbent were characterized using BET Surface Area Analyzer and Field Emission Scanning Electron Microscope (FESEM) for textural properties and surface morphology of the adsorbent. Further, the adsorbent will be analyzed to see the adsorption performances using fixed bed reactor at ambient conditions. Surface effect will be studied applying adsorption studies on different compositional modified adsorbent surface. In this study, hydrotalcite based adsorbent were consisted with magnesium (Mg), lithium (Li) and aluminium (Al) with different molar ratio and later the adsorbent will be modified by palladium (Pd) to activate surface for hydrogen adsorption. The synthesized adsorbent is expected to achieve the optimum hydrogen adsorption capacity as suggested by Department of Energy (DOE).

# ACKNOWLEDGEMENT

First and foremost, I would like to express my deepest gratitude to my father, Tahir Bin Awang and my mother, Maimunah Binti Mohd Nor for their best support emotionally and financially in aiding the succession of this project. A very special note of thank to my supervisor, Dr. Md Abdus Salam for his willingness and determination to help the completion of this project. Through the consultation period, I have received numerous share of insight on the different aspects to be assessed for this project to become feasible. His excellent support, patience and effective guidance have brought a great impact to the progress of the project. Nevertheless, I would also like to thank panel of examiners for being supportive and providing me with lots of tips to ensure that this project can be improved in the future.

Next, I would like to give token of appreciation to the Chemical Engineering Department of Universiti Teknologi PETRONAS (UTP) for providing me a platform to undertake this remarkable Final Year Project (FYP) course as a medium to enhance skills and knowledge regarding the undergraduate studies in Chemical Engineering.

Not to forget, my heartfelt gratitude goes to the my friends for providing me continuous support throughout the easy and challenging times.

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# LIST OF ABBREVIATION

| | |
|---|---|
| $H_2$ | Hydrogen gas |
| DOE | Department of energy |
| BET | Brunauer Emmette Teller |
| FESEM | Field Emitted Scanning Electron Microscopy |
| wt% | Weight percentage |
| Al | Aluminium |
| Li | Lithium |
| Mg | Magnesium |
| $Na_2CO_3$ | Sodium Carbonate |
| Pd | Palladium |

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# CHAPTER 1
# INTRODUCTION

## 1.1 Background of Study

Energy is essential to life. Without it, billions of people would be left cold and hungry. The major source of energy comes from fossil fuels, and the dominant fossil fuels used today by most industrialized and developing countries are oil, coal, and natural gas. Among these fossil fuels, oil is the most consumed for energy conversion, followed by coal, then natural gas (Riddle, et. al., 2003). Fossil fuels are the largest greenhouse gas emitters in the world, contributing three quarter of all carbon, methane and other greenhouse gas emissions. Burning of fossil fuels, apart from giving energy as fuel source also gives out pollutants to the atmosphere, which later accumulated and end up increasing the worlds temperature every minutes it were burn. This greenhouse effect, later will no longer be a minor concern as within few years ahead, the thinning of ozone will be the main issues talked over the world including the increasing pollutant levels in each country. In addition, these pollutants will eventually cause severe health effect towards humankind and eventually will lead to death.

Besides, as world population continues to grow and the limited amount of fossil fuels begins to diminish, it may not be possible to provide the amount of energy demanded by the world by only using fossil fuels to convert energy. Thus, it is crucial to have renewable resources play a larger role in the supply of energy.

Answering the call for renewable energy, the world now had diverted the attention to one abundant yet promising resources which is hydrogen based fuel. Hydrogen is a clean energy fuel that has potential to replace those fuel derived from fossil fuels such as diesel and petrol. Due to its importance as alternative fuel resources, several studies has been made to discover the storage of hydrogen. Hydrogen in nature exists primarily in combination with other elements. For hydrogen to be useful as a fuel, it must exist as free hydrogen ($H_2$).

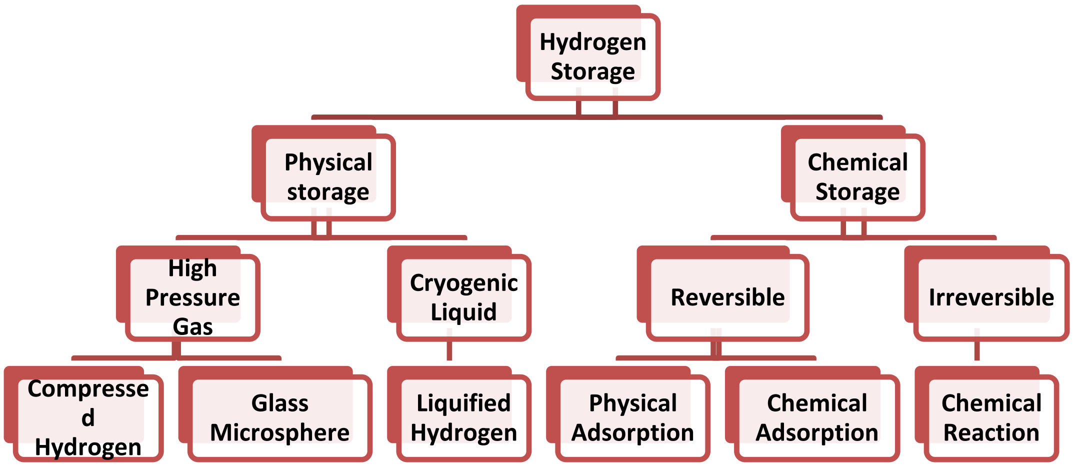


FIGURE 1.1 Types of Hydrogen Storage

From the studies conducted, it was found that clay minerals, which are abundant in the world, can acts as hydrogen adsorbent with few alterations made to its structure. Clay minerals have many applications in the industry sector because of its microporous structure especially as an adsorbent. However, some modification are being made to restructure the clay as an effective source of hydrogen adsorbent with aims to achieve hydrogen storage at 5.5 wt% at ambient temperature as stated by US Department of Energy (DOE).

This study intends to search on the potential of hydrotalcite like minerals as hydrogen storage media. The revolutionary method used to synthesize the hydrotalcite is co-precipitation method and wet impregnation method through Mg-Al and Li-Al combination ratio. Through this approach, the intended objective is to find the real capability of hydrotalcites hydrogen storage capability.

## 1.2 Problem Statement

Hydrogen is the cleanest fuel, and has a heating value three times higher than petroleum. However, it is not a natural source, but a man-made fuel; therefore, hydrogen bears a manufacture cost, which made it costing three times higher than the petroleum products. Therefore, any method of storage is not allowed to considerably increase the cost of hydrogen fuel. Besides, a technique of hydrogen storage has to meet the DOE criterion for the volumetric and gravimetric density of the stored hydrogen and the reversibility criterion for the charging or discharging processes (Zhou, 2005). Besides, Zhou also stated that there are basically five candidate methods that have attracted the common interest: compression, liquefaction, physisorption, metallic hydrides, and complex hydrides.

