HYDROGEN STORAGE CHARACTERIZATION OF HYDROTALCITE-DERIVED REDUCED MIXED OXIDES

By

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FINAL PROJECT REPORT

Submitted to the Chemical Engineering Programme
in Partial Fulfillment of the Requirements
for the Degree
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved:

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Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK

January 2010

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.

Ernie Nurazera Bt Zharani

ABSTRACT

Hydrotalcites compound have received much attention and view of their potential applications as adsorbents, as anion exchangers, in nucleophilic halide exchanger and most importantly as catalyst support. The synthesis and characterization of hydrotalcite-like compound (HTLcs) for hydrogen storage purposes is described. The HTLcs is synthesized by using Magnesium Nitrate Hexahydrate and Aluminium Nitrate Nanohydrate as the starting material by coprecipitation with sodium carbonate. The characterization analysis on the HTLcs synthesized is carried out by using Powder X-ray Diffraction (XRD), and Fourier Transform Infrared Spectroscopy. This study also focuses on the effect of thermal treatment on HTLcs during calcinations process which formed a mixed oxides compound. After that, the adsorption/desorption behavior study of H_2 on HTLcs is conducted by using Temperature programmed reduction (TPR)/Temperature Programmed Desorption (TPD).According to the FTIR analysis before and after adsorption, it was found that there is a significant amount of H_2 adsorbed after the mixed oxides reduced under hydrogen flow for a period of time. This outcome also supported by the H_2 consumption curve obtained in TPR analysis where it has shown that H_2 adsorption occur on metal formed after an amount of reducible mixed oxides completely reduced. Furthermore, during TPD analysis, it was found that small amount of H_2 desorbed with low rate of adsorption.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my gratitude to AP Dr Ye Lwin, my supervisor for Final Year Project He had been very supportive during the entire of the project period. He spent so much time and energy to guide me throughout these two semesters despite his other commitments and packed schedule as lecturer in UTP. Under his constant supervision, I managed to start this project with a proper planning and proceed until completion according to the timeframe scheduled.

I would like to acknowledge few of our lecturers namely Dr Chong, for her constant supports in helping me directly or indirectly throughout progression to complete this project. She had showed her concerns by providing guidance to me on the work concept of one of the device I used during the project, which provided me with relevant information to progress further until the completion.

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LIST OF ABBREVIATIONS

HTLcs : Hydrotalcite-like compound
H_2 : Hydrogen
CO2 : Carbon Dioxides
TPR/TPD : Temperature Programmed Reduction/Adsorption
FTIR : Fourier Transform Infrared Spectrometry
XRD : X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Energy is a requirement for any civilization, whether from wood, fossil fuels, nuclear or renewable sources (solar, wind and tidal) .However, due to increasing energy demand, there are significant concerns about the rising level of CO_2 emissions and the impact to our environment. A potential solution is to develop a low-carbon future, where fossil fuel use is reduced, replacing it with zero-carbon energy sources such as Hydrogen fuel cells which have a higher energy density than current battery technologies. The chemical energy per mass of hydrogen (142 MJ kg–1) is at least three times larger than that of other chemical fuels (for example, the equivalent value for liquid hydrocarbons is 47 MJ kg–1).Hydrogen fuel cells with certain mass of hydrogen have a range of potential applications with certain range of power requirement. Over the past decade, there have been many significant advances in the storage of hydrogen in porous media, complex hydrides and liquid hydrides, and in catalysts to accelerate the cycling kinetics for these materials. The conventional hydrogen storage technologies are compressed gas and liquid storage. In compressed gas, the solution currently uses presurised cylinders to store H_2.The cylinders used usually have a very high working pressure of 350-700 bar. Compressed gas storage is relatively cheap solution especially when lower pressure is suffice, but for portable application, compressed gas storage is too bulky. Liquid hydrogen storage or Cryogenic storage is another mature technology, but very low temperatures are needed to liquefy hydrogen making it not suitable and convenient for certain application.

Currently, metal hydrides are important energy store materials where it is likely favored application with weight and space issues provided by the hydrogen storage method discussed before. Hydrogen reacts with many metal elements and alloys, providing a range of metal hydrides to choose for hydrogen storage and the most commercial ones are magnesium hydrides, MgH_2. Magnesium in metal hydride has attracted substantial interest for hydrogen storage applications because of its low density and reactivity.

This study intends to investigate the potential of hydrotalcite-like compound as hydrogen storage material. Hydrotalcite-like compound used in this study is derived from Magnesium-Aluminium type based on the magnesium hydrides concept. Hydrotalcite-like compound having wide range of application including as an adsorbent to gasses such as carbon dioxide is expected to be a good hydrogen adsorbent due to its Layered Double Hydroxide (LDH) structure and other characteristic that will further elaborate throughout this study.

1.2 Problem Statement

The existence methods to store hydrogen currently are using metal hydrial such as MgH2 and also metal alloy's, prepared by conventional mechanical method. Due to that, another approach of soft method in preparing Hydrogen storage material has been purposed by using hydrotalcite-derived compound (HTLcs) of metal oxides which have also been used to adsorb other gasses such as carbon dioxide.[7]

1.3 Objectives

- This study aims to prepare hydrogen storage material by synthesize a composite consist of hydrotalcite-derived of Mg-Al mixed oxides.
- Next, the study of characterization of HTLcs is carried out to determine the structure of the synthesized material.
- Furthermore, the study also intends to investigate the hydrogen storage capabilities of synthesized material in terms of capacity and rate of adsorption/desorption

1.4 Scope of Study

- The hydrotalcite-derived compound of Mg-Al mixed oxides is synthesized using co precipitation method. The molar ratio of M^{2+}/M^{3+} is set at low value of 1.5 , 2.5 and 3.5.
- The structural characteristic of the hydrotalcite compound synthesized is studied by using X-ray Diffraction and FTIR analysis.
- The study of the performance of synthesized material in hydrogen adsorption/desorption is carried out in terms of the kinetics and equilibrium
- The adsorption and desorption performance are studied by using Temperature Programmed Desorption (TPD)/ Temperature Programmed Reduction (TPR)

1.5 The Feasibility and Relevancy of Project

- Another alternatives for chemically bound hydrogen storage technology that is comparable to the current conventional method, Metal Hydride.

- Gain more information and understand the characteristics of Hydrotalcite compound.

- Estimate the hydrogen loading capabilities of Hydrotalcite compound during adsorption process in order to predict the range of application

- Overcome current method, Metal Hydride challenges in terms of adsorption and desorption kinetics by introducing hydrotalcite reduced metal oxides element.

- Establish a new application of Hydrotalcite as an adsorbent. Prior to this research, Hydrotalcite has been used commonly to adsorb Carbon Dioxide.

Based on objectives and scope of study, the research project is feasible enough within the scope and time given (12months) as long as the project sticks to the Schedule and Planning (Gantt Chart), time period predicted for each activity.

CHAPTER 2
LITERATURE REVIEWS

2.1 Hydrotalcite-like Compound

Hydrotalcite-like compound (HTLcs) are bi-dimensional basic clay which occurs naturally or usually synthesized for research purposes [1] HTLcs are a class of layered compounds known as layered double hydroxides (LDHs), consisting of positively charged brucite (MgOH)-like layers and an interlayer space containing charged compensating anions and water molecules [1].

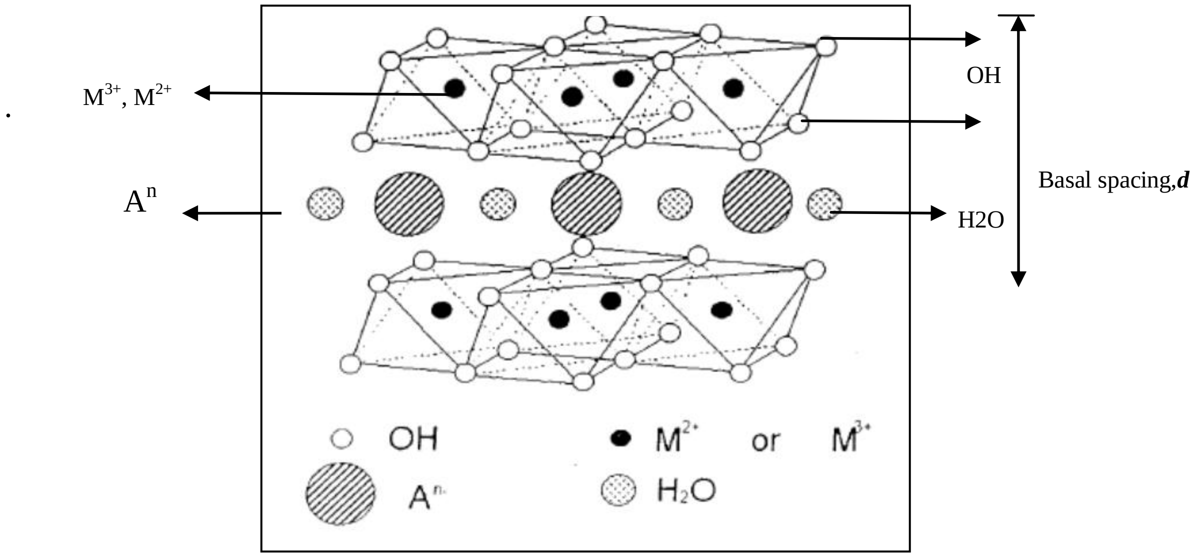


Figure 1 The general structure of hydrotalcite-like [1]

The metal cations (M^{3+}, M^{2+}) occupy the centers' of the octahedral whose vertices contain hydroxide ions(OH). The general formula for HTLcs is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}$ $A^{n-}_{\ x/n}$. yH_2O where M^{2+} are divalent cations (e.g Mg^{2+}, Zn^{2+}, Ni^{2+},etc) and M^{3+} are trivalent cations (e.g AL3+, Cr3+,etc).Where else, A^{n-} is a non-framework charge anions (e.g CO^{2-}_3, Cl^- , SO^{2-}_4, etc). [1] The value of x is the molar ratio of $M^{3+}/ (M^{3+}+ M^{2+})$ which normally varies between 0.17- 0.33 and usually x=0.25[1][5] .

The enthalpies of formation from the elements of a series of Mg/Al – CO_3 HTLcs with different Mg/Al ratios have been measured. It was found that the HTLcs compound is more stable by 10-20 kJmol-1 compared with a mixture of $Mg(OH)_2$, $Al(OH)_3$, $MgCO_3$ and water. [16].

Main Chemical & Physical Properties of Three Commercial Hydrotalcite-like Compound from CONDEA[9]

Property	PURAL MG30	PURAL MG50	PURAL MG70
chemical description	aluminum magnesium hydroxide	aluminum magnesium hydroxide	aluminum magnesium hydroxide
Form	powder	powder	Powder
Al2O3:MgO (%)	70:30:00	50:50:00	30:70
L.O.I.a (%)	35	40	45
Thermal stability Surface area (m2/g)			
3h/550 °C	271	228	201
3h/950 °C	110	90	120
3h/1150 °C	30	25	65
pore volume (mL/g)	0.55	0.45	0.35
loose bulk density (g/mL)	0.44	0.58	0.59
particle size < 25 ím (%)	27.1	32.9	59.2
particle size < 45 ím (%)	49.7	61.5	92.9
particle size < 95 ím (%)	91.4	97.1	100
Al2O3 (Mg-dop, 100%) (%)	70.9	49.3	29.2
MgO (Mg-dop, 100%) (%)	29.1	50.7	70.8

Hydrotalcite-like compound or Layered Double Hydroxide compound possess high versatility, tailored properties and low cost, which make it possible to produce materials designed to fulfill specific requirements and applications including adsorption.[17] In this study, Mg-Al Hydrotalcite-like compound with different molar ratios (Mg^{2+}/ Al^{3+}) will be used.

2.2 Preparation of Hydrotlcite-like compound

There are few numbers of synthesis techniques have been successfully carried out in the preparation of HTLcs. The commonly used in the industry is simple coprecipitation method. It has been reported that most of the HTLcs preparation for Carbon Dioxide adsorption process are based on coprecipitation. [1][2]. In the coprecipitation method, aqueous solutions of M^{2+} (or mixtures of M^{2+} species) and M^{3+} (or mixtures) containing the anion that is to be incorporated into the HTLcs are used as **precursor**.[18]. A preparation method of well-crystalline Cu-Al hydrotalcite-like compound by using copper nitrate trihydrate (M^{2+}) and aluminium nitrate nonahydrate(M^{3+}) is described in detail in [3]. This aqueous solution of cations is then mixed with a solution acted out as **precipitant** containing the desired interlayer anions.

To ensure there are no anions from the metal salts incorporated by competing reactions with our desired interlayer anions, the anions that is to be introduced should have high affinity for the HTLcs and be present in excess(eg CO_3^{2-})$^{.}$ The metal salts usually being selected are nitrate and chloride based because of the low selectivity of HTLcs towards this anions.

There are two types of coprecipitation method generally [18]:

2.2.1 Precipitation at Low Supersaturation

This technique is carried out by adding slowly the divalent-trivalent metal salts mixture with chosen molar ratio into a reactor which containing an aqueous solution of desired interlayer anions in our structure. To maintain/control the pH, a second solution of alkali is added simultaneously into the reactor.

Advantages: (1) Precise control of pH, thus allows control of the molar ratio (M^{2+}/M^{3+})

(2) Higher crystallinity because rate of crystal growth is higher than rate of nucleation

2.2.2 Precicpitation at High Supersaturation

This technique involves the addition of a mixed M^{2+}/M^{3+} salt solution to an alkaline solution containing the desired interlayer anion. Many types of hydrotalcite mostly for adsorption purposes are prepared by this method including [1][2][4].

Disadvantages: (1) Changes in pH, leads to impurity with undesired molar ratio. Thermal treatment performed to this solution may help to increase the crystallinity.

