CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The literature review which is relevant to the study is presented in this chapter. First of all, the theory of adsorption is discussed. In this section, the types of adsorption isotherms are presented. Next, information on current hydrogen storage technologies is described. Following this, the potential hydrogen storage adsorbents are reviewed. Reviews of the literature associated with hydrotalcite-like compounds are also presented.

2.2 Adsorption

In an adsorption process, one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent [40]. The unsaturated and unbalanced molecular forces present on every solid surface causes adsorption to occur [41]. The term adsorption refers to the process when gas molecules attaches on the surface of a solid when it is brought into contact with the solid and it is an exothermic process [42].

Meanwhile, the term absorption is used when gas molecules that are in contact with a solid enters the inside of the solid by diffusion. Sorption on the other hand, is a process where adsorption and absorption occurs simultaneously. On the other hand, the term desorption refers to the transfer of molecules sticking to the surface of the solid back to its bulk phase (gas or liquid) and it is usually an endothermic [42].

Additionally, the adsorption can also be described as a process where the separation of a substance from one phase is accompanied by its accumulation on the surface of another. The adsorbent refers to the adsorbing phase and in gas separations, is the solid. The adsorbate is the material adsorbed or concentrated on the surface of the adsorbent [43]. Adsorption can also be defined as the accumulation of concentration at a surface. This process occurs because the surface forces of an adsorbent solid are unbalanced. Both the repulsive and attractive forces between the adsorbate and adsorbent are balanced when adsorption occurs [44].

Adsorption process developed for commercial purpose usually consists of small adsorbent particles in a fixed bed. The solid adsorbent particles will adsorb components from the fluid that is passed through the bed. Approaching saturation, the flow in the bed is stopped and the bed is regenerated thermally or by other methods that causes desorption. The adsorbate is recovered and the solid adsorbent is prepared for another adsorption cycle [40].

The adsorption process plays a major role in the chemical, petrochemical and also pharmaceutical industries. It has been utilized for various industrial applications such as gas separation and purification and also for the purification of waters and wastewaters [45]. Among the applications of liquid phase adsorption include the removal of coloured impurities from organics and separation of fructose from glucose. Furthermore, applications of gas phase adsorption include removal of water from hydrocarbon and removal of solvents from air [44].

2.2.1. Physisorption and Chemisorption

Adsorption occurs due to the interaction between the solid and the molecules in the fluid phase. There are two kinds of forces in adsorption which either results in physical adsorption (physisorption) or chemical adsorption (chemisorption) [46]. In physisorption, only relatively weak intermolecular forces are involved, while in chemisorption, the formation of a covalent bond between the adsorbate molecule and the surface of the adsorbent takes place. As a result, the bond between the adsorbate and the adsorbent will be much stronger than the bond resulting from physisorption [41]. Physisorption is an exothermic process and heat is always released when adsorption occurs. Meanwhile, chemisorptions may be either exothermic or endothermic. Some general features that can be used to distinguish between physisorption and chemisorption are listed in Table 2.1.

Table 2.1: Features of Physisorption and Chemisorption [47]

Physisorption	Chemisorption
• Non specific and monolayer or multilayer	• Highly specific and monolayer only
• No dissociation of adsorbed species	• May involve dissociation
• Only significant at low temperatures	• Possible over a wide range of temperatures
• Low heat of adsorption (less than 2 or 3 times latent heat of evaporation)	• High heat of adsorption (more than 2 or 3 times latent heat of evaporation)
• Rapid, reversible (physisorbed molecules can be recovered via desorption)	• Activated, may be slow and irreversible (chemisorbed molecules cannot be recovered via desorption)
• No electrons transfer although polarization of sorbate may occur	• Electron transfer causing bond formation between sorbate and surface.
	• Chemisorbed molecules are linked to reactive parts of the surface

As shown in Table 2.1, the two types of adsorptions have many differences. The most important difference between physisorption and chemisorption is the magnitude of the enthalpy of adsorption. Many factors determine the type of adsorption that will occur and this includes the nature of the adsorbate, the nature of the adsorbent, the reactivity of the surface, the specific surface area of the adsorbate and the temperature and pressure of adsorption [41].