Among these five methods, physisorption is an interesting part to focus in term of hydrogen storage due to its inexpensive cost. Storage of hydrogen via physisorption such as through porous medium however, have few disadvantages when operated at ambient temperature. Usually very small amounts (< 1 wt%) of hydrogen are adsorbed at room temperature and up to 100 bar (Chen. et. al., 2008). This phenomena is concerning researches since the optimum hydrogen adsorption capacity needed at ambient temperature is 5.5 wt%. Thus, to counter the temperature dependence issue, the hydrogen surface interactions need to be increased. This project will focus on the adsorbent surface and effect of different surface structure in hydrogen adsorption.

## 1.3 Objectives

The main objectives of this project are:

i. To synthesis and characterize hydrotalcite based adsorbent for hydrogen adsorption.
ii. Hydrogen adsorption analysis of Mg-Al and Li-Al hydrotalcite.

This research will be focusing on synthesizing Mg-Al and Li-Al hydrotalcite clay. The Mg-Li-Al hydrotalcite clay will be prepared for different molar ratio to get optimum performance of the adsorbent. The characterization of the hydrotalcite clay will be tested using FESEM and BET Surface Area Analyzer. Both synthesized hydrotalcite will then, tested for their capacity to adsorb hydrogen.

# CHAPTER 2
# LITERATURE REVIEW

## 2.1 Hydrogen Demand

Hydrogen is the simplest and most abundant element on earth. Hydrogen combines readily with other chemical elements, and it is always found as part of another substance, such as water, hydrocarbon, or alcohol. Hydrogen is also found in natural biomass, which includes plants and animals. For this reason, it is considered as an energy carrier and not as an energy source. Hydrogen can be produced using diverse, domestic resources, including nuclear, natural gas and coal, biomass, and other renewable sources. The latter include solar, wind, hydroelectric, or geothermal energy. This diversity of domestic energy sources makes hydrogen a promising energy carrier and important for energy security.

It is desirable that hydrogen be produced using a variety of resources and process technologies or pathways. The production of hydrogen can be achieved via various process technologies, including thermal, electrolytic, and photolytic. The annual production of hydrogen is estimated to be about 55 million tons with its consumption increasing by approximately 6% per year (C.M. Kalamaras and A.M. Efstathiou, 2013). Besides, according to Navigant Research (2013), the global demand for hydrogen is at 250 million kg in 2013 and they forecasted that the global hydrogen demand will continue to increase in the future as indicated in Figure 2.1.

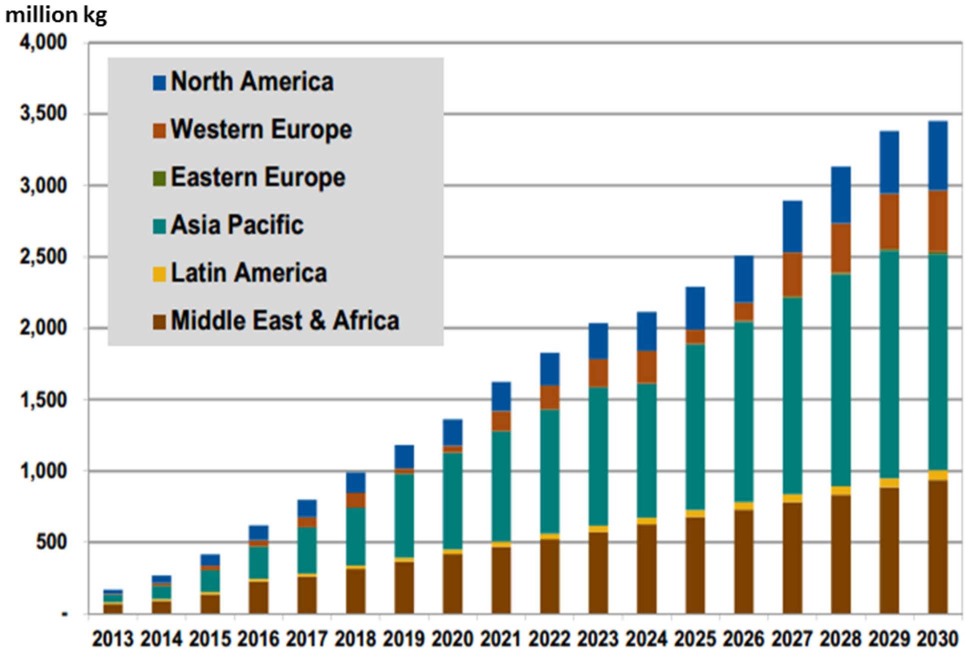


FIGURE 2.1 Forecast on Hydrogen Demand (Data from Navigant Research, 2013)

However, since hydrogen is not a natural source, but a man-made fuel; therefore, hydrogen bears a manufacture cost, which made it costing three times higher than the petroleum products. Therefore, any method of storage is not allowed to considerably increase the cost of hydrogen fuel. There are still problems in the realization of the renewed hydrogen from water, but the market supply and the cost of hydrogen do not constitute the bottleneck of hydrogen vehicles today although the hydrogen used presently may not be renewed. There is only one bottleneck for the hydrogen vehicle program, the storage of hydrogen.

Hydrogen storage describes the methods for storing hydrogen gas for subsequent use. The methods span many approaches, including high pressures, cryogenics, and chemical compounds that reversibly release hydrogen gas upon heating (Mills et. al., 2012).

To overcome this problem, later this project will discuss on the effective hydrogen storage via adsorption on porous material with synthesizing of hydrotalcite clay.

## 2.2 Adsorbent

An adsorbent is a material that has the ability to extract certain substances from gases, liquids, or solids by causing them to adhere to its surface without changing the physical properties of the adsorbent.

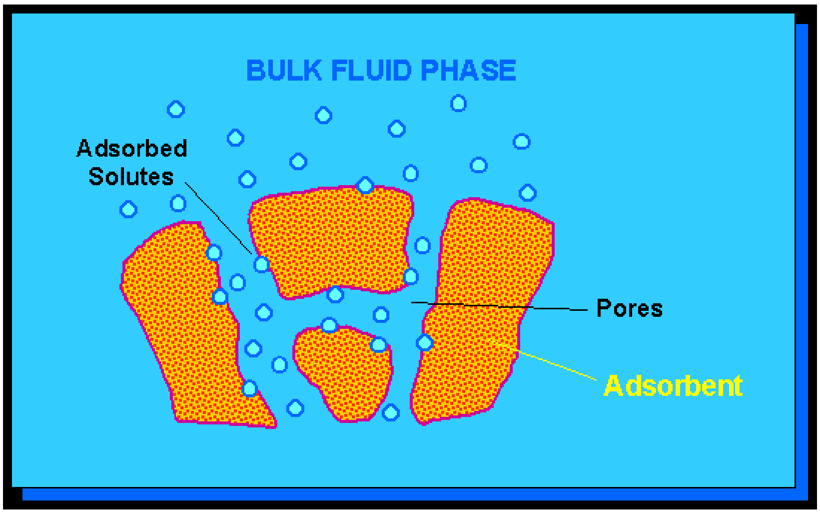


FIGURE 2.2 Illustration of Hydrogen Adsorbent and Adsorption Process

There are many types of adsorbent available in the earth. During the last 15 years new classes of solid adsorbents have been developed, such as activated carbon fibres and carbon molecular sieves, fullerenes and heterofullerenes, microporous glasses and nanoporous both carbonaceous and inorganic materials. Nanostructured solids are very popular in science and technology and have gained extreme interest due to their sorption, catalytic, magnetic, optical and thermal properties ( Dabrowski, 2001). Examples of adsorbent were tabulated in Table 2.1.