(2) Higher number of crystallization nuclei compared to crystal growth

Following coprecipitation method usually will be the **thermal treatment** which aims to increase crystallinity or badly crystallized material.[10] Other alternatives in preparing HTLcs includes Ion Exchange method, Rehydration Using Structural Memory Effect, Hydrothermal Methods and many more. [18]

2.3 Characterization of Hydrotalcite Compound

2.3.1 X-Ray Diffraction Analysis

The results of hydrotalcite diffraction pattern generally can be refer to Figure 2 below [10] :

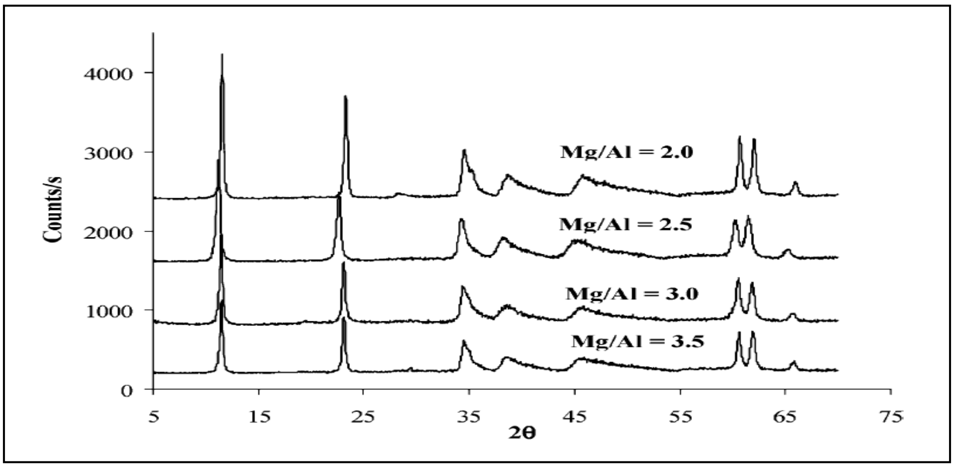
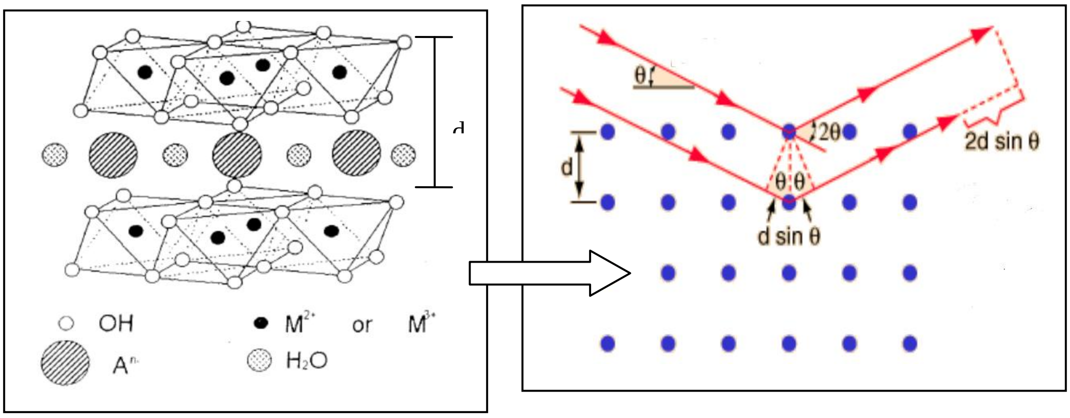


Figure 2 Powder X-ray diffraction patterns of hydrotalcite of varying Mg/Al molar ratio [10]

This pattern can be used as a reference to identify the presence of HTLcs structure. HTLcs structure in which cationic layers and anionic layers show basal spacing or planes separation d=7.6-7.8 Å in powder X-ray diffraction (XRD) patterns when small inorganic anions are intercalated.[4] .It has also been reported Mg-Al Hydrotalcite with different anions species having basal spacing , in the range of d= 7.6-8.9 Å [1].In figure 2, the presence of CO_3^{2-} anions in the interlayer is confirmed by the characteristic basal spacing d003=7.65 Å [10]. The calculation of basal spacing can be carry out by using Bragg's Law.

$$d = \lambda / 2 \sin O \qquad \textit{with } 10\ \text{Å} = 1 \textit{ nanometer}$$



Sited from: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html

Figure 3 The Bragg's Law applied on hydrotalcite crystal

In additional, characterization of HTLcs samples also is done by FTIR analysis which is discussed further in **section 2.3.2**

2.3.2 Fourier Transform Infrared Spectroscopy Analysis (FTIR)

Infrared Spectroscopy is the study of the interaction of infrared light with matter. As what stated in [23], when infrared radiation interacts with matter it can be absorbed, causing chemical bonds in the material to vibrate. Chemical structural fragments within molecules, tend to absorb infrared radiation in the same wave number range regardless of the structure of the rest of the molecules the structural fragments is in.

In this study, FTIR analysis is done before and after the hydrogen adsorption stage. Analysis is done to investigate the hydrogen bonds presence in sample in order to determine whether hydrogen adsorption process occur on sample surface. FTIR analysis is also done characterized the samples prepared to confirm the structure presence.

Below are the FTIR plots measured infrared radiation intensity versus wavenumber that commonly known as an *infrared spectrum* [24] , that can used as a guideline during FTIR analysis in this study

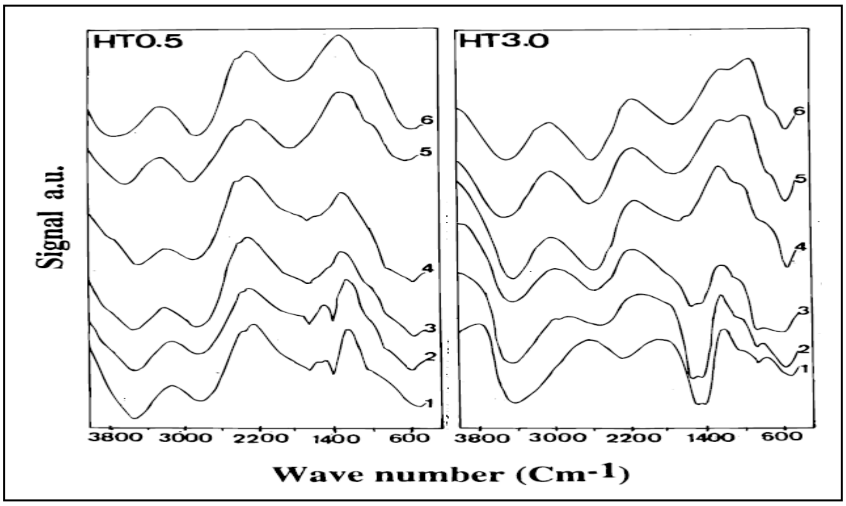


Figure 4 IR Spectra of 0.5 & 3.0 molar ratio calcined at different temperature (1) 333K (2) 473K (3) 673K (4) 873K (5) 1073K & (6) 1273K [24]

Mid –infrared radiation will be defined as lights between 4000-400 cm-1 and the majority of FTIRs operate in this wavenumber range.[23] It is expected the spectrum of noncalcined Hydrotalcite-like compound to rise peaks at wavenumbers = 3500 cm-1, 1640 cm-^{1},1370 cm^{-1}, 950 cm^{-1} and 760 cm^{-1}[10]

2.4 Application of Hydrotalcite-like Compound

It has been reported that HTLcs has been used for adsorption of gasses such as N_2,O_2,CO_2 and H_2 [5].Besides that, HTLcs has been used for other applications such as for propiolactone polymerization , usage in aldol condensation in the gas phase after thermal activation of samples containing first series transition cations in the brucite-like layers, usage in propene oligomerization field and halide exchange reactions using HTLcs[7].

There are few reports proved the multi-application of HTLcs and the most interesting one is as a catalyst. This includes as a catalyst supports, catalyst in Important Organic Reactions and Enviromental catalyst. [17].The recent growth in research in this areamainly comes from the use of Ni containing HTLcs-like materials a catalyst [6] Besides, it is also reported that HTLcs are applied in Ion Exchange and adsorption area, pharmaceutics, biochemistry, Photochemistry and also Electrochemistry.[17]

Recently, a number of researchers have shown that the copper based catalyst of hydrotalcite derived mixed-oxides give highly stable activity for synthesis of higher alcohols and hydrocarbons, water shift reaction, NOx and Sox reduction.[3] Due to these various applications these HTLcs materials are receiving considerable attention from researches in recent years. The usual HTLcs available are Mg-based and Cu-based. Many of their most important applications are due to their permanent anion-exchange and adsorption capacity, the mobility of their interlayer anions and water molecules, their large surface areas and the stability and homogeneity of the materials formed by their thermal decomposition.[8]

The important parameters determining the application of hydrotalcites are degree of crytallinity and textural properties.These properties are influenced by various paramaters such as the nature of the bivalent and trivalent cations anf their ratio, the concentration of metal salt solution and their alkali solution, the reaction pH and many more [10] Limited research as been made on textural properties of hydrotalcite, and one of them is reported in [7] whereas the writer discussed the effect of anions, cations, molar ratio,temperature and cycle number of adsorption.

2.5 Thermal Treatment on Hydrotalcite-like materials

Usually the usage of hydrotalcite as an adsorbent or catalyst require at high temperature condition. It has been reported that a popular method of preparing intercalated products is mixing calcined powder of hydrotalcite with aqueous solution of anions to intercalated.[4] Furthermore, study shows that HTLcs, both as directly prepared or after thermal treatment, are promising materials for a large number of practical applications in catalysis, adsorption, pharmaceutics, photochemistry, electrochemistry and other areas.[17] Plus, this study will be conducted at very high temperature for adsorption of H_2 right after its production. Thus, its vital and interesting to analyze changes take place in the structure of the solid as the temperature increase.[4][6].Under hydrothermal treatment, a change in the Mg-Al ratio is observed, together with a more ordered structure of the species existing in the interlayer space. Calcination at increasing temperature leads to decomposition of this compound, with the final formation of MgO and $MgAl_2O_4$ mixed oxides.[6] It has been stated that [6], thermal decomposition takes place in three steps : (1)correspond to elimination of water molecules from the interlayer space (2) tentatively correspond to elimination of carbonate anions (3) due to elimination of hydroxyl groups from the brucite layers[6]. From recently analysis conducted, removal loose bound water molecules from hydrotalcite pore occurred at around 220˚C , the removal OH^- groups which is mostly bonded to Mg^{2+} occurred at around 330-380˚C and the removal of CO_3^{2-} at the temperature around 400-550˚C. After the removal of carbonate anions, the material become amourphous metastable mixed solids oxides.[10] It has been claimed that **mixed metal oxides** obtained bt controlled thermal decomposition of HTLcs have large specific surface area (100 – 300 m2/g) , basic properties, a homogeneous and thermally stable dispersion of the metal ion components, synergic effects between the elements, and the possibility of sturcture reconstruction under mild condition.[17]

The XRD pattern of hydrotalcite upon calcination which formed mixed-oxides generally can be referred to figure 5 below [6]:

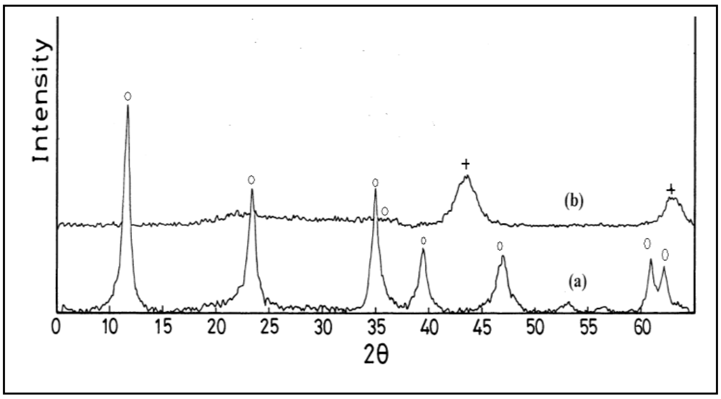


Figure 5 XRD profile of hydrotalcite sample at (a) 400 K and (b) at 773K with, (O)HTLcs and (+)MgO

As what have been discussed in 2.4, thermal treatment on sample leads to removal of certain components from the structures which are water molecules, interlayer anions and hydroxyl groups from the brucite-like layers. This will lead to the formation of new crystalline phases.[6][10] From Figure 4, it is expected that Mg oxides are formed after calcination at 773K .

2.6 Metal Hydride

Despite the advantages of hydrogen as energy source, it is difficult to store that its use as a fuel has been limited. The relatively advanced storage methods such as high-pressure gas or liquid cannot fulfill future storage goals. Chemically or physically combined storage of hydrogen in other materials has potential advantages over other storage methods [14]

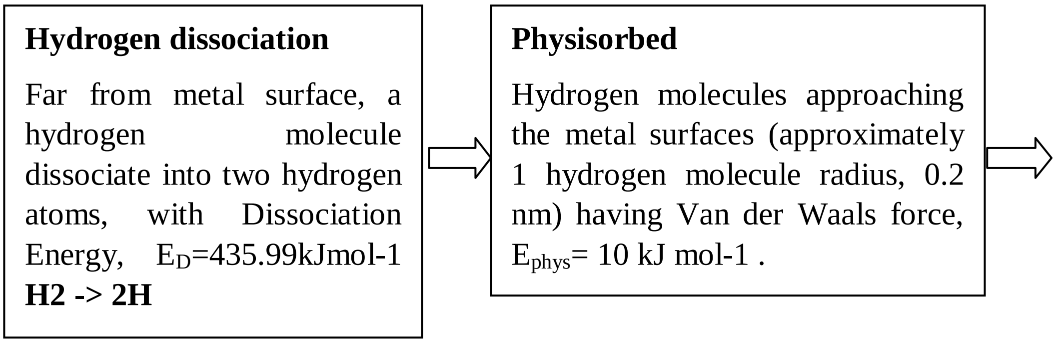
One method that has been rigorously studied involves the use of metals and alloys, where the solids are reacted with hydrogen to form metal hydrides (e.g MgH_2)[15].Qualities that make these alloys useful include their ability to absorb and release large amounts of hydrogen gas many times without deteriorating, and their selectivity (they absorb only hydrogen)[8].