2.2.2. Adsorption Forces and Energies

Adsorption introduces two types of forces which are physical forces and chemical forces. Physical forces in adsorption include dipole moments, polarization forces, dispersive forces or short-range repulsive interactions. Meanwhile, chemical forces of adsorption are valency forces arising out of the redistribution of electrons between the solid surface and the adsorbed atoms. Adsorption can either be physisorption or chemisorption depending on the nature of the forces involved [41], [46], [48].

The main forces that are responsible for physisorption are van der Waals forces (dispersion attractive interaction and the short range repulsion) and also electrostatic contributions which are only significant in adsorbents with ionic structure such as zeolite. The van der Waals forces are non-specific as they do not depend on the polar nature of the adsorbent or adsorbate [47].

Energy of adsorption can provide valuable information regarding the mechanisms of physisorption if the experimental measurements are made under carefully controlled conditions and the adsorption systems are well characterized. Barrer proposed the general expression for the adsorption energy at very low surface coverage, E_O which is

$$E_O = E_D + E_R + E_P + E_{F\mu} + E_{FQ} \tag{2.1}$$

There are two types of contributions in the above equation which are non-specific and specific contributions. The non specific contributions consist of dispersion contribution, E_D and repulsion contribution, E_R. Meanwhile, the specific contributions are polarization, E_P, field dipole, E_F and field gradient-quadrupole energies, E_{FQ}. Equation 2.1 can be rewritten as,

$$E_O = E_{NS} + E_S \tag{2.2}$$

Where, $E_{NS} = (E_D + E_R)$ is the non specific contributions and $E_S = (E_P + E_{F\mu} + E_{FQ})$, is the specific contributions. In order to study the adsorbent-adsorbate interactions, analysis of the isotherm data must be taken at very low surface coverage. This is because this condition will allow the elimination or the minimization of the adsorbate-adsorbate interactions. Therefore, at higher coverage, an addition (self-potential) term must be added to E_O to allow for the latter interactions [46].

The adsorption energy is governed by both the adsorbent and also the adsorbate. For the above equation, the magnitude of the non-specific contribution is dependent on the polarizibilities of the adsorbate and the adsorbent and the density of the force centres in the outer part of the adsorbent (i.e. in the surface layer). Meanwhile, the polarity of the adsorbate molecule is important only when the specific contribution is large [46]. Adsorbate molecules entering small pores of molecular dimensions results in considerable increment in the adsorption energy compared to the adsorption energy given by physisorption of the same molecules on the corresponding open surface and this is due to the additive nature of the molecular interactions [46].

2.2.3. Rate of Adsorption and Adsorption Equilibrium

The exposure of a solid surface to a gas will result in the gas molecules striking the solid surface and some of these molecules will stick to the surface and become adsorbed while the other molecules will rebound back. For any system, the rate of adsorption will initially be large because the adsorbent surface is vacant but as the surface is covered by the adsorbent molecules, the adsorption rate will start to decrease. [41] [42].

On the other hand, the rate of desorption (rate of adsorbed molecules that rebounds from the surface) which takes place from the covered adsorbent surface is fast initially. As the time proceeds, the desorption rate will continuously decrease while the adsorption rate increase continuously until the rate of adsorption is equal to the rate of desorption which indicates that equilibrium is achieved. During this stage, it is said that the solid is in adsorption equilibrium with the gas. The equilibrium which occurs is considered as a dynamic equilibrium because the number of molecules sticking to the surface and the number of molecules rebounding from the surface is equal. However, if the flow of molecules which leaves and attaches to the adsorbent surface is not balanced, the process will either be adsorption or desorption [41] [42].

2.2.4. Adsorption Isotherms

The adsorption equilibrium can be presented either as an adsorption isotherm at constant temperature, the adsorption isobar at constant pressure and the adsorption isostere for a constant equilibrium adsorption. The presentation of the adsorption equilibrium in these various forms is possible since the amount adsorbed at the equilibrium of an adsorbate-adsorbent system depends on the pressure of the gas and the temperature of adsorption. The adsorption isotherm is most commonly used for representing equilibrium states of an adsorption system since in practice the most convenient determination of adsorption is at constant temperature [41].