Table 2.1: Types of Adsorbent Available

| Carbon Adsorbents | Mineral Adsorbents | Other Adsorbents |
|---|---|---|
| Active carbons<br>Activeted carbon fibres<br>Molecular carbon sieves<br>Mesocarbon microbeads<br>Fullerenes<br>Carbonacceous<br>Nanomaterials | Silica gels<br>Activated alumina<br>Oxides of metals<br>Zeolites<br>Clay mineral<br>Pillared clays<br>Porous clay hetero-structures<br>Inorganic nanomaterials<br>Hydrotalcite-like clay | Synthetic polymers<br>Composite adsorbents<br>Mixed sorbents |

As alternatives for hydrogen adsorption, this project will later discussed on the potential of modified clay mineral namely hydrotalcite clays, to be one of the effective adsorbent for hydrogen adsorption.

## 2.3 Adsorption

Adsorption is defined as a selective concentration or retention of one or more components from a gaseous mixture on a solid surface. The real adsorption system can be defined as an equilibrium one including the adsorbent being in contact with the bulk phase and the so-called interfacial layer. This layer consists of two regions: the part of gas residing in the force field of the solid surface and the surface layer of the solid. The term ‘adsorption’ deal with the process in which molecules accumulate in the interfacial layer, but desorption denotes the converse process.

The fundamental concept in adsorption science is that named as the adsorption isotherm. It is the equilibrium relation between the quantity of the adsorbed material and the pressure or concentration in the bulk fluid phase at constant temperature. The adsorption phenomenon provides an excellent method of separation particularly at low concentrations and hence it is recognized as an important mass transfer operation. There are various adsorption isotherms available which relates the amount adsorbed per unit mass of the adsorbent to the partial pressure of the adsorbate in the gas phase at equilibrium, depending upon the nature of adsorbent and adsorbate. Fixed bed adsorption studies are very important in adsorption which basically tells us the performance of the adsorbent under various operating conditions such as bed height, flow rate, inlet adsorbate concentration and many more by drawing a breakthrough curve which can be found out experimentally or can be predicted through mathematical modeling. There is physical adsorption where the force of attraction between adsorbate and adsorbent is Van Deer Waal's forces and also chemical adsorption in which the strength of its force of attraction is almost the same as chemical bond. The important factors that influence adsorption capacities are:

- The nature of adsorbent and adsorbate
- The surface area of adsorbent
- Operating condition of experiments

Depending on the type of phases in contact, adsorption involves the following systems: liquid-gas, liquid-liquid, solid-liquid and solid-gas. The major development of adsorption processes on a large, industrial scale deals mainly with the solid-gas and solid-liquid interfaces, but in various laboratory separation techniques all types of interfaces are applied. The term 'fluid' is commonly used to denote gas or liquid in contact with the boundary surface of solids. Later, this project will discuss on the development of surface effect of newly synthesized hydrotalcite clay on the adsorption of hydrogen.

## 2.4 Hydrotalcite based adsorbent

Hydrotalcite (HTLC) are a family of clay minerals consisting of a double-layered hydroxide structure, with the general formula $Mg_6Al_2(CO_3)(OH)_{16}.4(H2O)$ (Cavani et. al, 2000) and can be found in nature in white or colourless with molecular weight 603.98 g/mol. Synthetic hydrotalcite is anionic clays also known as layered double hydroxides (LDH) which is similar to brucite, $Mg(OH)_2$ structure. The name of hydrotalcite is referring to its resemblance to talc and its characteristic which is high in water content. Hydrotalcite can be used as additives for polymer, anion exchange, antacids, and catalyst to accelerate reactions, catalyst support, nuclear waste treatment and also sorbents (Stephenson, 2013). Due to the demand for larger surface area for adsorption, these hydrotalcite were put under thermal treatment known as calcined hydrotalcite with larger surface area and high porosity (Gutierrez, 2009).

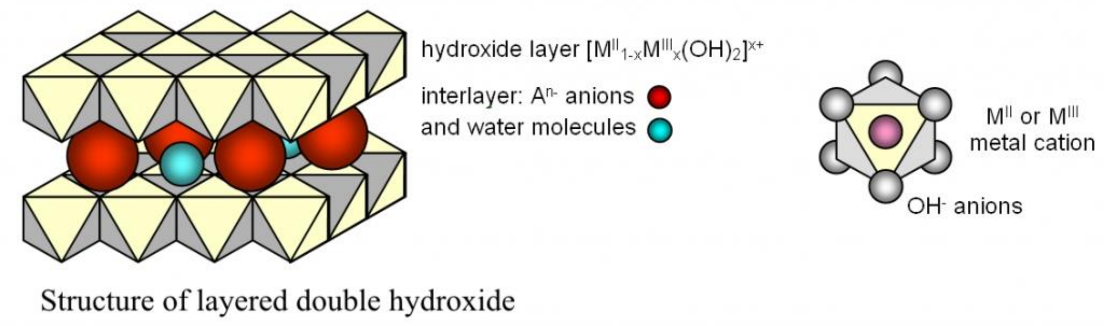


FIGURE 2.3 Structure of Hydrotalcite (Cavani et. al., 2000)

Coprecipitation is the process of precipitation of more than one substance simultaneously. It has been recognized that coprecipitation is one of the most reliable and reproducible techniques for the preparation of non-noble metal-based catalysts (Cavani et. al, 2000). This is because, this technique allows homogeneous precursors to be used as starting materials, where two or more elements are intimately mixed together, and synergic effects are favored. The thermal stability and the activity of the catalyst also had to be attributed to the nature of the precursor.

Clays are characterized by a layered structure because of which they are slippery when wet. They are broadly classified into cationic and anionic clays. Cationic clays are widely spread in nature. They have negatively charged layers with cations in the interlayer. Structurally, anionic clays are the mirror images of cationic clays and contain positively charged layers and anions in the inter layers. Anionic clays are represented by the general formula, where M2+ is a divalent or monovalent cation and AIl- is the interlayer anion. The value of x is usually between 0.2 and 0.33. The structure of anionic clays is best understood starting from the structure of brucite, $Mg(OH)_2$ The brucite-like sheet is formed by the edge sharing of $M(OH)_6$ octahedra. The isomorphous substitution of M2+ ions by trivalent cations leads to the generation of positive charge in the brucite- like sheet. This results in the formation of a layered structure with the charge compensating anions and water in the interlayer region.