Hydrogen reacts at elevated temperature with many transition metals and their alloys to form hydrides [20] From what reported in [19] molecular hydrogen is dissociated at the surface before absorption; two H atoms recombine to H2 in the desorption process. Hydrogen is located in the form of atoms, never molecules, on interstitial sites of the host metal lattice. The formation of magnesium hydride, for instance, by

$$\mathbf{Mg(s) + H_2\,(g) \qquad MgH_2\,(g)}$$

is an exothermic reaction and hydrogen desorption from the hydrides can be achieved endothermally under appropriate thermodynamic conditions.[22]

The process of physisorbed and chemisorbed of hydrogen on the metallic compound are described as below: [20]



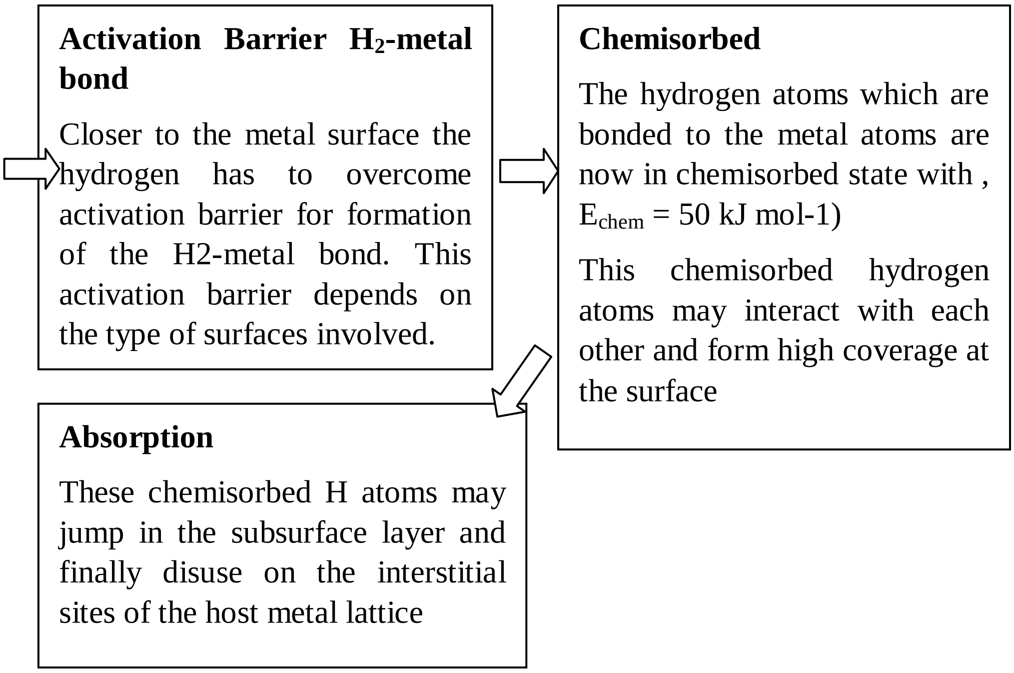
Hydrogen dissociation

Far from metal surface, a hydrogen molecule dissociate into two hydrogen atoms, with Dissociation Energy, E_D=435.99kJmol-1

H2 -> 2H

Physisorbed

Hydrogen molecules approaching the metal surfaces (approximately 1 hydrogen molecule radius, 0.2 nm) having Van der Waals force, E_{phys}= 10 kJ mol-1 .



Activation Barrier H_2-metal bond

Closer to the metal surface the hydrogen has to overcome activation barrier for formation of the H2-metal bond. This activation barrier depends on the type of surfaces involved.

Chemisorbed

The hydrogen atoms which are bonded to the metal atoms are now in chemisorbed state with , E_{chem} = 50 kJ mol-1)

This chemisorbed hydrogen atoms may interact with each other and form high coverage at the surface

Absorption

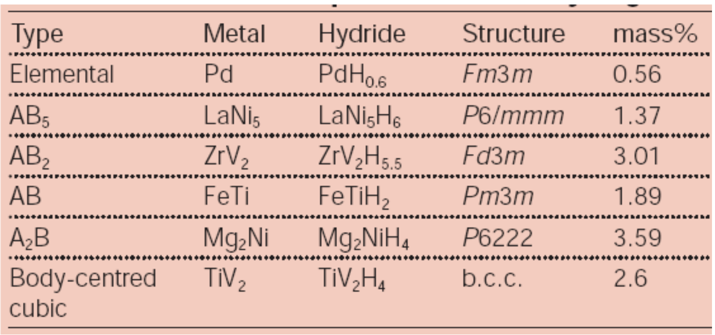
These chemisorbed H atoms may jump in the subsurface layer and finally disuse on the interstitial sites of the host metal lattice

For this hydrogen storage study using HTLcs, we aim for the process to be up until chemisorbed process as it will be easier for the adsorbed hydrogens to be desorb for usage purposes.

Recently, there is considerable research on magnesium and its alloys for on-board hydrogen storage due to Mg-based hydrides possess good-quality functional properties, such as heat-resistance, vibration absorbing, reversibility and recyclability (e.g Mg-10 wt% Al_2O_3) [14] A group og Mg-based hydrides stand as promising candidate for competitive hydrogen storage with reversible hydrogen capacity up to 7.6 wt% H_2 for on-board applications [14] but they are not reversible within the required range of temperature and pressure. The formation of MgH_2 from bulk Mg and gaseous hydrogen is extremely slow, it is reported at 1 bar requires not room temperature but more than 300 C.[19]

Alloying Mg before the hydride formation is one of the approach. The alloys such as Mg_2Cu, $Mg_{17}La_2$ and MgAl, proved to have the ability to form hydrides: Mg_2Ni forms a ternary complex hydride Mg_2NiH_4, which still contains 3.6 mass% hydrogen.[19] In the systems studied so far (Mg–Cu, Mg–Al), the temperature for 1 bar equilibrium pressure could be lowered the reversible temperature. It is not a large improvement, and it has the penalty that the mass density is thereby reduced as well.

Typical Intermetallic compounds and their hydrogen-storage properties [19]



Type	Metal	Hydride	Structure	mass%
Elemental	Pd	$PdH_{0.6}$	*Fm3m*	0.56
AB_5	$LaNi_5$	$LaNi_5H_6$	*P6/mmm*	1.37
AB_2	ZrV_2	$ZrV_2H_{5.5}$	*Fd3m*	3.01
AB	FeTi	$FeTiH_2$	*Pm3m*	1.89
A_2B	Mg_2Ni	Mg_2NiH_4	P6222	3.59
Body-centred cubic	TiV_2	TiV_2H_4	b.c.c.	2.6

For gaseous hydrogen fuel tanks to be used in vehicles, however, we need some 4–5 mass% (indeed, 6.5 mass% and 62 kg H2 m–3 are the targets of the US Department of Energy[19]). Batteries are the most common application for hydrogen storage alloys. These hydride-forming alloys are the M in Ni-MH (nickel-metal hydride) batteries, the negative electrode in the battery cell.[8]

Based on this literature review gathered, it is relevance to chemically synthesize hydrotalcite-like compound of Mg-Al, and subsequently to Mg-based metal hydrides for hydrogen storage purposes in this project.

2.7 Hydrogen Storage in Metal Oxides

As what been stated before, the conventional method in hydrogen storage is by mechanically adsorption in metal hydride form[8].In case of magnesium hydride, MgH_2 for instance, the theoretical hydrogen storage capacity is rather interesting, but the practical use of this system is limited by the slow rate of adsorption-desorption phenomena. For this reason, a great deal of work is devoted to increase the kinetics performances of the system and one of them is by using metal oxides[11] Recently by carrying out different preparation procedures, it has been shown that $CeNi_5$ oxide, reduced under H_2 could store as much hydrogen as $CeNi_5$ alloy [12]. Furthermore, few studies has been conducted to investigate the interaction of hydrogen with a series of mixed oxides.[11][12][13]. It has been reported that after treatment under H_2 at 473K or 573 K, CeMxOy mixed oxides contain anionic vacancies produced by the elimination of H_20[12] Based on thermogravimetric profile of CeZr0.5Ni3O*y* mixed oxides treated under H_2 , it can be observed that the weight loss up to ~120° , corresponds to the elimination of phisisorbed water, while for higher temperature more distict domain is observed at about the temperature reduction CeZr0.5Ni3O*y* with the creation of anionic vancancies by water elimination.[14]

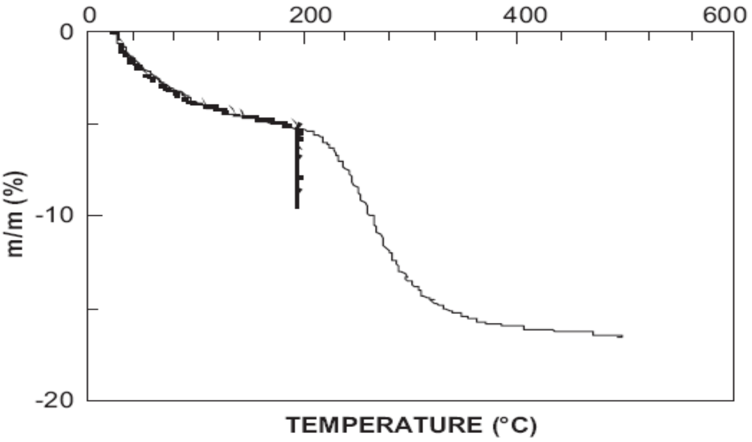


Figure 6 Thermogravimetric profiles of the CeZr0.5Ni3O*y* compound treated

From experiment conducted, it has been found that when NiO metal oxides been treated under H_2 flow for temperature above 150˚C reduction process observed, where NiO becomes metallic Ni , with the creation of anionic vacancies by elimination of water. [13]

$Ni^{2+} + O^{2-} + H_2 \longrightarrow Ni^0 + H_2O + \square$ (with□ : anionic

The anionic vacancy, created in the bulk and at the surface of the solid, by the loss of water is able to receive hydrogen in hydride form according to heterolytic dissociation. [14].

It has also been proposed that, besides Equation (1), the anionic vacancies if filled with hydride species by heterolytic splitting can be summarized as. [13]

$O^{2-} \quad M^{N+} \quad \square + H_2 \longrightarrow OH^- \quad M^{N+} \quad H^-$ (with□ : anionic

It is already reported that metallic Nickel is able to adsorp hydrogen to formed metal hydride which will be elaborated more in section 2.6 [12]

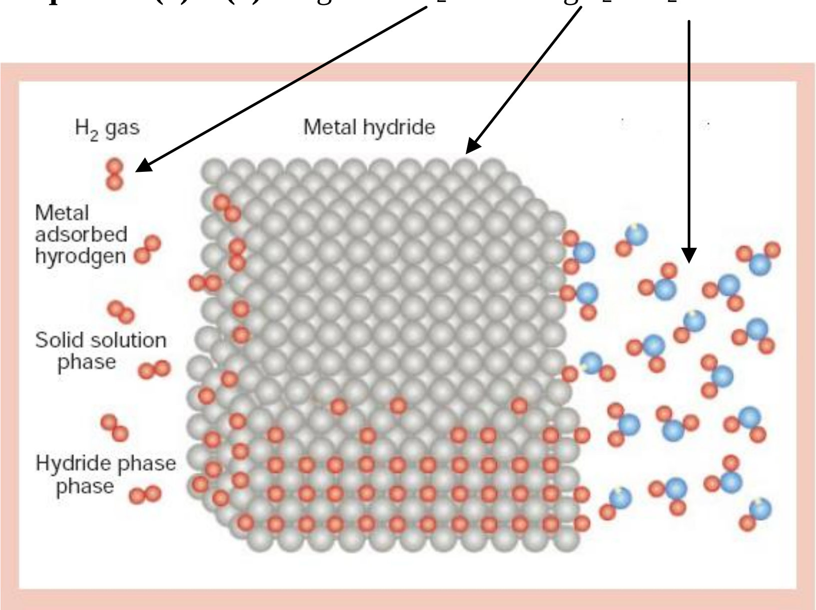
Thus it is expected the behavior of Mg-Al oxides will be similar to what have been discussed while undergo reduction process and hydrogen adsorption. The overall equation based on concepts in section 2.5, 2.6 & 2.7 for HTLcs compound this project is :

(1) $2 Mg + O_2 \longrightarrow 2 MgO$ (During Calcination, Section 2.5)

(2) $MgO + H_2 \longrightarrow Mg + H_2O$ (During Reduction in TPR analysis)

(3) $Mg + H_2 \longrightarrow MgH_2$ (During Adsorption in TPR analysis)

Overall equation (2) + (3) : $MgO + 2\,H_2 \longrightarrow MgH_2 + H_2O$



2.8 Carbon Dioxide Adsorption by using Hydrotalcite-like compound(HTLcs)

The combustion of fossil fuels, such as coal or natural gas, releases large volumes of carbon dioxides to the environment. A number of techniques can be used for separation of carbon dioxide from the fuel gas stream. Recently, it was reported that HTLcs could well meet all the CO2 adsorbent criteria and such compounds are one of the most promising adsorbent for reaction process for hydrogen production[7].The adsorbent must have (1) high selectivity and adsorption capacity for carbon dioxide, (2) satisfactory adsorption/desorption kinetics, (3) moderate heat of adsorption, (4) stable adsorption capacity for repeated cycles.[2] Based on literature reviews, extensive research on equilibrium and kinetics of carbon dioxide adsorption of HTLcs have been conducted.[7][1][6][2].The effects of composition,types of anions and temperature has been investigate as well.[9] It has been known that the acidic properties of CO_2 and H_2 makes the study on hydrogen adsorption by HTLcs is comparable and relevance with the current conventional CO_2 adsorption by HTLcs.

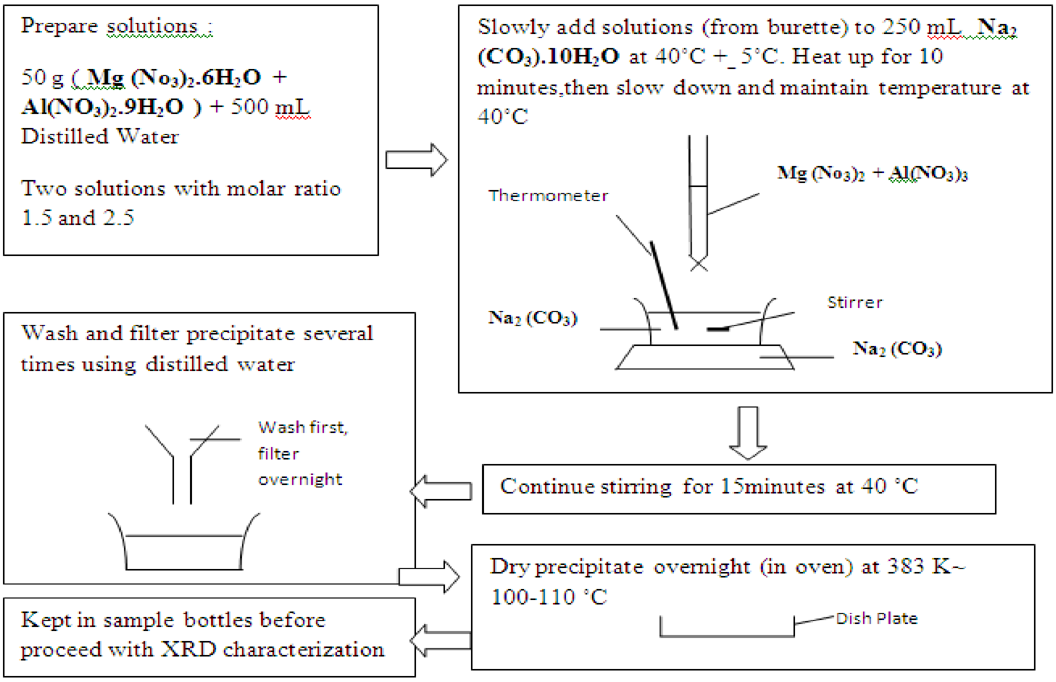
CHAPTER 3

METHODOLOGY

3.1 Sample Preparation

The Mg/Al Hydrotalcite-derived compound is prepared by co precipitation techniques. In preparation stage, two solutions each containing 50g of Magnesium Nitrate Hexahydrate, **Mg $(No_3)_2.6H_2O$** and Aluminium Nitrate Nanohydrate, **$Al(NO_3)_3.9H_2O$** used as starting materials are mix into 500mL of distilled water.[3] In this experiment, Mg/Al molar ratios suggested in both three solutions are 1.5, 2.5 & 3.5.The proportion of each chemical solution ($MgNO_3$& $AlNO_3$) is calculated according to Appendix I . Each solution is slowly added into 0.5M sodium carbonate hydrate, **Na_2 $(CO_3).10H_2O$.** [3] The resulting precipitates are filtered, washed and dried in a conventional oven [1].