The adsorption isotherm is the relationship between the amount adsorbed by unit mass of solid and the equilibrium pressure (or relative pressure) at a constant temperature. The relative pressure is the ratio of adsorptive pressure p to the saturated vapour pressure of the bulk liquid, p^0 [49]. The experimental adsorption isotherm is usually presented in graphical form. The adsorption isotherm can be generally represented by the following equation [46].

$$n^a / m^s = f(p/p^o)_T \tag{2.3}$$

Where, n^a is the amount of gas adsorbed, m^s is the mass of solid adsorbent, p is the equilibrium pressure and p^o is the standard pressure (equal to saturation pressure of adsorbate at T and usually 1 bar).

The adsorption isotherm can be measured using two principle method which is the volumetric method and gravimetric method. Irrespective of the measurement method, the adsorbent is held at a constant temperature which is approximately equal to the boiling point of the adsorptive. Subsequently, the adsorptive pressure is gradually increased and held constant for some time to enable the adsorption process and to allow the adsorbent temperature reach equilibrium [49].

In the volumetric method, the amount adsorbed is determined by measuring the pressure change and comparing it with the pressure change that would occur when there are no adsorbent. Meanwhile, for gravimetric measurement, the amount of mass adsorbed is shown by the mass increase [49].

2.2.4.1. IUPAC Classification of Adsorption Isotherms

There are six classes of adsorption isotherms classified by the International Union of Pure and Applied Chemistry (IUPAC) where the majority of them are obtained from physical adsorption. The different adsorption isotherms are shown in Figure 2.1.

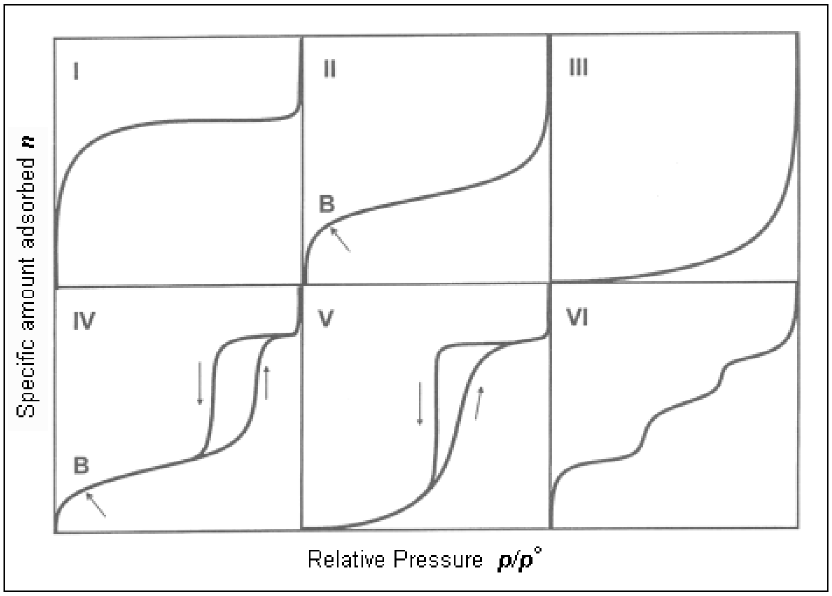

Figure 2.1: Gas physisorption isotherms according to IUPAC classification [46]

The adsorption isotherm with the Type I isotherm which exhibits a curve concave to the p/p_0 that rapidly rises at low relative pressure before reaching a plateau is the characteristic of physisorption on microporous material. Type II isotherm is initially concave before finally being convex to the relative pressure and it describes adsorption by non-porous or macroporous adsorbents with high energy of adsorption. Additionally, the Type III isotherm is convex to the relative pressure and indicates weak adsorbent-adsorbate interaction which is usually displayed by non-porous or macroporous materials. Next is the Type IV isotherm which is similar to the Type II isotherm but with addition of hysteresis loop. This isotherm indicates adsorption by mesoporous material. Type V isotherm is initially convex before levelling off at high pressure and also contains a hysteresis loop, indicating occurrence of pore filling and pore emptying and is mesoporous. Finally the Type VI isotherm is the stepwise multilayer adsorbates and shows the layer by layer adsorption on very uniform surface [49].