In the case of adsorption of water, the interaction between water and a solid surface can be viewed as a chemical reaction characterized by certain energy, which is the product of surface area and the energy per unit of surface area. The understanding of the interaction deals mainly with the analysis of the energy and free energy changes per unit area associated with the contact of water and clay minerals. The global behavior of the clay-water interface can be viewed as a combination between two processes: physical adsorption and progressive building of the interface between a charged surface and water, namely the electric double layer. At microscopic level, three main interactions can be considered referring to water-hydrotalcite clay interaction. Firstly, the dispersive interaction where the complexity of the sandwiches structure enhances the attraction force. Secondly, the donor-acceptor interaction, which occurs between polar group and water. The active surface polar group of clay is mainly silica rings. The third major type of interaction is due to cations. Water adsorption onto cations located inside sites creates two competitive charge transfers. The first is between the electrons of an oxygen atom from the solid, and a hydrogen atom from a water molecule. The second is between the cations and the oxygen atom of water molecules.

## 2.5 Hydrogen Adsorption

Hydrogen storage is one the main concern in hydrogen fueled energy. This is due to the limited storage of hydrogen. Hydrogen can be stored in three ways which are via compressed gas, liquid hydrogen and condensed state. However, for these storage to take place few requirements need to be fulfilled considering the volumetric density, gravimetric density, kinetics, heat transfer, efficiency, reversibility, and operation temperature of each storage system. In condensed state storage system, hydrogen can be stored via two ways either physisorption or chemisorption.

This study will focus on the physisorption of hydrogen that is the adsorption of hydrogen on surface of materials. Physical adsorption exhibits several advantages over chemical hydrogen storage as for example the complete reversibility and the fast kinetics. In addition, a very small amount of energy ($< 10$ kJ mol$^{-1}$) is involved both in the adsorption and in the release of hydrogen in physisorption process (B. Panella, 2006).

Van der Waals interactions are the origin of the physisorption of gas molecules onto the surface of a solid. Once a monolayer of adsorbate molecules is formed, gaseous molecules interact with the surface of the liquid or solid adsorbate. The binding energy of the second layer of adsorbate molecules is, therefore, similar to the latent heat of sublimation or vaporization of the adsorbate. Consequently, a single monolayer is adsorbed at a temperature equal to or greater than the boiling point of the adsorbate at a given pressure.

## 2.6 Characterization of Adsorbent

The characterization of hydrotalcite clay in the meantime was tested using FESEM and BET analyzer. BET Surface Area Analyzer measures the surface area and pore size distribution of hydrotalcite by using gas adsorption and mercury porosimetry. Hydrotalcite in experiments are labelled as HT and tested for various degasification temperature and degasification time.

### 2.6.1 BET and FESEM Analysis

BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer. The technique encompasses external area and pore area evaluations to determine the total specific surface area in $m_2/g$ yielding important information in studying the effects of surface porosity and particle size in many applications. This technique characterizes pore size distribution independent of external area due to particle size of the sample. Field Emission Scanning Electron Microscope (FESEM) is a microscope that uses electron to form surface morphology of a sample.

Hydrogen adsorption studies is important since the time required for refueling and discharging in dynamic application such as for automotive fuel cell purpose. The rate of hydrogen adsorption can be measured with a fixed bed apparatus. The set-up of fixed bed are as follows:

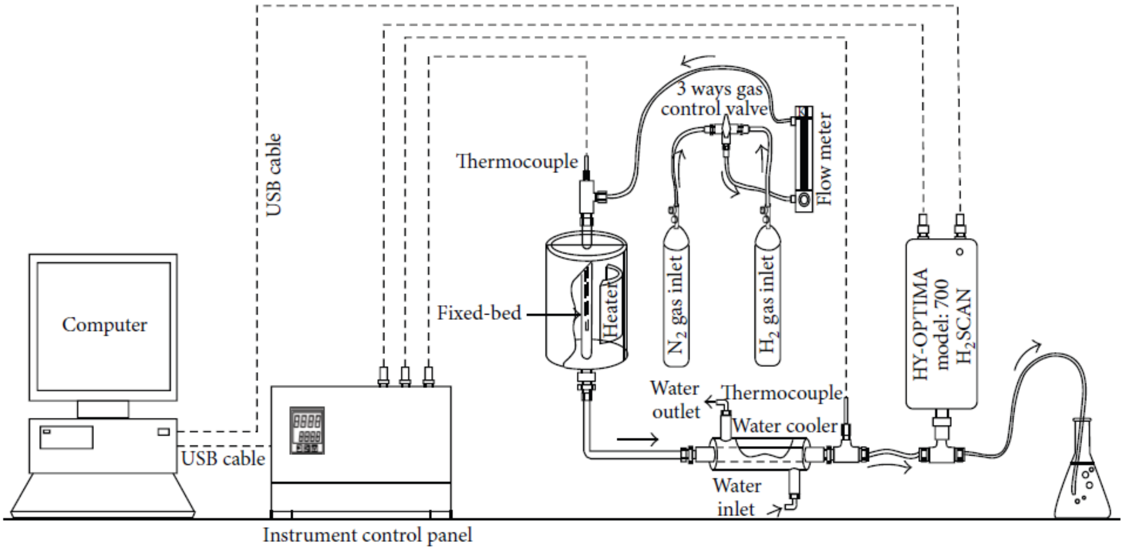


FIGURE 2.4 Diagram of the full fixed bed set up (Salam et. al., 2013).

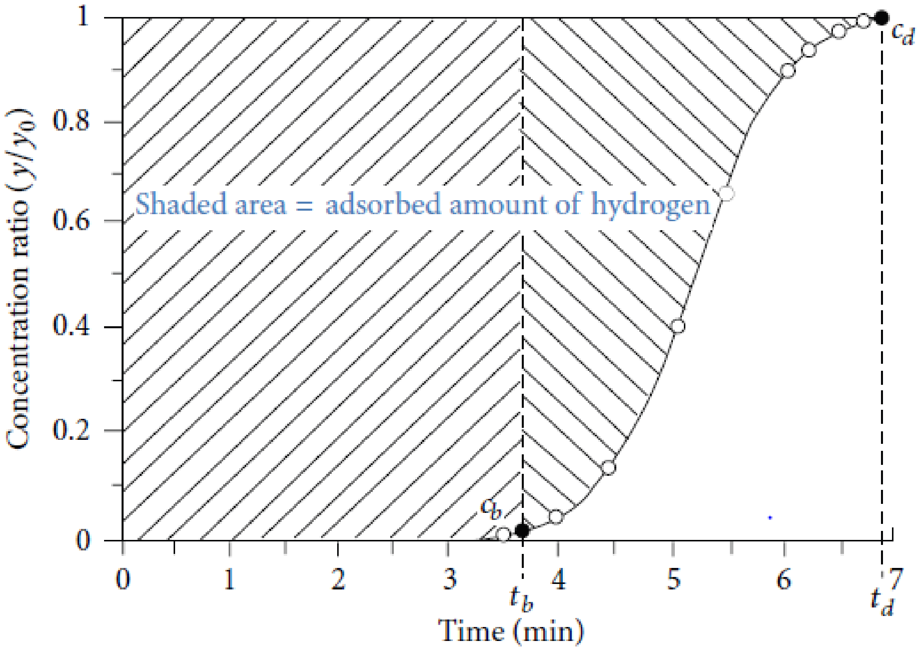


FIGURE 2.5 Typical breakthrough curve of hydrogen gas adsorption

( Salam et. al., 2013)