3.1.1 Flow of hydrotalcite synthesis preparation



Prepare solutions :

50 g (**Mg $(No_3)_2.6H_2O$** + **$Al(NO_3)_2.9H_2O$**) + 500 mL Distilled Water

Two solutions with molar ratio 1.5 and 2.5

Slowly add solutions (from burette) to 250 mL **Na_2 $(CO_3).10H_2O$** at 40°C +_ 5°C. Heat up for 10 minutes,then slow down and maintain temperature at 40°C

Continue stirring for 15minutes at 40 °C

Wash and filter precipitate several times using distilled water

Dry precipitate overnight (in oven) at 383 K~ 100-110 °C

Kept in sample bottles before proceed with XRD characterization

3.2 X-ray Diffraction

The presence of Mg-Al HTLcs as the main compound in the dried precipitates was confirmed by Powdered X-ray Diffraction (XRD) pattern analysis [2].The characterization of the HTLcs compound also determines the degrees of crystalline [3].The scans is conducted at room temperature on samples that had not been degassed or heat treated. The resulting patterns are compared to the reference patterns for naturally occurring hydrotalcite mineral [1]. The basal spacing, ***d,*** of cationic layers and anionic interlayers in the hydrotalcite structure can be calculated by using Bragg's Law, based on the resulting diffraction pattern.[4]. Usually samples for XRD characterization required an amount more or less 0.1-0.2 grams and the parameter used is $2\theta = 2° - 70°$. For this project, the XRD test is carried out after synthesis stage

3.3 Calcination

Before the samples undergo hydrogen adsorption/desorption capacity analysis, they undergo calcinations process or thermal treatment at around 500 ˚C for one day in a furnace. Few studies on the effect of thermal treatments on hydrotalcite structure have been carried out and reported.[4][6].

3.4 BET Areas Analysis

The surface area of calcined hydrotalcite before undergo hydrogen adsorption process is to be determined from Nitrogen adsorption isotherm at 77K using Micromeritics,ASAP 2010 USA . [24] The specific surface area of the samples is to be calculated according to the Brunauer, Emmet, Teller (BET) method and the pore size distribution of sample is to be calculated from desorption branch using Barret,Joyner and Helenda method [10]

3.5 Temperature Programmed Reduction (TPR)/ Temperature Programmed Desoprtion (TPD)

The hydrogen adsorption/desorption capacity is measured by using Temperature programmed reduction (TPR) /Temperature Programmed Desorption (TPD)[1].All the analysis using TPR/TPD is monitored by thermal conductivity detector (TCD) in the exhaust of the gas stream. The analysis is divided into two parts:

3.5.1 TPR Analysis first run (1st)

The sample undergoes pre-treatment from room temperature by heating at 10˚C/min up to 600˚C under Hydrogen flow (5% H_2/95% N_2) at 30mL/min.

The process is carried out based on temperature profile Figure 7.After this stage complete, the samples undergo XRD characterization again and FTIR analysis to confirm that reduction process is completed and the structure of the elements/compound presence in the sample is determined.

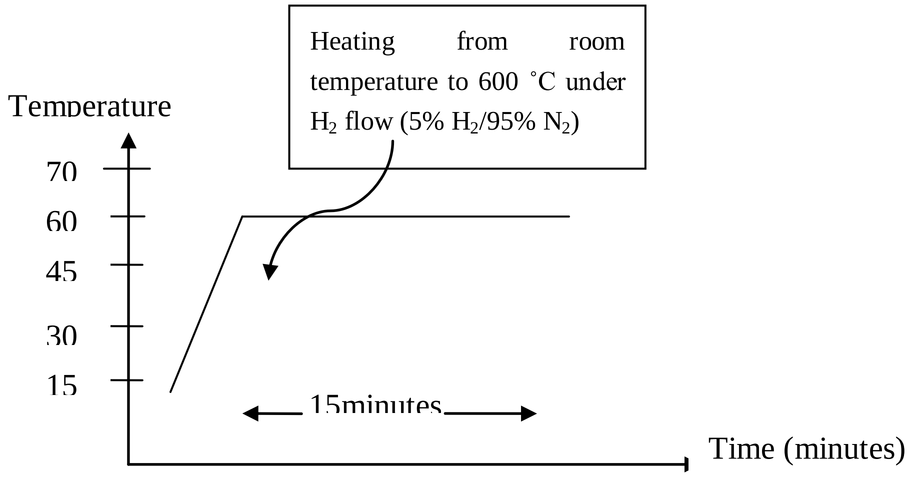


Figure 7 The programmed temperature profile for First run TPR

3.5.2 TPR/TPD analysis second run (2nd run)

The second part of this analysis is carried out based on the temperature profile in Figure 8 .First the sample is pre-heated from room temperature by heating at 10˚C/min up to 600˚C under Hydrogen/Nitrogen (5%H_2/95% N_2) flow at 30 mL/min, and is held at 600˚C for about 15minutes for reduction process to occur (follows temperature profile run 1) After the reduction process completed, the temperature is reduced to room temperature at the rate of 10˚C/min for adsorption process .For desorption purpose, the study is carried out by heating the sample from room temperature in the reserve path under pure nitrogen flow.

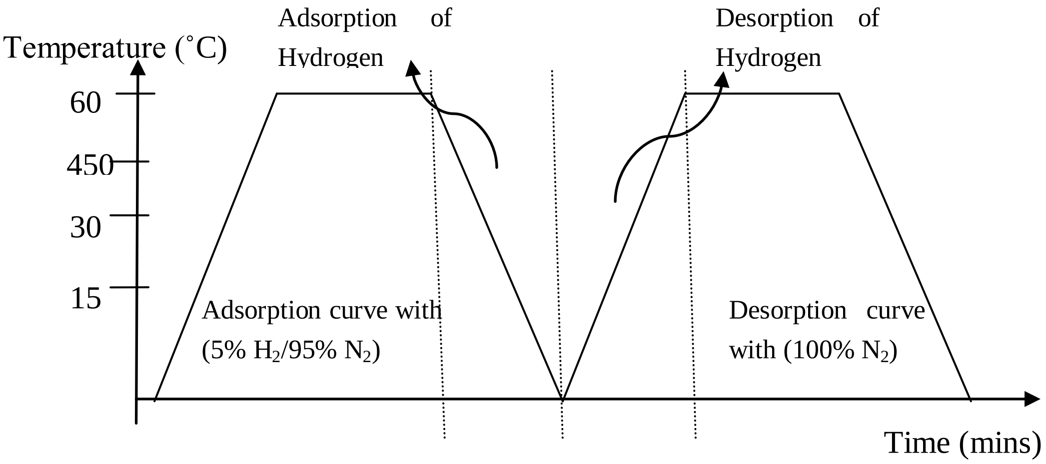


Figure 8 The programmed temperature profile for Second run

3.6 Fourier Transform Infrared Spectroscopy (FTIR)

The FT-Infrared spectra was recorded using a Perkin-Elmer Spectrum GX Fourier transform infrared apecttrophotometer (FT-IR) system in the region 400-4000 cm-1 using KBr pallets as background.[10] for samples at all molar ratio:

1) Before TPR analysis (after calcinations)
2) After First run TPR analysis
3) After Second run TPR analysis

3.7 Thermogravimetric Analyzer (TGA)

Start Experiment Hydrotalcite characterization and to measure the rate of Hydrogen adsorption by the HTLcs is to be carried out using Thermogravimetric Analyzer,TGA using temperature profile below.

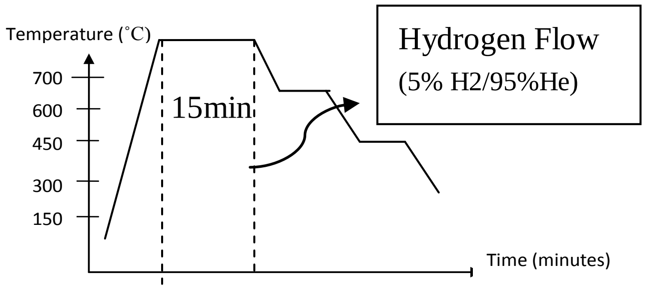


Figure 9 The programmed temperature profile in determination rate of adsorption

First the sample is heated at 10°C/min under Helium flow(30 mL/min), up to 600 °C and left constant for 15 min. Then, the temperature is reduced down to 450 °C at the rate of 15°C/min. Here the Hydrogen flow is introduced and the sample is continuously held at 450°C to reach steady state.

The procedures are then repeated for other holding temperatures 300 °C and 150°C, respectively. Derivative thermal gravity (DTG) curves produced the rates of adsorption on the fresh adsorbent at different temperatures.

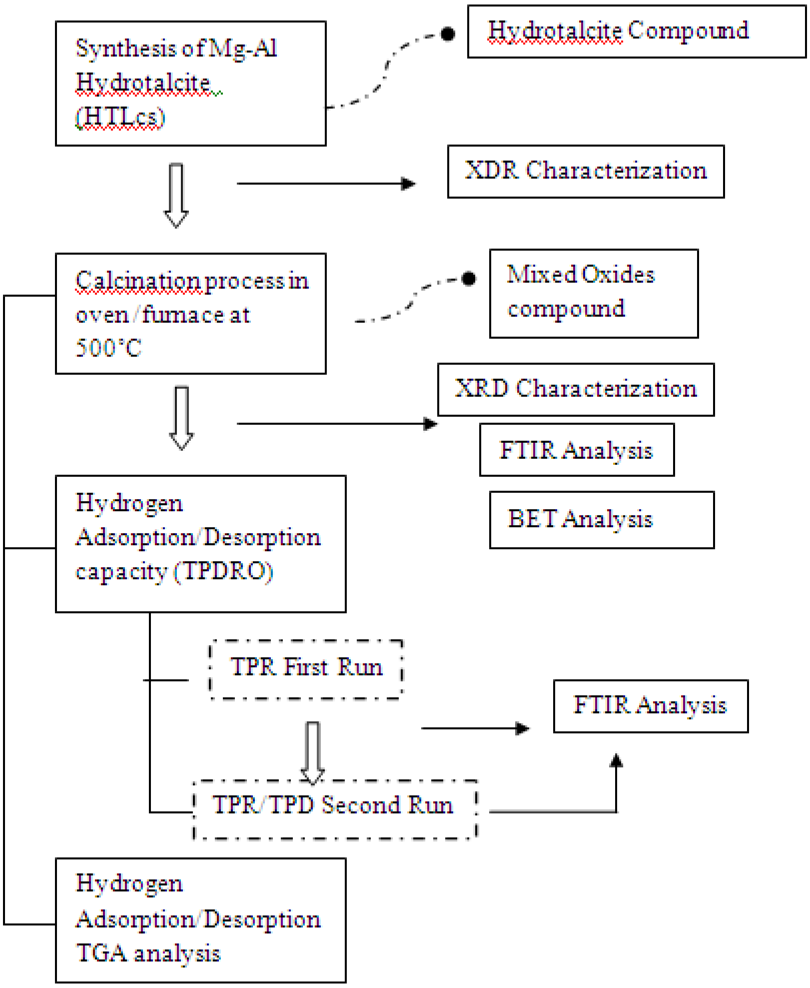


Figure 10 Flow chart of stages in hydrogen adsorption/desorption process using hydrotalcite compound at high temperature

CHAPTER 4

RESULTS & DISCUSSIONS

4.1 X-ray Diffraction Analysis

4.1.1 Hydrotalcite Compound

The X-ray diffraction analysis was performed at room temperature using samples that had not been heat treated. The XRD patterns of the hydrotalcite samples synthesized at three different molar ratio : 1.5 , 2.5 and 3.5 are shown in **Figure 11**. A well-crystalline phase which resembles the hydrotalcite-like compound was observed in all samples.

The basal spacing of each compound is calculated with Bragg's Law using d003 peak at low 2θ values (10-11 °). From the graphs shown, the basal spacing at different molar ratios is similar, falling in the range of 7.5-8.9 Å. These values are comparable the values gathered for Mg-Al Hydrotalcite from various literature just like what have been stated in section 2.3. The characteristic basal spacing within that range also confirmed the presence of CO_3^{2-} anions in the interlayer of hydrotalcite structure. Besides, the sharp, symmetric peak of the d003 at low 2θ (10-23°) and broad, asymmetric peak of d006 planes at higher 2θ (34-66°) were observed in all XRD curves, comparable with the results in [10]

Table 3 Comparison between values of d= basal spacing of hydrotalcite using Bragg's Law and from XRD

Sample	Manual calculation using Bragg's Law	Values from XRD curves
MA-1.5P	d = 9.398Å	d = 9.344 Å
MA-2.5P	d= 8.827 Å	d = 8.999 Å
MA-3.5P	d = 7.822 Å	d = 7.892 Å

The hydrotalcite samples are designed as MA-xP, whixh represents a Mg-Al precipitate with Mg/Al ratio of x

Based on XRD results, it has been proved that the samples synthesized presence in crystalline solid. The curves of intensities vs 2θ for all the samples are low almost everywhere except at certain angles where sharper peaks occur: these represent the diffracted beams. This is due to a large number of atoms arranged in a perfectly periodic array in three dimension in crystal structure that diffracts x-ray. Based on **Table 3** , the basal spacing of the crystalline structure decreases as the molar ratio increases. This is due to increasing amount of Magnesium within the cation plane in the structure that increases the degree angular measured between the X-ray incident beam to the crystal plane. It has been stated in [21] that phase of a sample determines the diffraction pattern of that substance or more specifically the shape and the size of the unit cell determines the angular position of the diffraction lines, and the arrangement of the atoms within the unit cell determines the relative intensities of the lines. As for extreme sharp peak appeared in **MA-1.5P** at around 2θ =29° and 39 °, it may be due to significant effects by the synthesis procedures and other factors such as temperature or presence of impurities.

4.1.2 Hydrotalcite Compound upon Calcination : Mg-Al Mixed Oxides

After calcinations process of hydrotalcite synthesized samples, the amount reduced around 40% proving the decomposition occurred. During decomposition, removal of few components involved, water molecules, interlayer anions and hydroxyl groups from the brucite-like layers. This changes taking place in the structure of the solid leads to formation of new crystalline phase, Mg-Al mixed oxides.