On the other hand, the isotherms of chemisorption generally exhibit a plateau at lower pressures than the micropore filling plateau. The completion of a chemically bound monolayer causes this limiting adsorption. The slow rate of chemisorption in some systems under certain conditions makes it hard to obtain equilibrium data. Additionally, it is possible that the chemisorption reaction is undetected at low temperature and pressure and only become significant with change of experimental conditions [46].

There are various adsorption isotherms that can be used to represent adsorption data. The most important isotherms include the Langmuir, the Freundlich, the Brunauer-Emmet-Teller (BET), and the Dubinin equations. The Freundlich isotherm applies to both physisorption and chemisorption while the Dubinin equations are applied in the analysis of physical adsorption of gases and vapours [41] [46].

2.2.4.2. Langmuir Adsorption Isotherm

The following section will present the classical Langmuir adsorption isotherm and some of its generalizations. The classical Langmuir adsorption isotherm published in 1916 is given in the following [42].

$$m(p,T,m^s) = m_\infty(T,m^s)\frac{b(T)p}{1+b(T)p} \tag{2.4}$$

In equation 2.4, m is mass of adsorbate, p is pressure, t is absolute temperature, m^s is mass of sorbent material, m_∞ is limiting value of mass adsorbed at constant T, $p \longrightarrow \infty$, also mass of monolayer adsorbate covering completely the surface of the sorbent.

The generalizations of the Langmuir adsorption isotherm include the following assumptions [42] ; adsorption occurs on a fixed number of sites, each site can take only one adsorbate molecule but no more, all sites are energetically equivalent (same heat of adsorption), interactions between adsorbed molecules are negligible compared to the sorbate/sorbent interactions.

The Langmuir isotherm model has been used together with the Freundlich model in a previous study to correlate the adsorption isotherms of hydrogen in a metal-organic framework, MO-177 produced from zinc nitrate hexahydrate and BTB ligand [37].

2.3 Hydrogen Storage Technologies

Hydrogen has become an attractive possible alternative to fossil fuels due to its possession of the highest heating value (39.4kWh/kg) among all chemical fuels and also a specific energy content of 33.3kWh/kg which is approximately three times higher than gasoline or diesel [36]. Additionally, hydrogen is also renewable when it is produced from a renewable source and it is environmentally friendly. On earth hydrogen is in the form of water and it has to be produced [2]. The various methods for hydrogen production include water electrolysis, steam methane reforming [1], coal gasification and also biomass gasification.

Hydrogen storage is an important aspect that needs to be considered in order to use hydrogen as an energy source. Due to its low critical temperature (33K/-240°C) that makes hydrogen a gas under at standard temperature and pressure. There are various ways of storing hydrogen and it is conventionally done via compression and liquid storage [1]. The hydrogen is stored as compressed gas in pressurized cylinders at about 350 - 700 bars. The disadvantages of compressed gas technology for storing hydrogen are safety concerns since high pressure is used, space limitations and high energy consumptions (about 18% of lower heating value (LHV) of Hydrogen when compressed to 700bar). On the other hand hydrogen is also stored as liquid in cryogenic tanks. However, the hydrogen liquefaction process is even more energy intensive than compression (consumes at least 30% of energy contained in hydrogen) [36] and very low temperatures are required. Besides that there are problems such as boil-off (leading to loss of hydrogen) and the relatively high cost of liquefying hydrogen in the cryogenic storage of hydrogen [1].

2.3.1. Physically Bound Hydrogen

In physisorption, low temperatures are required since the enthalpy of adsorption for physically bound hydrogen ΔH_a is between 4 and 10kJmol^{-1}. Physisorption of hydrogen is usually measured at 77-80K since at this temperature, liquid N_2 can be used [1]. The physisorption of hydrogen is a surface phenomenon thus it encourages hydrogen storage study on materials with high specific surface area or high porosity.