The breakthrough curves obtained from the experiments were used to determine the amount of hydrogen adsorbed with function of time where ($y/y_0$) is the concentration ratio (Salam et. al., 2013).

$$\frac{y}{y_0} = \frac{t}{(t + A.e^{-B.t})} \qquad (1)$$

Where $A$ and $B$ are the fitting parameters, $y$ and $y_0$ are the final and initial concentrations of hydrogen, respectively, and $t$ is the adsorption time. Using the typical breakthrough curve as stated in figure 2.5, the capacity of the fixed bed for hydrogen adsorption or mass adsorbed by the bed ($M_{ads}$) can be calculated using the following equation (Salam et. al., 2013):

$$M_{ads} = \frac{Q_T\ (MW)}{(RT/P_A)} \left[\Delta t - \int_0^t \left(\frac{y}{y_0}\right) dt\right] \qquad (2)$$

where $t$ is the time, equivalent to the total or stoichiometric capacity, $M_{ads}$ = adsorbed mass, $Q_T$ = flow of gas, $y_0$ =inlet gas concentration and $P_A$= partial pressure of inlet hydrogen gas. All parameter units were converted to SI unit for calculation and adsorption capacity of the bed determined by using the following equation(Salam et. al., 2013):

$$W = \frac{M_{ads}}{M_{bed}} \qquad (3)$$

Where $M_{bed}$ = mass of the bed.

# CHAPTER 3
# METHODOLOGY

## 3.1 Research Methodology and Project Activities

The chosen methodology for this research is based on extensive literature researches and experimental studies because the effectiveness of the synthesized hydrotalcite clays were not apparent and has to be investigated. Later, the synthesized hydrotalcite were to be evaluated based on their efficiency in adsorbing hydrogen at 5.5 wt% at ambient temperature. Figure below demonstrates the flow of the research work in this study.

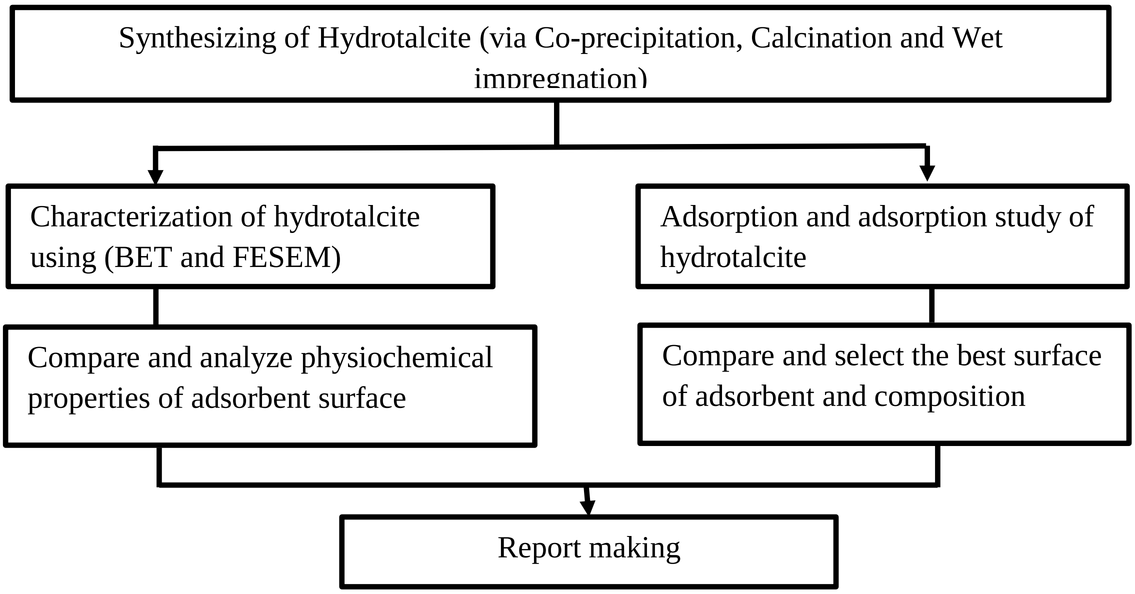


FIGURE 3.1 Schematic diagram depicting the flow of the FYP project

## 3.2 Raw Materials and Chemicals Needed

The list of chemicals will be required are:

Table 3.1: List of chemicals

| Section | Items | Unit |
|---|---|---|
| CHEMICALS | Magnesium nitrate hexahydrate | 500g |
| | Aluminium nitrate nanohydrate | 500g |
| | Lithium nitrate | 500g |
| | Sodium carbonate decahydrate | 1kg |
| | Palladium drop | Few drops |

## 3.3 Equipment Required

There are two kinds of instruments that were widely employed in this research work, which are analytical instrument and experimental instrument. Analytical instruments will be used for the characterization of the catalysts which are listed below together with its functionality:

i) Brunauer-Emmet-Teller (BET) Surface Area Analysis

ii) Field Emission Scanning Electron Microscope (FESEM)

The equipment which is required for the catalyst preparation is listed as follows:

a) Weighing Balance

b) Hotplate Magnetic Stirrer

c) Furnace chamber

## 3.4 Preparation of Hydrotalcite

In this research work, the hydrotalcite will be prepared by using two methods, which are the co-precipitation method and wet impregnation method. Mg-Al and Li-Al hydrotalcite was prepared with two different molar ratio with Mg-Al and Mg-Li composition of 3:1. The coprecipitation method was conducted with Sodium Carbonate as the precipitating agent. The reactions involved in the synthesizing are as below:

$2Mg(NO_3)_2.6H_2O + 2Na(CO_3).10H_2O \longrightarrow Mg_2(OH)_2CO3 + 4NaNO_3 + 30H_2O + H_2CO_3$……………………………………………………………………………….(4)

$2LiNO_3.3H_2O + Na_2(CO_3).10H_2O \longrightarrow Li_2(OH)_2CO_3 + 2NaNO_3 + 14H_2O + H_2$…(5)

$2Al(NO_3)_3.9H_2O + 3Na_2(CO_3).10H_2O \longrightarrow 2Al(OH).CO_3 + 6NaNO_3 + 46H_2O + H_2CO_3$…………………………………………………..………………………...(6)

Table below shows the mass of Mg, Li, and Na used to synthesize both ratios of hydrotalcite:

Table 3.2: Mass of Mg, Li, Al and $NaC0_3$ used in synthesizing hydrotalcites

| **Molar Ratio** | **Magnesium (g)** | **Lithium (g)** | **Aluminium (g)** | **Sodium Carbonate (g)** |
|---|---|---|---|---|
| **Mg-Al = 3:1** | 33.61 | 0.0 | 16.39 | 61.88 |
| **Li-Al = 3:1** | 0.0 | 32.54 | 17.46 | 63.44 |

### 3.4.1 Co-precipitation Method

The procedure of synthesizing Mg-Al and Li-Al hydrotalcite are as below:

**The first step to synthesize the catalysts by using co-precipitation method is to prepare the standard stock solution**. In this research work Mg solution, Li solution and Al solution are prepared by dissolving the correct amount of the chemicals in crystal/powder form into the volumetric flask. After that, the solution is stirred for 30 minutes by using magnetic stirrer at 200 rpm.