The XRD profiles for hydrotalcites at molar ratios 1.5, 2.5 and 3.5 calcined at 500 °C are shown in **Figure 12**. Based on all three profiles, a highly amorphous material is formed with main diffraction peaks close to 2θ = 45° & 65° which may due to the crystallization of MgO. Moreover, a weak peak at 2θ =35° should be ascribed to hydrotalcite compound that do not transform into mixed oxides phase. The basal spacing peak originated from 2θ = 12° in original XRD profile before calcinations did not appeared due the decrease in interlayer spaces during decomposition of water molecules.The XRD profiles obtained from the samples are comparable to the one mentioned in [6] for hydrotalcite calcined at 500°C hence the formation of Mg-Al oxides is confirmed.As for sharp peaks appeared at 2θ =19 & 29, they may be due to trace or disturbance from the XRD device.

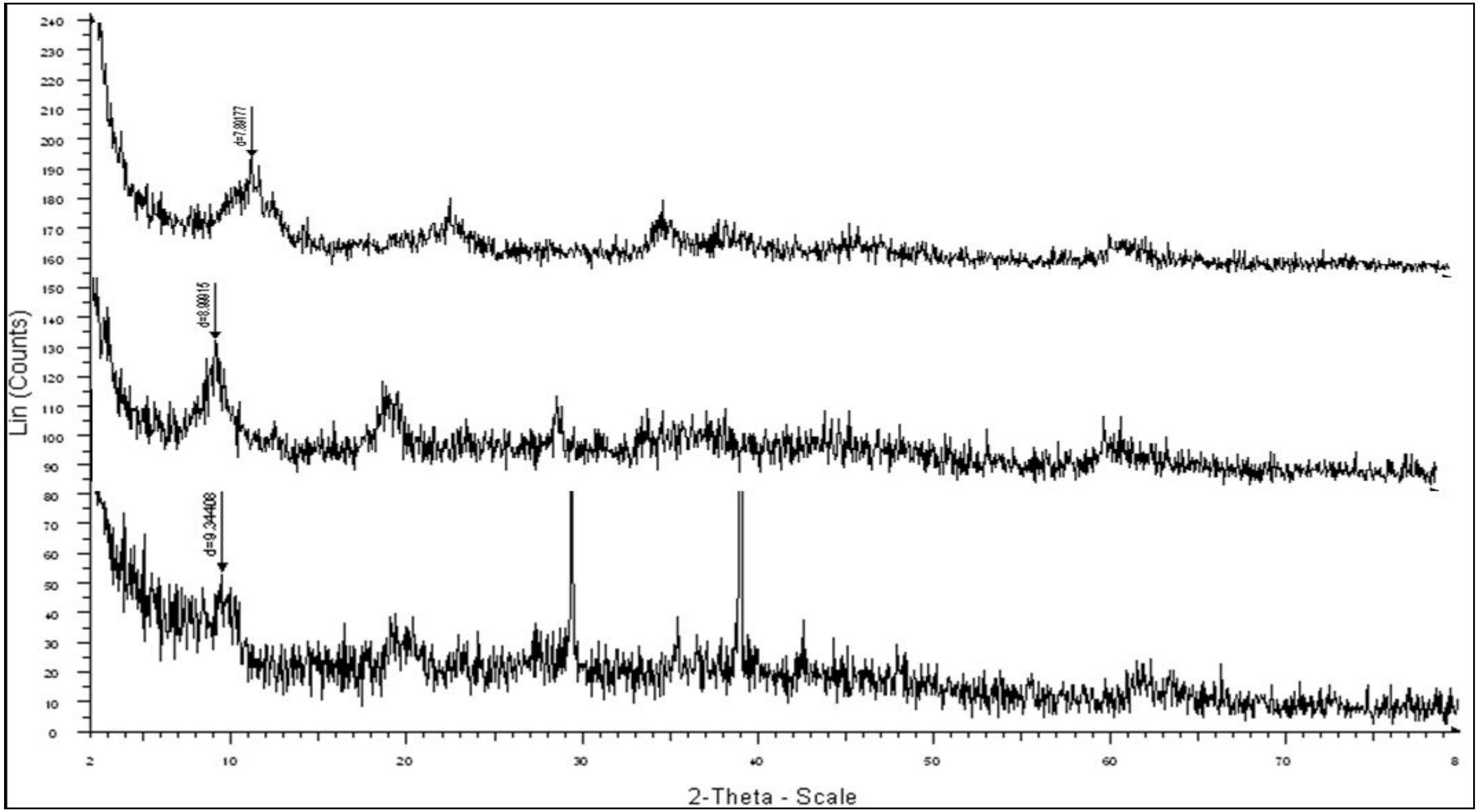


Figure 11 X-ray diffraction pattern for hydrotalcite compound at three molar ratios, MA-1.5P, MA2.5P and MA-3.5P

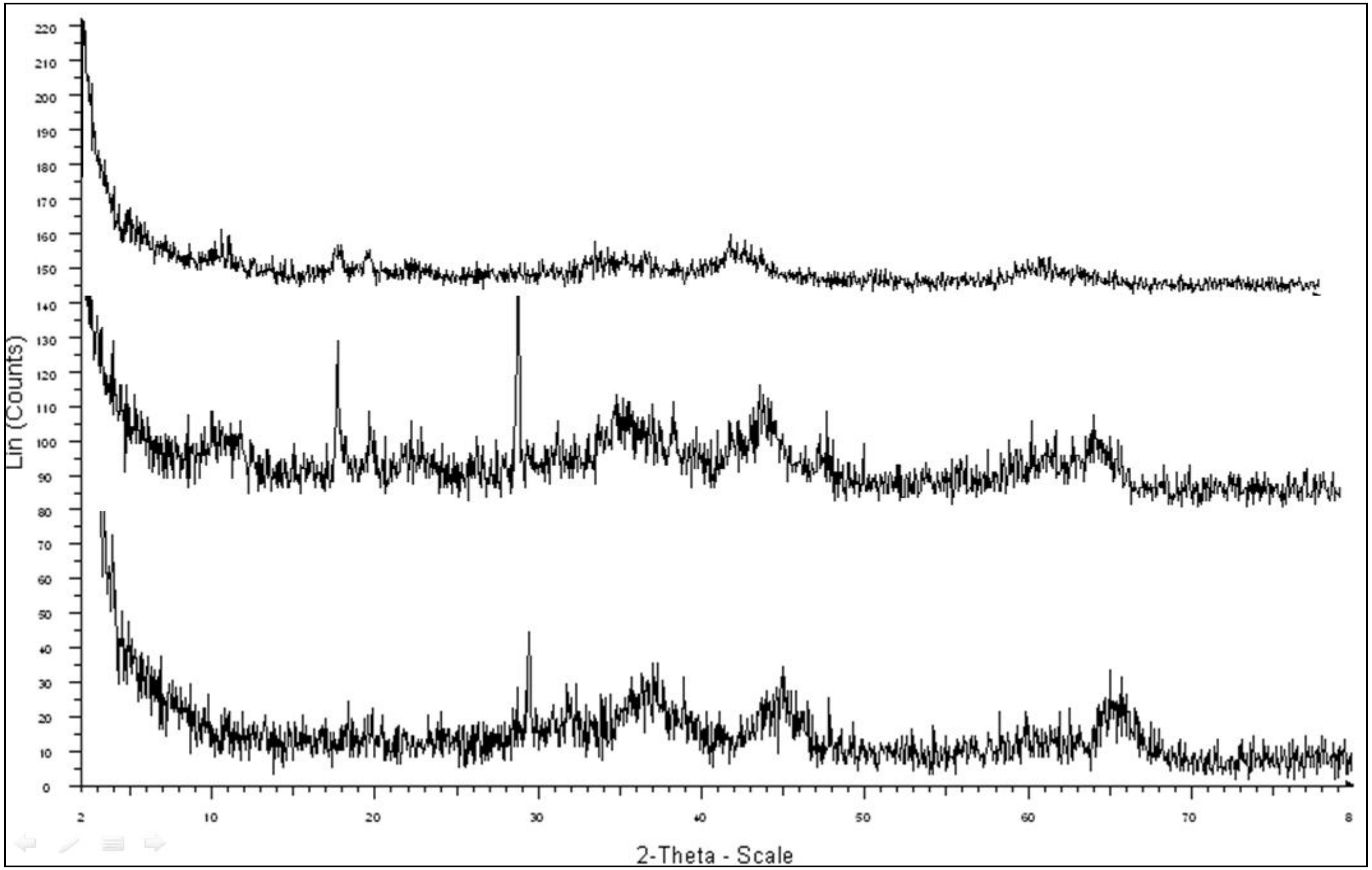


Figure 12 X-ray diffraction pattern for hydrotalcite compound after calcinations at 500 ° at three molar ratios, MA-1.5P, MA2.5P and MA-3.5P

4.2 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis is done on samples at stages after calcination, after the reduction process and after adsorption process take place. FTIR analysis results in absorption spectrum which provides information about the chemical bonds and molecular structure of a material. Plus, it also provides an analytical technique used to identify mainly organic materials. However in this project, this analysis is mainly to detect Hydrogen bonds at different process stages.

A hydrogen bond is the attractive force between the H_2 attached to an electronegative atom of one molecule and an electronegative atom of a different molecule. Usually the electronegative atom is oxygen, nitrogen, or fluorine, which has a partial negative charge.In this case, we are concentrating on attractive forces of H_2 atoms with O_2.

The FTIR spectrum collected is analyzed by looking at three parameters:

- Intensity (Weak, Medium Strong)
- Shape (Sharp & Broad)
- Position (wavenumber, cm^{-1})

Figure 13 shows the infrared spectrum of the samples after calcinations (prior to TPR analysis) at three different molar ratios. According to XRD results for samples prior to TPR analysis in **4.1. 2,** there are significant amount of HTLcs compound presence after calcinations hence it is expected to observe HTLcs infrared spectrum. All samples show quite similar pattern with peaks appeared from the same wave numbers. Moreover, the FTIR spectrum obtained for all samples are in good agreement, with only slight variations in the peak positions as compared to the data available in the literature for HTLcs compound. [10]

The broad peak at 3400-3500 cm^{-1} is attributed to the H-bonding stretching and bonding vibrations of the OH group in the brucite-like layer. The shoulder present around 3000 cm^{-1} is attributed to hydrogen bonding between H_2O and interlayer CO_3^{2-} anions. The intensity of this shoulder increases with decreases molar ratio, indicating stronger layer-interlayer interaction and a well-ordered interlayer region. The appearance of a shoulder at around 1640 cm-1 represents bands of H_20. A sharp peak appears at region 1380 cm-1 could be assigned to interlayer carbonates. The peaks at 960 cm-1 represent the deformation of Al-OH and peaks at 750 cm-1 for the Al-OH translation were observed. The band at 550 cm-1 is assigned to the translation modes of hydroxyl groups, influenced by Al3+ cations (Mg/Al-OH).

For samples after reduction process, where Magnesium metal is formed from MgO, the spectrums observed has slightly difference compared to the one after calcinations (Before TPR analysis). Based on **Figure 14**, it is observed that peaks were still observed at respective wavenumbers however certain peaks become weaker and broader. This corresponds to the reduction process taken place where H_2 consumed is used to reduce Mg oxides to Mg metal.

$$MgO + H_2 \longrightarrow Mg + H_2O$$

In this process, H_2O is produced and because this process is taken place at high temperature (up to 600 °C) the H_2O formed is released. Thus it is expected less Hydrogen bonds appeared in samples as less H_2O molecules presence. From **Figure 14**, peaks situated at wavenumber approximately at 3000 cm^{-1} and 1640 cm^{-1} becomes weaker and broader because originally, just like what have been discussed before, the peaks at those respective wavenumbers represent the hydrogen bonding of H_2O and interlayer CO_3^{2-} anions and also bonds among H_2O molecules themselves.

For samples after adsorption process, where Mg metals formed during reduction process is further exposed to H_2 flow, the spectrums observed has only small difference compared to the one after reduction process. This maybe due to the low rate of adsorption of H_2 and this is discussed further at the next section. During this process H_2 is adsorbed to formed Mg Hydrides compound.

$$Mg + H_2 \longrightarrow MgH_2$$

It can be seen in **Figure 15** the peaks appeared at location 3500 cm-1 and 1300 cm-1 seems stronger and sharper compared to the weak and broader peaks appeared before. These respective wavenumbers represent Hydrogen bonds between H_2 in Hydrides formed and OH (3500 cm-1) group as well as with interlayer CO_3^{2-} (1300 cm-1). The adsorption consumed increasing H_2 in form of hydrides that behave likely like anions, thus increasing the negativity of the structure. Hence, Hydrogen bonds are stronger represented as sharp & strong peaks at those respective wavenumbers.

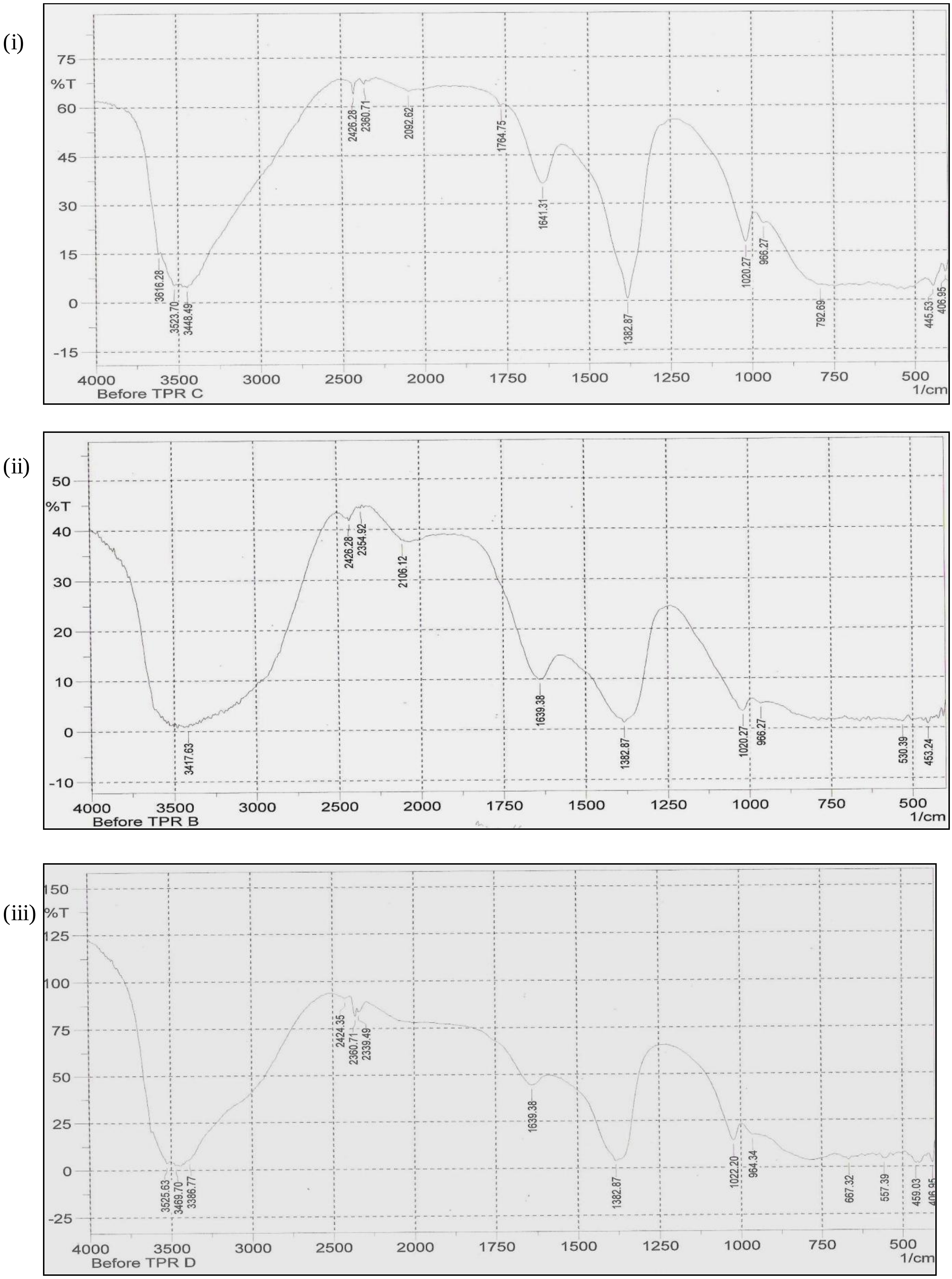


Figure 13 FTIR Spectrum for hydrotalcite after calcinations for molar ratio (i) MA1.5P, (ii) MA2.5P & (iii) MA3.5