Numerous investigations have been conducted on the potential of porous materials to store hydrogen and they include the work by Zhou et al. [50] which studied the hydrogen physisorption on superactivated carbon. Meanwhile, Zubizaretta et al. [9] studied hydrogen adsorption on various carbon materials such as activated carbons, carbon cloths and carbon nanotubes. Other porous materials that have been studied for physisorption of hydrogen are zeolites [10] and metal organic frameworks (MOFs) [51]. The study on physisorption of hydrogen for hydrogen storage has gained wide interest since the gas adsorption via this method is reversible which makes the adsorbent recyclable. The physisorption method may also offer high hydrogen storage capacity and also fast hydrogen desorption [10]. Nijkamp et al. [4] investigated the hydrogen physisorption using carbonaceous and silica-alumina-based sorbent at 77K and 1 bar. It was found that large hydrogen storage capacity can be attained only when the adsorbents contains a large volume of micropores with a suitable diameter (e.g. 0.9nm).

Physisorption of hydrogen has a number of advantages which makes it attractive to researchers. The major advantage of hydrogen storage using physisorption is the low operating pressure, the relatively low cost of materials involved. Additionally, this method also has fast kinetics of sorption compared to chemical adsorption and it is also reversible [37]. Nonetheless, the drawbacks of this method for hydrogen storage applications are the small amount of adsorbed hydrogen on the carbon material and the low temperature requirements of this method [2].

2.3.2. Chemically Bound Hydrogen

The hydrogen storage via the chemisorption of hydrogen is commonly done using metal hydride adsorbent [1]. Hydride is formed through the reversible reaction of many metals with hydrogen where the hydrogen is chemisorbed onto the metal surface and subsequently the hydrogen atom diffuses into the crystal lattice [52]. The generic reaction of metal hydride formation is given by the following equation:

$$2M + xH_2 \Leftrightarrow 2MH_x \tag{2.5}$$

The formation of the metal hydride is an endothermic reaction while the regeneration of the metal is an exothermic reaction [1]. The metal can be regenerated by either increase the temperature or lowering the pressure. There are various metal hydrides that have been studied for hydrogen storage purpose and the most common examples are Fe-Ti hydrides, La-Ni hydrides and Ti-Zr-V series of hydrides [53]. However, the most widely studied would be magnesium hydride due to its high hydrogen storage capacity of about 7.6 percent.

Besides that, complex hydrides have also been of interest to researchers as they are lightweight and the number of hydrogen atoms per metal is generally two. Complex hydrides can be differentiated from the previously mentioned metal hydrides mainly by the transition of the metal to an ionic or covalent compound when it absorbs hydrogen. Furthermore, complex hydrides are stable and decompose only at elevated temperatures. The structure of the complex hydride consists of the hydrogen atom which is located in the corners of a tetraeder with boron or aluminum in the centre. A cation such as Li or Na is used to compensate the negative charge of the anion, $[BH_4]^-$ and $[AlH_4]^-$. Presently, lithium borohydride, $LiBH_4$ is the compound which has the highest gravimetric hydrogen density at room temperature with 18mass% [2], [13].

However, challenges of hydrogen storage using complex hydrides are the kinetics and thermodynamics limitations [13]. For example, $NaAlH_4$ when catalyzed decomposes at room temperature. Meanwhile, $LiBH_4$ has high dehydrogenation enthalpy [1]. Studies on the destabilization of $LiBH_4$ by aluminium was carried out although the dehydrogenation reversibility was improved, the system experienced severe capacity loss during the dehydriding/rehydriding cycles [54]. Additionally, to improve desorption conditions, Zuttel et al. [55] used SiO_2 as catalyst for the hydrogen adsorption using $LiBH_4$ and considerable desorption could be detected starting at 100°C. Apart from metal hydrides, hydrogen storage can also be conducted on non-metallic hydrides of carbon (organic hydrocarbons) and nitrogen (ammonia) [1].