**Prepare sodium carbonate solution** by dissolving it in dissolved water at 60-70°C while stirring at speed of 300-400 rpm until the solutes were completely dissolved and produced clear solution

↓

**Mix Mg and Al solution in a 1L beaker with glass rod. Titrate the solution with Sodium Carbonate with the metal oxide mixture for 30 minutes at** speed of 300-400 rpm while maintaining temperature at 55°C. Control the pH

↓

**Filter the solution (after titration) and washed five times with deionized water**. Then, **dried the sample** at 120℃ overnight and calcined at 500℃ for 6 hours in flowing oxygen (20mL/min).

↓

**Repeat the same step for Li-Al component.**

↓

**Start the wet impregnation of Mg-Al and Li-Al**

### 3.4.2 Wet impregnation method

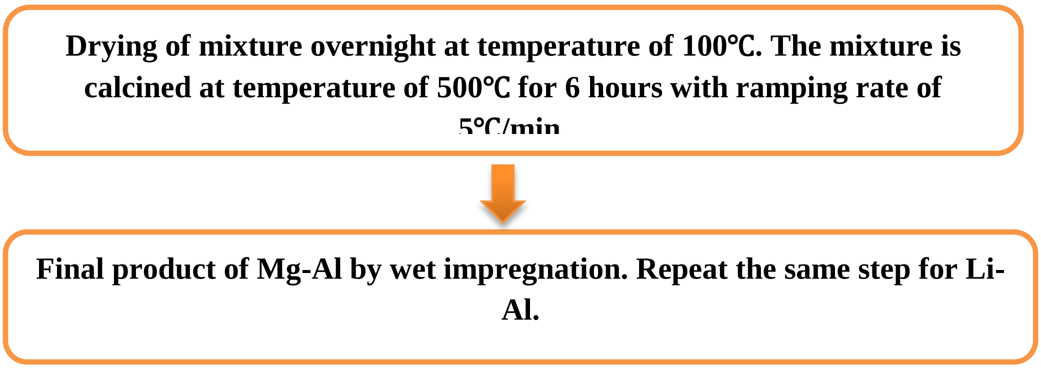
Method to synthesize modified hydrotalcite catalyst by using the wet impregnation method is indicated as follows:

**Addition of Pd standard solution by drop wise into Mg-Al hydrotalcite (about 1 -2 grams)**

↓

**Addition of 30 mL of deionized water into solution. The solution is stirred for 1 hour at 500 rpm at room temperature to ensure homogenenous mixing**

↓



Drying of mixture overnight at temperature of 100℃. The mixture is calcined at temperature of 500℃ for 6 hours with ramping rate of 5℃/min

Final product of Mg-Al by wet impregnation. Repeat the same step for Li-Al.

## 3.4 Gantt chart and flowchart

### 3.4.1 Gantt Chart FYP 1

| No | Activities | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Confirmation of Project Title | 🟨 | 🟨 | | | | | | | | | | | | |
| 2 | Preliminary Research Work | | 🟨 | 🟨 | 🟨 | 🟨 | | | | | | | | | |
| 3 | Submission of Extended Proposal | | | | | | 🟨 | 🟨 | | | | | | | |
| 4 | Oral Proposal Defense | | | | | | | | 🟨 | 🟨 | | | | | |
| 5 | Preparation of Chemicals and Glassware | | | | | | | | | | 🟨 | 🟨 | 🟨 | 🟨 | |
| 6 | Preparation of Interim Report | | | | | | | | | | | | 🟨 | 🟨 | |
| 7 | Submission of Interim Draft Report | | | | | | | | | | | | | 🟨 | |
| 8 | Submission of Interim Report | | | | | | | | | | | | | | 🟨 |
| 9 | Synthesis of Hydrotalcite | | | | | | | | | | | | | 🟨 | 🟨 |

### 3.4.2 Gantt Chart FYP 2

| No | Activities | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Laboratory experiment | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 |  |  |  |  |
| 2 | Preliminary Research Work | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 |  |  |  |  |
| 3 | Submission of Progress Report |  |  |  |  |  |  | 🟨 |  |  |  |  |  |  |  |
| 4 | Test Hydrogen Adsorption via fixed bed reactor |  |  |  |  |  |  | 🟨 | 🟨 | 🟨 |  |  |  |  |  |
| 5 | Characterization of Hydrotalcite |  |  |  |  |  |  |  |  | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 |  |
| 6 | Submission of Draft Final Report |  |  |  |  |  |  |  |  |  |  | 🟨 |  |  |  |
| 7 | Pre Sedex |  |  |  |  |  |  |  |  |  | 🟨 |  |  |  |  |
| 8 | Submission of Dissertation (soft bound) |  |  |  |  |  |  |  |  |  |  |  | 🟨 |  |  |
| 9 | Submission of Technical Paper |  |  |  |  |  |  |  |  |  |  |  | 🟨 |  |  |
| 10 | Viva |  |  |  |  |  |  |  |  |  |  |  |  | 🟨 |  |
| 11 | Submission of Hard Bound |  |  |  |  |  |  |  |  |  |  |  |  |  | 🟨 |

### 3.4.3 Flowchart

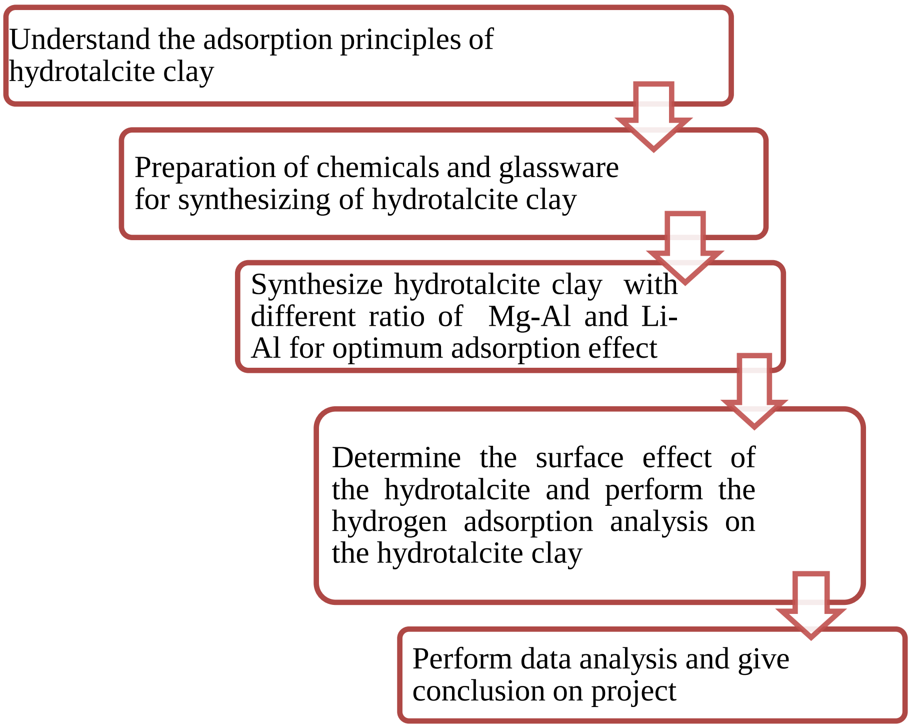


FIGURE 3.2 Flowchart of Project

# CHAPTER 4

# RESULT AND DISCUSSION

This chapter discussed about the results that is obtained from this research work. Besides, in order to provide clear and significant understanding on the surface effect of Mg-Al and Li-Al hydrotalcite, thorough discussion and analysis is performed via surface morphology characterization and adsorption studies for both hydrotalcite synthesized.