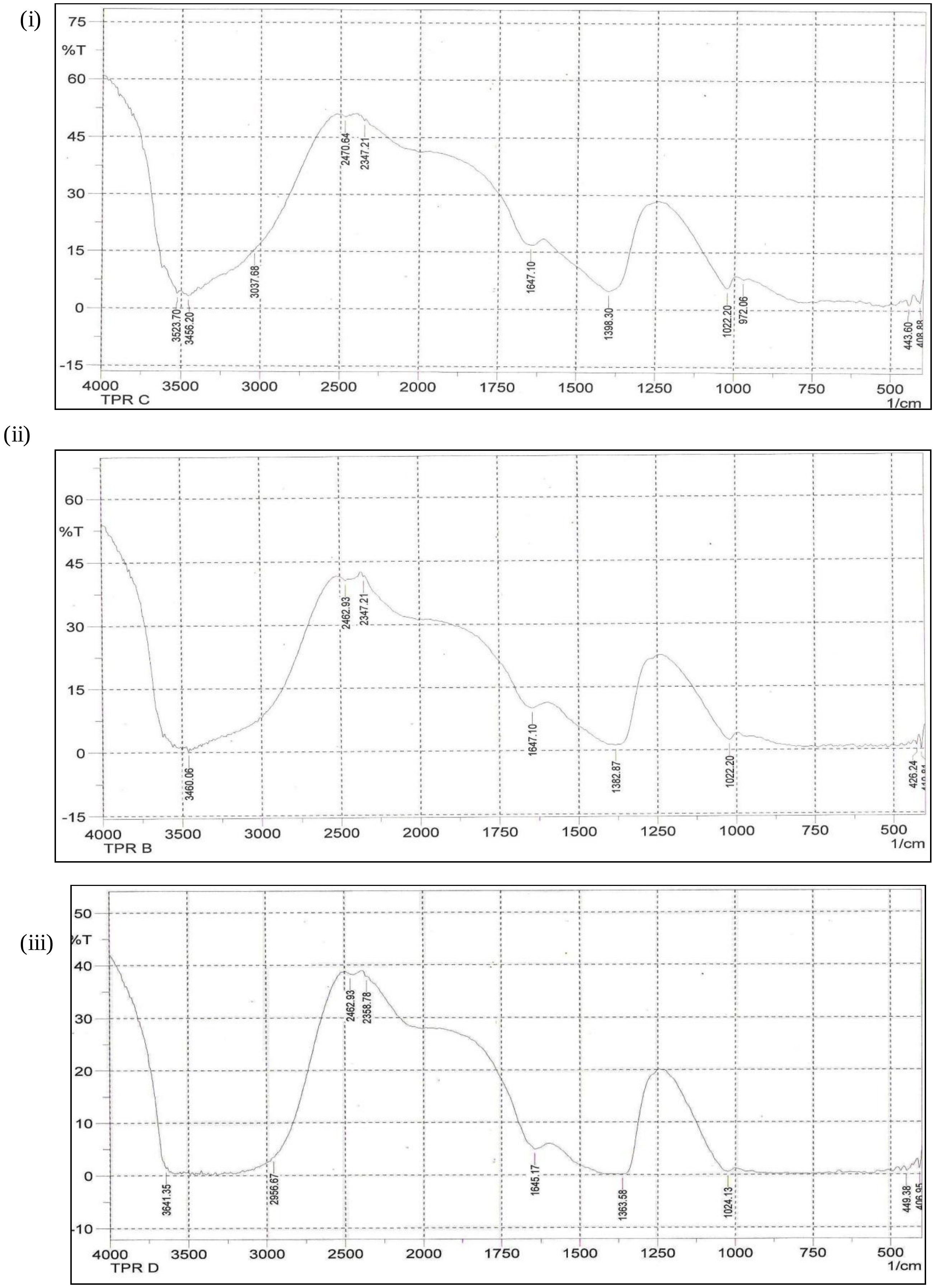


Figure 14 FTIR Spectrum for hydrotalcite during TPR Analysis (after Reduction) for molar ratio (i) MA1.5P,(ii) MA2.5P & (iii) MA3.5P

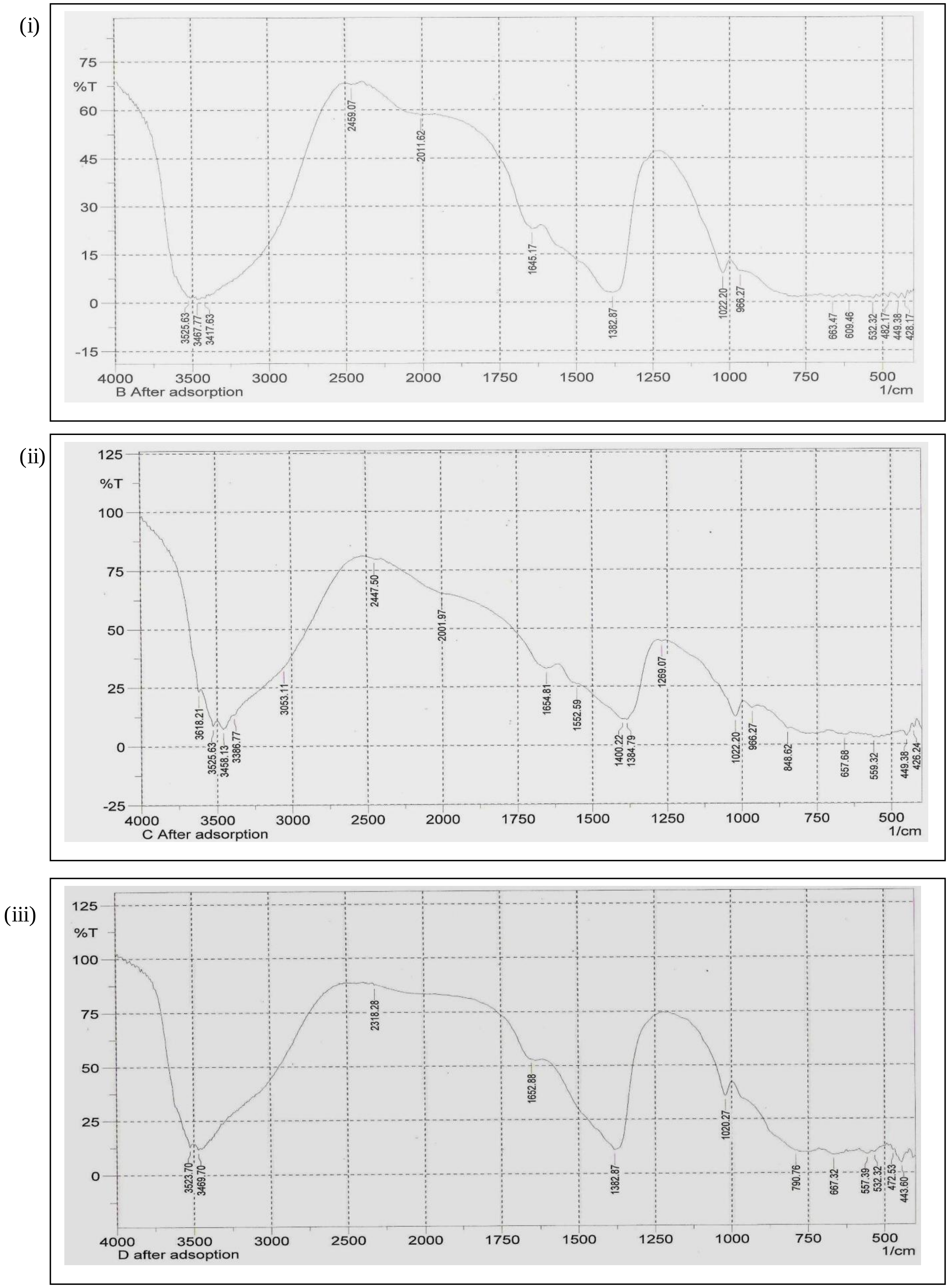


Figure 15 FTIR Spectrum for hydrotalcite after TPR Analysis (after Adsorption) for molar ratio (i) MA1.5P, (ii) MA2.5P & MA3.5P

4.3 Temperature Programmed Reduction (TPR) in Hydrogen

The temperature programmed reduction (TPR) profiles of the samples for three molar ratios are shown in **Figure 16,17** and **18** up to adsorption stage according to Figure 8. It is convenient to measure the uptake of hydrogen by the difference in the thermal conductivity (Signal mV) of the gas before and after reduction across time & temperature and this thermal conductivity represents the change in H_2 concentration (H_2 consumption). Since the gas flow is constant, the change in H_2 concentration is proportional to the rate of reduction. [25]

The peaks appeared in all samples represent the reduction process where the highest reduction rate occurred at temperature around 600°C . Starting at room temperature, the signal of H_2 consumption is at the original baseline. As the time and temperature increases, the H_2 consumption increases as well indicating that the rate of reduction increases. This shows that the H_2 consumed is used for reduction process of MgO to Mg metal until the reduction rate reaches the maximum at temperature 600°C. Beyond this temperature, the signal, or H_2 consumption decreases with increasing time .This shows that the rate of reduction process becomes slow until the signal reach the original baseline and this is the point where reduction process is assumed to be completed. At this point, we assumed all reducible Mg oxides reduced completely and formed Mg metal. From **Table 4**, the percentage MgO reduced to Mg from total amount of sample is highest for sample MA2.5P, followed by MA1.5P and MA3.5P in the range of 7.027-11.18 % only. These figures from Table 4 are calculated from amount H_2 adsorbed during reduction and total amount of samples provided by the TPR analysis. (refer Appendix B) It is expected there are still large amount of oxides presence which is difficult and require higher temperature to reduce. Thus, the H_2 adsorption only occurred on surface of the portion of oxides which has been reduced to metal.

Table 4 Percentage of MgO reduced to Mg metal during reduction process

Samples	Total amount of sample MgO(g)	Total hydrogen for reduction (umol/g)	Total hydrogen for reduction (µmol)	Equivalent MgO reduced to Mg based on stoichiometry (g)	% MgO reduced to Mg
MA-1.5P	0.155	2532.002	392.46	0.015	10.12
MA-2.5P	0.152	2875.367	437.06	0.017	11.18
MA-3.5P	0.1423	1756.543	249.96	0.0100	7.027

The amount of H_2 adsorbed is calculated by integrating the reduction peak (from baseline to baseline) and multiply with the calibration factor of the device.

Figures 15,16 and 17 , (i) were all generated from TPR curve in (ii) using a software called Digitizer. From these figures, the signal of H_2 consumption continues to increase slowly with decrease in temperature until it reaches room temperature. This significant increasing signal proves there is H_2 uptake for storage by the material after the material has been reduced completely by H_2. The rate of adsorption is calculated for each sample based on the curves showed in **Table 5**. It can be seen that the sample MA-2.5P has the highest rate of adsorption, followed by MA1.5P and MA3.5P. Sample MA-2.5P shows the highest rate of adsorption because the percentage MgO reduced to Mg metal is the highest thus larger metal surface for H_2 uptake available. According to [9], incorporating different amount of Al content by introducing different molar ratio has two functions: (1) Increase the density of layers in HTLcs with increasing Al content, which is favorable for H_2 adsorption. (2) Decreasing interlayer space when more Al contained in brucite-like layers, thus reduce the number of high-strength H2adsorption sites. Therefore, there is an optimum Al content, or optimum molar ratio, in HTLcs for adsorption of H_2 and from results, **MA2.5P** seems to be the optimum molar ratio.

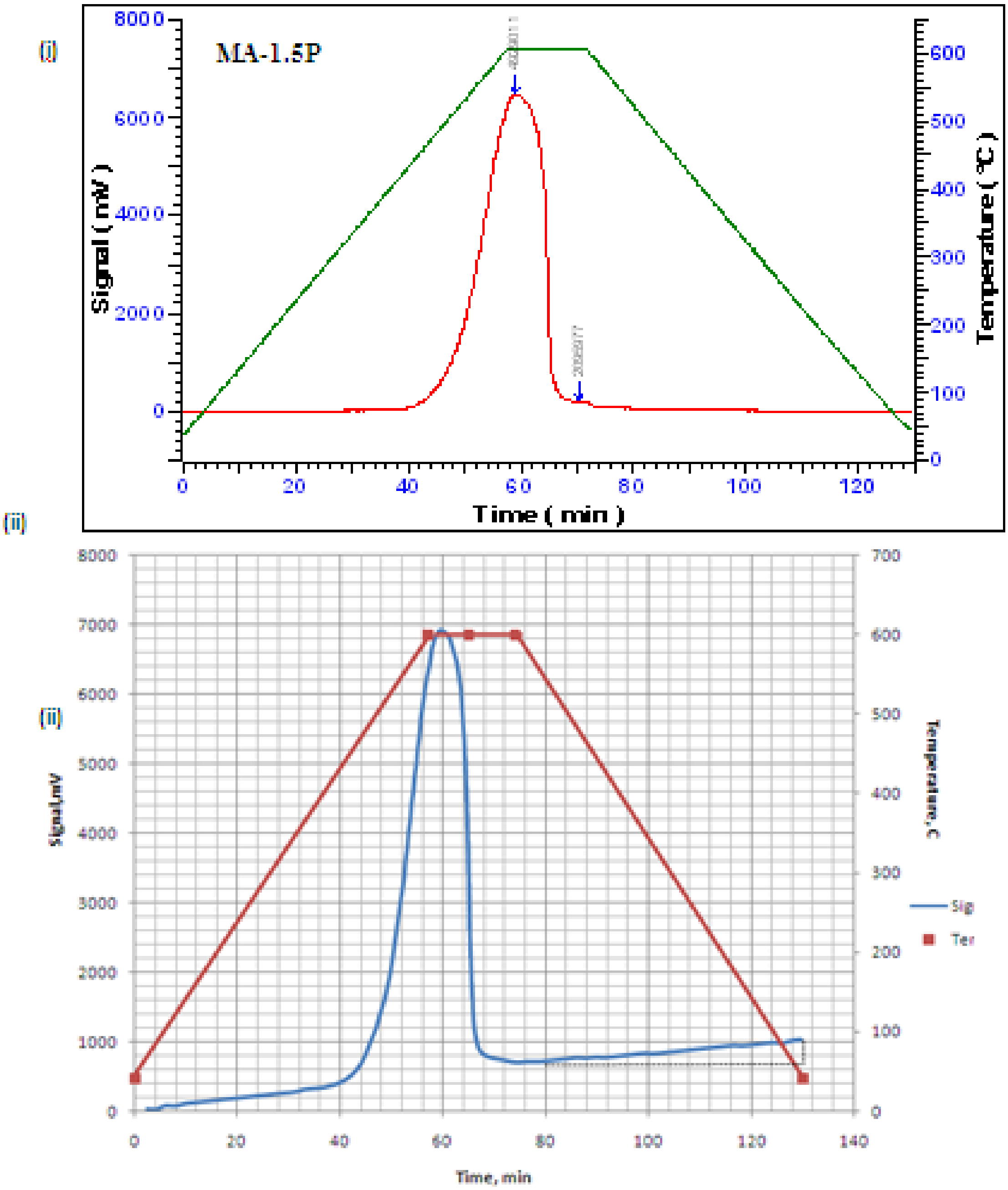
Table 5 Hydrogen uptake correspond to three samples with different molar ratio from Figure 16,17 & 18

Samples	**Total H_2 uptake for storage (µmol)**	**Total H_2 uptake for storage (g)**	**Capacity (H_2 uptake for storage/Total amount) %**	**Rate of adsorption of Hydrogen uptake for storage (µmol/s)**
MA-1.5P	46.568	0.000093	0.06	0.0158
MA-2.5P	51.966	0.000104	0.07	0.01843
MA-3.5P	41.44	0.000083	0.06	0.0144

The capacities of all samples are extremely small compared to what have been reported; capacity Mg-based metal hydride is up to 7wt%. However, this figures proved that there is H_2 uptake and this HTLcs material is capable in adsorbing H_2 and further research work needs to be carry out to improve the capacity.

(i)

(ii)

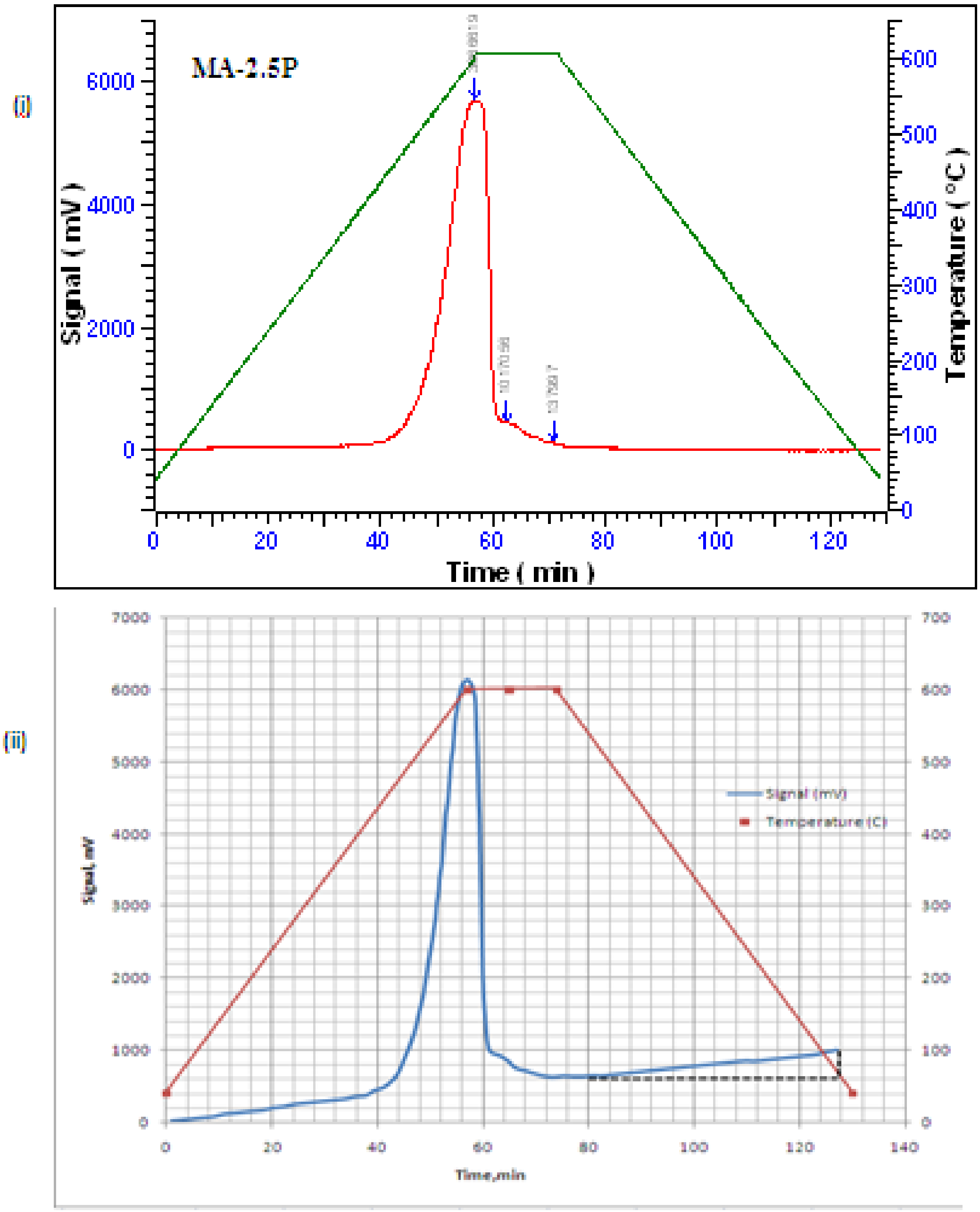


Area = 1/2 x (129-80) x (1033-727)
= 7497 mV.min = 449820 mV.s

Calibration Factor : 103.526705 x 10-9 mmol/ mV.s

Amount of Hydrogen adsorbed = 449820 mV.s x 103.526705 x 10-9 mmol/ mV.s
= 0.046568 mmol
= 46.568 μmol
Rate of adsorption = 46.568 μmol / (129-80) x 60 s
= 0.015 μmol/s

Figure 16 (i) TPR curves for molar ratio 1.5 from TPDRO device (ii) TPR curves for molar ratio 1.5 generated from Digitizer



Area = 1/2 x (127-80) x (1006-650)
= 8366 mV.min = 501960 mV.s

Calibration Factor : 103.526705 x 10-9 mmol/ mV.s

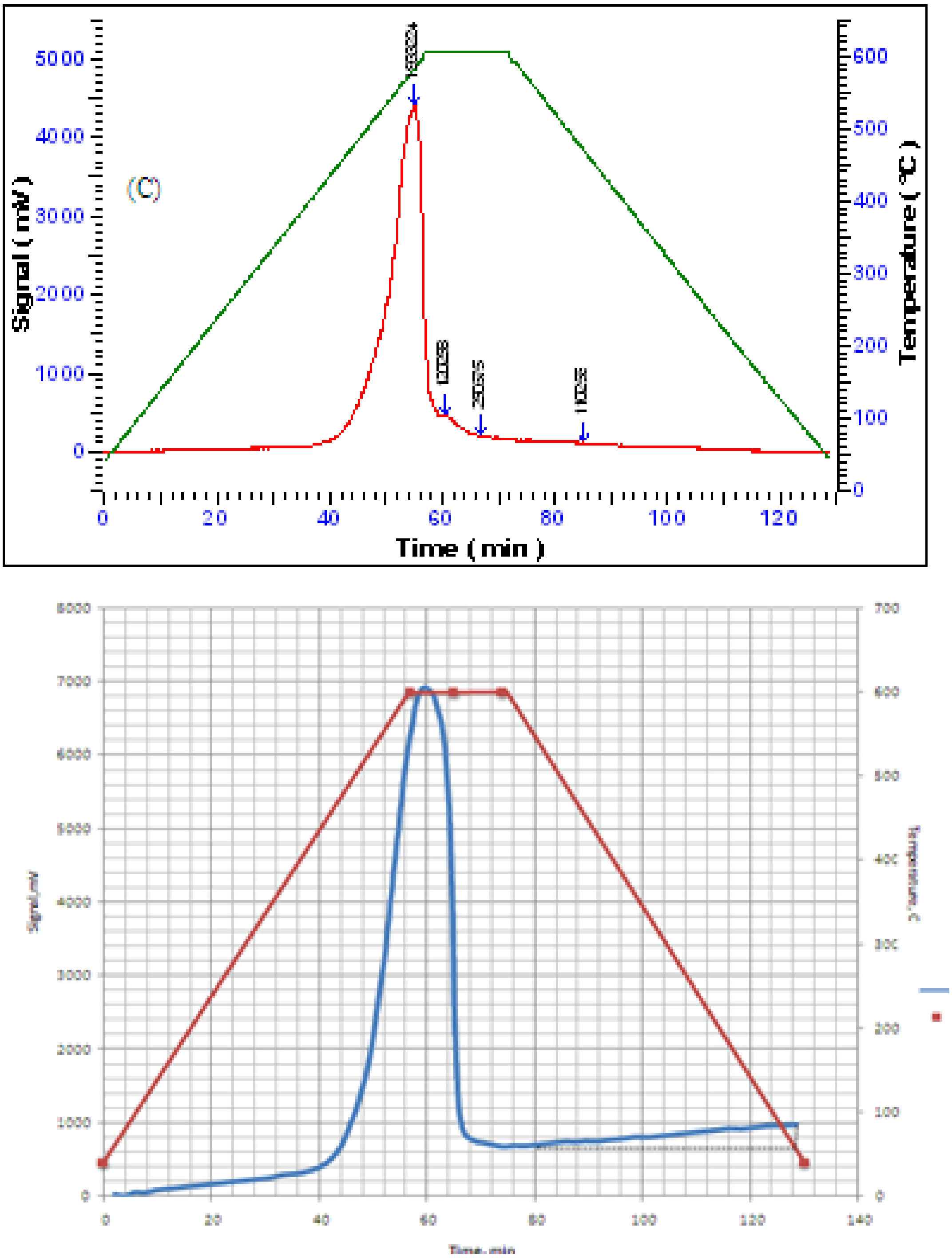
Amount of Hydrogen adsorbed = 564000 mV.s x 103.526705 x 10-9 mmol/ mV.s
= 0.0519662 mmol

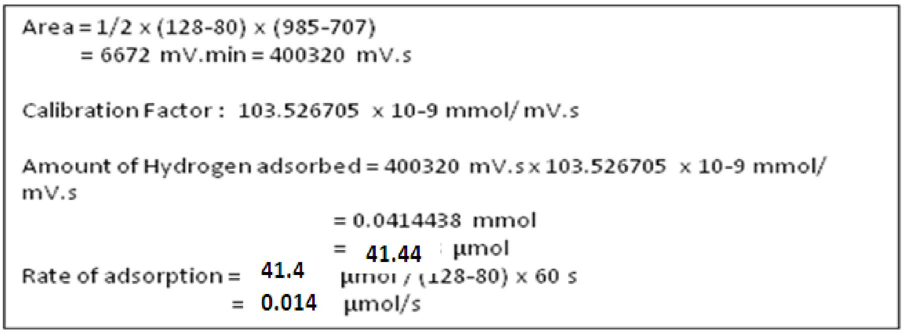
51.996 µmol
Rate of adsorption = 51.996 µmol / (127-80) x 60 s
= 0.0184 µmol/s

Figure 17 (i) TPR curves for molar ratio 2.5 from TPDRO device (ii) TPR curves for molar ratio 2.5 generated from Digitizer

(i)

(ii)




Area = 1/2 x (128-80) x (985-707)
= 6672 mV.min = 400320 mV.s

Calibration Factor : 103.526705 x 10-9 mmol/ mV.s

Amount of Hydrogen adsorbed = 400320 mV.s x 103.526705 x 10-9 mmol/ mV.s
= 0.0414438 mmol
= 41.44 µmol

Rate of adsorption = 41.4 µmol / (128-80) x 60 s
= 0.014 µmol/s

Figure 18 (i) TPR curves for molar ratio 3.5 from TPDRO device (ii) TPR curves for molar ratio 3.5 generated from Digitizer

4.4 Temperature Programmed Desorption (TPD) in Nitrogen

After the samples reached room temperature in TPR analysis, the H_2 flow is switched off and replaced by N_2 flow only for desorption analysis (refer **Figure 8**). The polarity of the device is changed and during TPD the signal represents the hydrogen desorbed instead of hydrogen consumed in TPR analysis.

The TPD curves for all samples are shown in **Figure 19**. The temperature is increased from room temperature and is held constant at 600°C under N_2 flow (refer **Figure 8**). This analysis illustrated in Figure 18 reveals that the signal (H_2 desorbed) increases with temperature and slows down with temperature held constant. The total amount of H_2 desorbed from materials is described in **Table 6** in terms of capacity. It can be seen that sample MA-2.5P which has the highest rate of adsorption (Table 10) now has the lowest rate of desorption indicating that the more H_2 molecules adsorbed the more tendency they have to jump into bulk of HTLcs material thus requires more energy to desorbed and this lead to low rate of desorption.