## 4.1 Characterization of synthesized catalysts

Characterizations of synthesized hydrotalcites are performed via the BET and FESEM analysis. It is significant because it enables the researchers to have a better insight on the surface morphology and the textural properties of synthesized hydrotalcites. The textural properties of the hydrotalcite may include pore size and surface area of the carrier and the geometry and strength of the support.

### 4.1.1 Brunauer Emmet Teller (BET) Surface Area Analysis

Brunauer-emmet-Teller (BET) analysis conducted by measuring nitrogen multilayer adsorption as a function of relative pressure using surface area analyzer. It provides precise specific surface area analysis of material tested. The technique used can determine the total specific surface area in $cm^2/g$ which later, are essential for the study of the effects of surface porosity and particle size in many application. Physical adsorption (physisorption) of gas on the surface of hydrotalcite were used to determine the specific surface area of hydrotalcite. This is done by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Besides, it must be noted that relatively weak forces (Van der Waals forces) between the adsorbate gas molecules and the adsorbent surface area of the test powder were affecting the physisorption mechanism. The BET surface area of the hydrotalcite was determined by using equation (7):

$$S_T = \frac{X_m L_{av} A_m}{M_V} \tag{7}$$

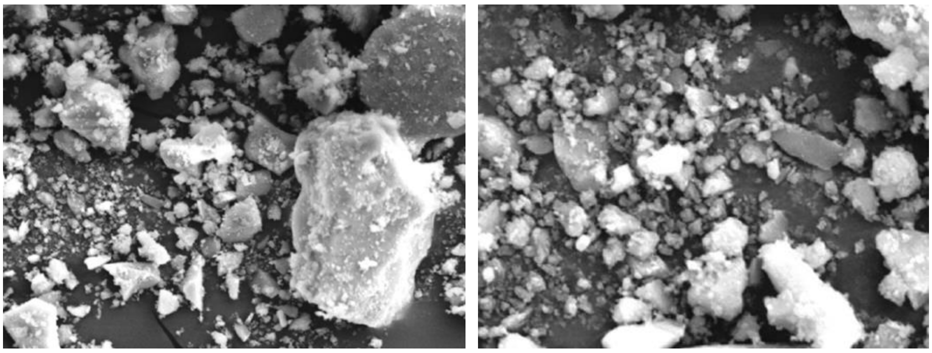
where $S_T$ is the total surface area of the catalysts, $X_m$ is the monolayer capacity, $L_{av}$ is the Avogadro's number, $A_m$ is the cross sectional area of the adsorbate, and $M_V$ is the molar volume.

Table 4.1: Surface area and pore volume of Mg-Al Hydrotalcite

| Hydrotalcite | | Surface Area ( $m^2/g$) | Pore Volume ($cm^3/g$) |
|---|---|---|---|
| Mg-Al | Before Impregnation | 97.0671 | 0.39979 |
| | After impregnation | 70.018 | 0.27306 |
| Li-Al | Before Impregnation | 88.5213 | 0.41057 |
| | After impregnation | 73.2149 | 0.31216 |

### 4.1.2 Scanning Electron Microscopy (SEM) Analysis

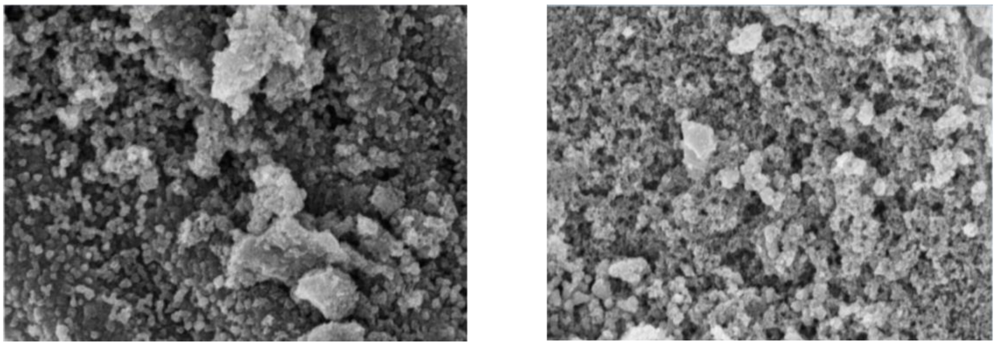
Scanning electron microscopy (SEM) images represent morphology of the hydrotalcite and were recorded on a Philips XL30/FEI ESEM operating at an accelerating voltage from 5 to 30kv. The samples are taken at 5000x magnification.



(a) (b)

FIGURE 4.2 SEM images of Li-Al Hydrotalcite before impregnation (left) and after impregnation (right) at 5000x magnification

Figure below shows the surface morphologies of Mg-Al hydrotalcite before (left) and after (right) doped with Palladium with 50.00 kx magnification.



(a) (b)

FIGURE 4.3 FESEM images of Mg-Al Hydrotalcite before (a) and after (b) impregnation with Pd

The hydrogen adsorption studies are currently done using the synthesized Mg-Al and Li-Al Hydrotalcite with the flow of 10% Hydrogen gas and 90% nitogen gas. After the hydrogen adsorption study is conducted, all the data are used to construct breakthrough curve graphs.