Generally for all samples, it is also revealed that very small amount of H_2 was physisorbed on the sample surface and that the majority of H_2 stored in the sample during TPR analysis was chemisorption (peaks at approximately high temperature, 550°C). From **Table 5 & 6**, it can be seen that the rate of desorption is very slow compared to the rate of desorption. This maybe due to the majority of H_2 stored through chemisorption during adsorption process requires higher energy (temperature) in order to break the bond with sample's surface and desorbed. This TPD- H_2 results further confirmed the ability of HTlcs materials to adsorbed and stored H_2 though the process can be further improvise in terms of H_2 capacity uptake and desorbed.[15]

Table 6 Hydrogen uptake correspond to three samples with different molar ratio

Samples	**Total amount of sample MgO(g)**	**Total H_2 Desorbed (µmol)**	**Total H2 Desorbed (g)**	**Capacity desorbed (Total H2 Desorbed/Total amount) %**	**Rate of desorption x 10^-3 (µmol/s)**
MA-1.5P	0.155	5.94	0.0000119	0.0076	2.48
MA-2.5P	0.152	5.677	0.0000113	0.0074	2.36
MA-3.5P	0.1423	6.772	0.0000135	0.0095	2.82

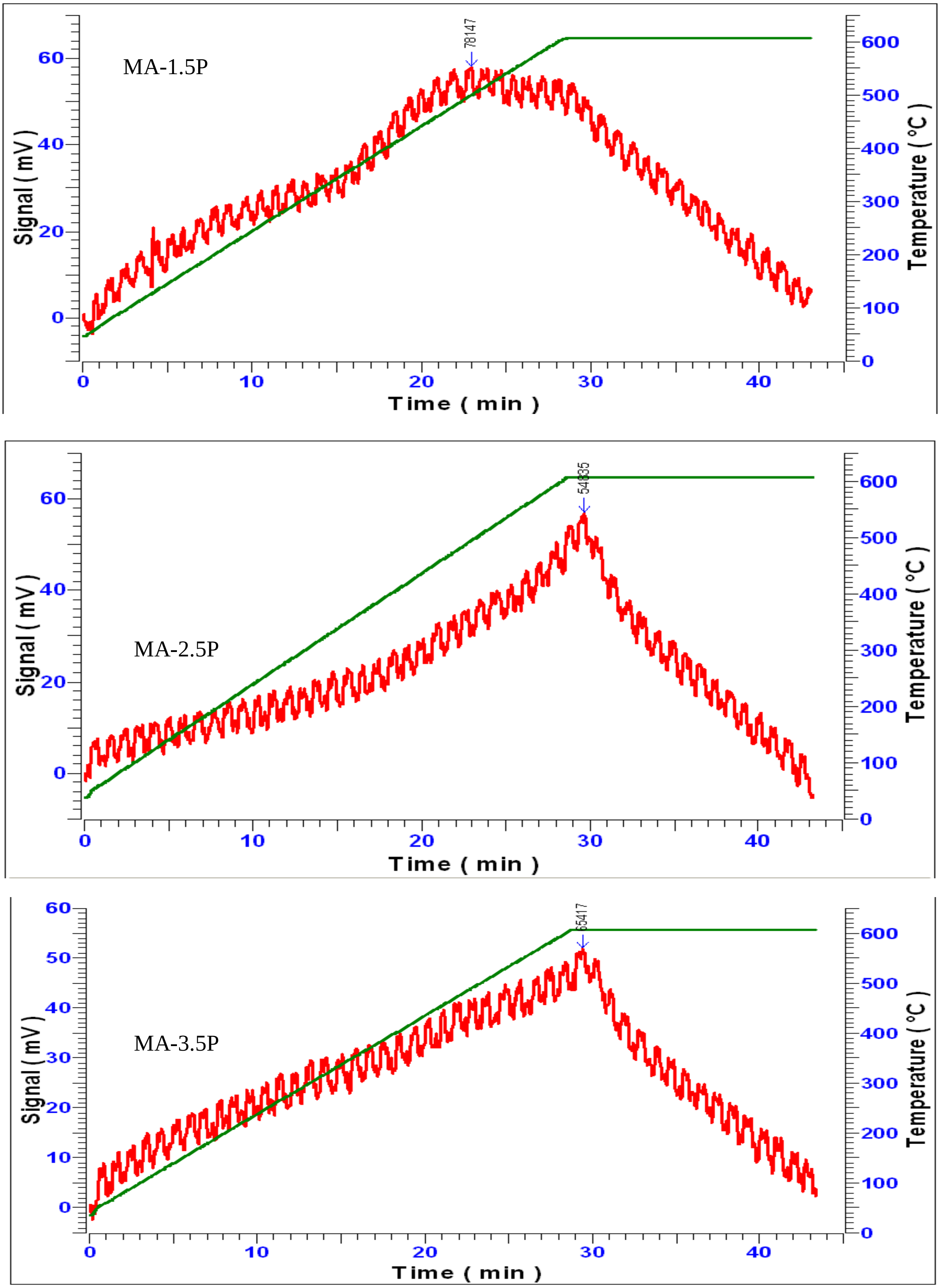


Figure 19 TPD curves for molar ratio A :1.5, B :2.5 & C :3.5

CHAPTER 5

CONCLUSION

The hydrotalcite-like compound is prepared through co-precipitation method with three different Mg/Al molar ratio : MA1.5P, MA2.5P & MA3.5P. The compound prepared is subjected to characterization stage that includes X-ray Diffraction and FTIR analysis. Both analyses showed that hydrotalcite synthesized are in good shape, with only slight difference with results obtained in the literature. Further analysis on H_2 adsorption shows that HTLcs samples, MA-2.5P has the highest rate of adsorption followed by MA1.5P and MA3.5P. On the other hand, the analysis on H_2 desorption shows that sample MA-3.5P has the highest rate of desoprtion followed by MA-1.5P and MA-2.5P. From the results gathered, though the amount obtained is low, it is proved that hydrotalcite-like compound synthesized is capable to be a potential hydrogen storage material. Therefore, it is very relevance to chemically synthesize hydrotalcite-like compound of Mg-Al, and subsequently to metal hydrides in order to adsorb hydrogen at specific temperature and pressure. Nevertheless, there are still rooms for improvement in terms of raw materials used and kinetics.

CHAPTER 6
RECOMMENDATIONS

Few recommendations can be applied in order to improve the capacity and rate of adsorption and desorption of H_2 process in future:

6.1 Sample Preparation

- Incorporate metal element such as:
  - Cobalt which expected to reduce the reduction temperature.[26] The current reduction temperature used is around 600° C which is quite high for industrial application thus by reducing the reduction temperature, the H2 adsorption process will be more practical.
  - Lithium which expected to be more reactive than Mg and help to reduce Mg and formed metal hydride easily. Thus, this can improve the H_2 uptake in adsorption process.
  - Nickel which is expected to easily formed hydride to increase the H_2 uptake during adsorption process
- During synthesis process, the precipitation needs to be washed several time to take out NO_3^- to prevent impurities presence during characterization analysis.

6.2 Analysis

- Temperature programmed Reduction/Desorption

  - Increase the time at holding temperature to ensure entire Mg mixed oxides has been reduced to increase the H_2 uptake during adsorption process after that.

- From TPR graphs, it can be seen the H_2 uptake is still increasing by the time the temperature reached room temperature. It is wise to lower the heating rate from 10 ° C/min to obtain a peak in order to estimate the total amount of H_2 uptake during adsorption.
- It is recommended to use higher flow rate of H_2/N_2 mixture to increase the capacity of HTLcs in adsorbing H_2

- Other method for analysis
  - Using other device such as TGA analysis that will provide both capacity (amount og H_2) in terms of weight and also rate of adsorption/desorption at the same time.
  - Other device such as Chemisorption, Analysis that introduces pulses of H_2 flow through samples, and straight away obtained the amount adsorbed by the calculating the difference area of the pulses.

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APPENDICES

APPENDIX A

CALCULATION IN SYNTHESIZING STAGE

A = $Mg(NO_3)_2.6H2O$, M_A= 284 g/g-mole

B= $Al(NO_3)_3.9H2O$, M_B=417g/g-mole

C= $Na_2(CO_3).10H2O$, M_C= 286 g/g-mole

Equations :

i $2[Mg(NO_3)_2.6H2O] + Na_2(CO_3).10H2O \rightarrow Mg_2(OH)_2CO_3 + 2NaNO_3 + H_2O$

ii $Al(NO_3)_3.9H2O + Na_2(CO_3).10H2O \longrightarrow Al(OH)CO_3 + 2NaNO_3 + H_2O$

To get the amount of $Mg(NO_3)_2.6H2O$ & $Al(NO_3)_3.9H2O$ needed

Molar ratio = M^{2+}/M^{3+} = Mg/Al = moles of Mg, N_A/moles of Al, N_B

x = mass of A , y = mass of B , z = mass of C

a) Molar ratio = 1.5
Given x + y = 50 ———————— (1)
Molar ratio = $N_A/N_B = (x/M_A)/(y/M_B) = 1.5$
$= (x/284)/(y/417) = 1.5$
x = 1.0216 y———————— (2)
Substitute (2) into (1) ,

x = **25.267 g**
y = **24.733 g**

b) Molar ratio = 2.5
Given x + y = 50———————— (1)
Molar ratio = $N_A/N_B = (x/M_A)/(y/M_B) = 2.5$
$= (x/284)/(y/417) = 2.5$
x = 1.703 y ————————(2)
Substitute (2) into (1) ,

x = **31.502 g**
y = **18.498 g**

c) Molar ratio = 3.5
Given x + y = 50———————— (1)
Molar ratio = $N_A/N_B = (x/M_A)/(y/M_B) = 3.5$
$= (x/284)/(y/417) = 3.5$
x = 2.383 y ————————(2)
Substitute (2) into (1) ,

x = **35.220 g**
y = **14.780 g**

To get the amount of $Na2\ (CO_3).10H2O$ needed

Based on equation **i** and **ii**

(a) Mg : Na = 2:1

$N_A/N_B = 2$

$(x/M_A) / (z1/M_C) = 2$

$(x/284) / (z1/286) = 2$

$z1 = 0.504x$ ―――――― (3)

(b) Al : Na = 1 : 1

$N_B/N_C = 1$

$(y/M_B) / (z2/M_C) = 1$

$(y/417) / (z2/286) = 1$

$z2 = 0.685y$ ―――――――
(4)

zT = z1 + z2

= 0.504x + 0.685y ―――――― (5)

For molar ratio = 1.5 , substitute x and y calculated before in (5)

zT = 0.504 x + 0.685 y

= 0.504 (25.267) + 0.685 (24.733)

= 29.676 g

For extra 10% usage ,

zT = (1.1)(29.676) = **32.644 g**

For molar ratio = 2.5 , substitute x and y calculated before in (5)

zT = 0.504 x + 0.685 y

= 0.504 (31.502) + 0.685 (18.498) = 28.548 g

For extra 10% usage ,

zT = (1.1)(28.548) = **31.403 g**

For molar ratio = 3.5 , substitute x and y calculated before in (5)

zT = 0.504 x + 0.685 y

= 0.504 (**35.220**) + 0.685 (**14.780**)

= 27.875g

For extra 10% usage ,

zT = (1.1)(27.875) = **30.663 g**

APPENDIX B

THEORETICAL CALCULATION ON AMOUNT OF HYDROGEN

Theoretical calculation on amount of Hydrogen needed to reduced MgO

Sample	Sample amount(g)	Total hydrogen for reduction (µmol)	Hydrogen needed for reduction(g)	Percentage different (theoretical & TPR) %
MA-1.5P	0.155	392.46	0.00774	**89**
MA-2.5P	0.152	437.06	0.0076	88
MA-3.5P	0.1423	249.96	0.0071	92

For **MA-1.5P**,

Molecular weight of MgO =40.3045 g/mol

Molecular weight of Hydrogen = 2.0159 g/mol

Amount of MgO sample used in TPR analysis = 0.155g/40.3045 g/mol

= 0.00384 mol

From equation ,

$$MgO + H_2 \longrightarrow Mg + H_2O$$

1 mol of MgO $\longrightarrow$ 1 mol of H_2

So 0.00384 mol MgO $\longrightarrow$ 0.00384 mol MgO/1 mol MgO) x 1 mol H_2 = 0.00384 mol H_2 x 2.0159 g/mol

= 0.00774 g H_2

From Table 2 section 4.3,

Hydrogen adsorbed during TPR = 392.46 umol x 2.0159

= 0.0008 g

Percentage difference = (0.0008-0.00774/0.00774) x 100

= **89.664**%

The percentage difference of H_2 amount adsorbed during reduction process theoretically and actual are very high , indicates that the actual H_2 adsorbed during TPR are very low. This may due to:

(a) We assumed samples are 100% MgO where as there might be other compound presence such as Hydrotalcite, impurities or any other compound

(b) MgO in TPR analysis is not completely reduced. This may be due to inappropriate temperature and the Mg compound itself is hardly reduce able.

Theoretical calculation on percentage of MgO reduced to Mg metal

Based on assumption no.2 , the amount of MgO reduced to Mg metal during the reduction process can be calculated by the actual amount of H2 adsorbed during reduction.

From equation,

$$MgO + H_2 \longrightarrow Mg + H_2O$$

1 mol of $H_2 \longrightarrow$ 1 mol of MgO

So 392 µmol $H_2 \longrightarrow$ 392 µmol H_2/1 mol H_2) x 1 mol MgO = 392 µmol H_2 x 40.3045 g/mol

= 0.015 g MgO

Percentage MgO reduced to metal Mg :

= (Total MgO reduced using stoichimetric/ total amount sample)

= 0.015/0.155 **= 9.67** %

Table 9 : Percentage of MgO reduced to Mg metal during reduction process (From Chapter 4 , section 4.3)

Samples	Total amount of sample MgO(g)	Total hydrogen for reduction (umol/g)	Total hydrogen for reduction (µmol)	Equivalent MgO reduced to Mg based on stoichiometry (g)	% MgO reduced to Mg
MA-1.5P	0.155	2532.002	392.46	0.015	**9.67**
MA-2.5P	0.152	2875.367	437.06	0.017	11.18

APPENDIX C

GANTT CHART FOR FINAL PROJECT

Details/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
First Semester (FYP I)														
Literature Review/Research More on : • Hydrotalcite/LDH characteristic & structure • Hydrotalcite preparation methods • Hydrogen Storage methods/ technology • Identify analysis to be done in project	**x**	**x**	**x**	**x**	**x**	**x**	**x**							
Preparation for hydrotalcite synthesis								**x**	**x**	**x**				
* Hydrotalcite Synthesis in lab											**x**	**x**		
*XRD Characterization													**x**	**x**
*Gather results and synthesized hydrotalcite													**x**	**x**
Second Semester (FYP II)														
Continue literature reviews More on : • Hydrotalcite thermal treatment • Reduction process on mixed oxides • Adsorption/desorption process	**x**	**x**	**x**											
*Calcination process		**x**	**x**											
*BET Analysis									**x**	**x**				
*XRD Characterization				**x**	**x**	**x**								
* FTIR Analisys				**x**	**x**	**x**								
*TPD/TPR Analysis						**x**	**x**	**x**						
* TGA Analysis									**x**	**x**				
*Gather results and synthesized hydrotalcite											**x**	**x**	**x**	**x**

** Depend on time limitation and availability of devices involved in each stage*

APPENDIX D

WORK FLOW PROJECT