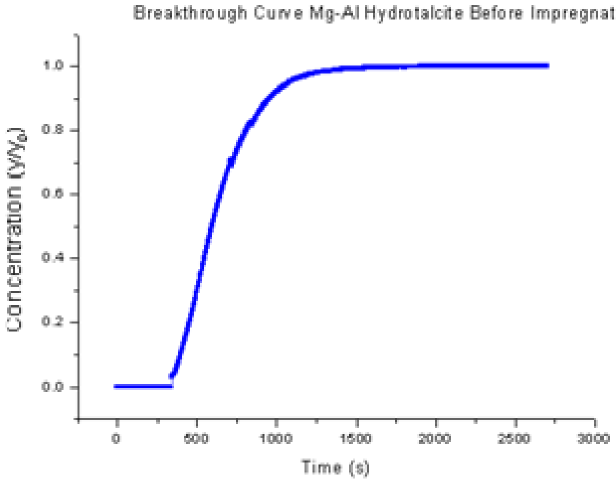


Figure 4.4 Breakthrough curve of Mg-Al Hydrotalcite Before Impregnation

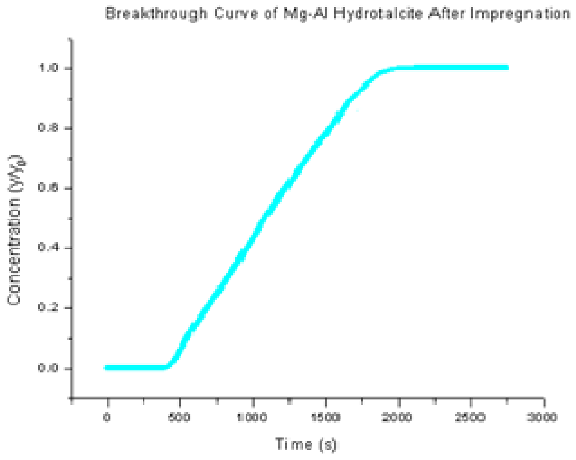


Figure 4.5 Breakthrough curve of Mg-Al Hydrotalcite After Impregnation

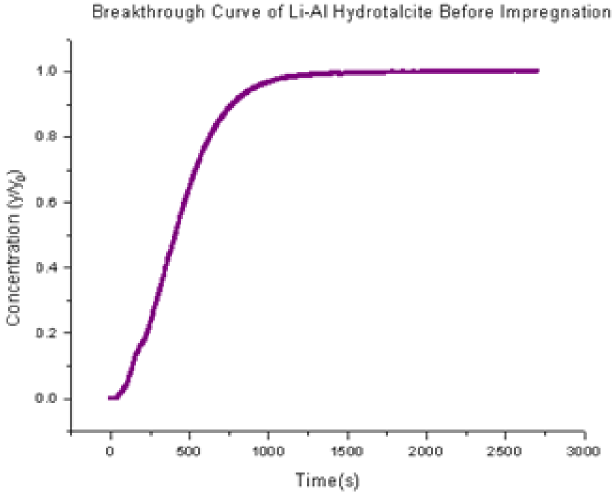


Figure 4.6 Breakthrough curve of Li-Al Hydrotalcite Before Impregnation

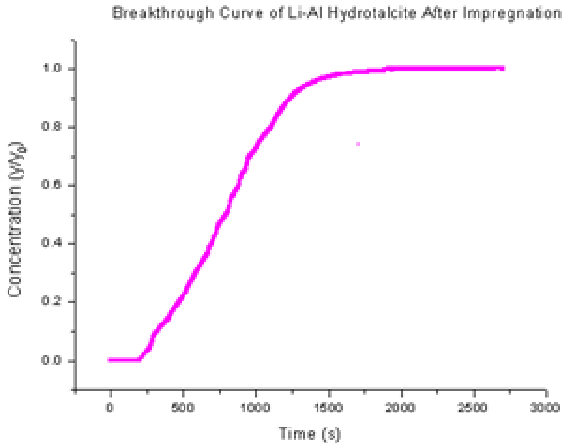


Figure 4.7 Breakthrough curve of Li-Al Hydrotalcite After Impregnation

Based on figure 4.1, the graph of hydrogen adsorption was plotted in order observe which hydrotalcite gives the higher reading of hydrogen adsorption capacity. The mass of the adsorption and weight percentage of the hydrogen adsorption can be calculated from the adsorption breakthrough curve and equations proposed by Rodriques et. al. (2007) as shown below:

$$\frac{\mathrm{y}}{y_0} = \frac{\mathrm{t}}{(\mathrm{t} + \mathrm{A.\,e}^{-\mathrm{B.t}})}$$

$$M_{ads} = \frac{Q_T\,(MW)}{(RT/P_A)}\left[\Delta t - \int_0^t \left(\frac{\mathrm{y}}{y_0}\right) dt\right] \qquad (8)$$

$$W = \frac{M_{ads}}{M_{bed}}$$

Where,

Therefore,

t = total adsorption time

y = initial concentration

$y_o$ = final concentrarion

$M_{ads}$ = adsorbed mass

$Q_t$ = gas flow

$P_A$ = partial pressure

$M_{bed}$ = mass of bed = 0.5g

Table 4.2: Hydrogen Adsorption of Hydrotalcites

| Sample | Adsorbed Mass (g) | Hydrogen Adsorption (wt%) |
|---|---|---|
| Mg-Al Before Impregnation | 0.02525 | 2.52593 |
| Mg-Al After Impregnation | 0.02997 | 2.99976 |
| Li-Al Before Impregnation | 0.02362 | 2.36285 |
| Li-Al After Impregnation | 0.02653 | 2.65310 |

Based on the figure above, the synthesized Mg-Al hydrotalcite has the maximum hydrogen adsorption uptake which is almost 3.0 wt% after impregnation of Pd compared to Li-Al hydrotalcite which gives the highest hydrogen uptake at about 2.65 wt% only after impregnation of Pd. Besides, the impregnation of 1wt% Pd into the synthesized increased the hydrogen adsorption capacity of each set of hydrotalcite. Compared to the value of hydrogen storage target by DOE at 5.5 wt%, the synthesized hydrotalcite were not yet satisfying the criteria. This may due to the limitation if few criterias such as the ratio of mixing the materials is not at its best value, or the amount of Palladium doped is insufficient in term of concentration. However, for future research, this limitation can be altered by increase the ratio of mixing and try doping the Palladium with different concentration.

# CHAPTER 5

# CONCLUSION AND RECOMMENDATION

The purpose of this research is mainly to synthesis Mg-Al and Li-Al hydrotalcites and then sent for characterization study by analytical techniques such as Brunauer Emmette Teller (BET) to find the pore size distribution and Field emission scanning electron microscopy (FESEM) to determine the surface morphology. Besides that, the hydrogen adsorption study will also be carried out by fixed bed reactor. The breakthrough curve for all the samples were analyzed and proves that hydrogen adsorption on impregnated Mg-Al and Li-Al hydrotalcite adsorbs 3.0 wt% and 2.65 wt% hydrogen, which is higher than Mg-Al and Li-Al hydrotalcite with less adsorption capacity of 2.53 wt% and 2.36 wt%. As a conclusion, this research has reached the objectives in term of synthesizing and analysis of hydrogen adsorption on modified adsorbents which are Mg-Al and Li-Al. In addition, since the hydrogen adsorption capacity did not satisfy DOE’s target of 5.5 wt% hydrogen adsorption, some recommendation can be done for future research as betterment of this project. The recommendation would be as follows:

a) To perform the hydrogen adsorption with different pairing of metal oxide.
b) To add more testing on the synthesized hydrotalcites using XRD to identify chemical composition and amorphous of materials.
c) To use the combination of Mg-Al-Li as new hydrotalcite.
d) To use hydrotalcite with different ratio combination.
e) To impregnate the synthesized hydrotalcite with Palladium in different weight percentage, wt%.

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