2.3.3. Hydrolytic Evolution of Hydrogen

When a metal with higher negative reduction potential than hydrogen reacts with water, hydrogen gas is released or produced. Simultaneously, the oxide or hydroxide of the metal is also formed as presented in the following reactions [1]:

$$M + xH_2O \rightarrow MO_x + xH_2 \tag{2.6}$$

$$M + 2xH_2O \rightarrow M(OH)_{2x} + xH_2 \tag{2.7}$$

For example, if sodium is used then it will react according to the second reaction and sodium hydroxide is formed. In order to make this reaction reversible, the sodium hydroxide can later be reduced to obtain the metallic sodium. In order to produce one hydrogen molecule two sodium atoms are required. The hydrogen molecule that is combusted will reproduce a water molecule which can be recycled for additional hydrogen generation. In this process, sodium gives a gravimetric hydrogen density of 3 mass %. However, the drawbacks of this process are the challenges in controlling the thermal reduction process and also issues of reversibility since the end products are thermodynamically very stable [1], [2]. Additionally, careful control of the quantities of the reactants is required to enable the control of the hydrogen evolution [1]. Nonetheless, Steinfield et al. [56] has successfully demonstrated the process using zinc.

2.4 Investigations on Solid Hydrogen Storage

2.4.1. Hydrogen Adsorption on Metal Hydrides

Metal hydrides are one of the potential hydrogen solid storage materials that have been extensively investigated. Numerous studies have been conducted using all three types of metal hydrides which are classical or interstitial metal hydrides, chemical hydrides and complex light metal hydrides [52]. As mentioned earlier the MgH_2 metal hydride has among the highest hydrogen storage capacity of 7.6wt%. Therefore the Mg-based hydrides have been widely investigated [5], [32], [34], [57].

However, Mg-based hydrides has three shortcomings for use in hydrogen storage which are slow adsorption-desorption kinetics, the hydrogen molecules do not readily dissociate at the surface of Mg to generate the hydrogen atoms that diffuse into the metal (transition metals can be used to catalyze the process but not main group elements) and high enthalpy of formation of the hydride [13], [58]. Due to those limitations, several authors have investigated hydrogen storage in metal hydrides with the addition of niobium catalyst in order to improve the sorption kinetics. However, it was found that the reaction kinetics below 300°C is still inconvenient to apply as hydrogen storage medium [32]. Mg-Al alloy was used in the study as Al was found to destabilize the MgH_2 and also generally the kinetics of the Mg/MgH_2 system [32]. Another approach used to improve the characteristics of Mg-based hydrides is by modification of the thermodynamics properties using alloyed Mg-based compounds such as MgNi and Mg_2Cu [32].

2.4.2. Hydrogen Adsorption on Activated Carbon

Activated carbon is a synthetic modified carbon containing small graphite crystallites and amorphous carbon with pore diameters less than 1nm and specific surface areas up to $3000m^2/g$. This material is attractive for use as adsorbent since it is low cost and is available on an industrial level [59]. There are numerous studies which investigated hydrogen adsorption on activated carbon. Early studies on hydrogen storage via activated carbon have been conducted in the 1960 to 1980s on activated carbon prepared using mineralogical or organic precursors via the thermochemical processing. The activated carbon previously used contained many types of carbon structures which provide adsorption sites for hydrogen. However, the adsorption sites could not stabilize hydrogen above the cryogenic temperature [12].

Early investigation on hydrogen adsorption using activated carbon was reported by Kidnay and Hiza in 1967 in which adsorption isotherms of hydrogen on coconut shell charcoal were reported at 76K and pressures up to 90 atm. Moreover Carpetis and Peschka, was first to suggest that hydrogen could be inexpensively stored on activated carbon by adsorption at cryogenic temperatures. In the work hydrogen adsorption isotherm for various carbon materials at 78 and 65K at pressure up to 41.5 atm. The paper excluded the amount of adsorbent used in the investigation making it impossible to compare hydrogen adsorption capacity of the cryogenically cooled container in absence of the adsorbent.

J. A. Schwarz group was also actively investigating hydrogen adsorption on activated carbon during the 1980s to early 1990s. Their work focused on the fundamental aspect of hydrogen adsorption on activated carbon in order to increase the operating temperature of the adsorbent. Nonetheless the best hydrogen adsorption capacity obtained was 4.8wt% at a temperature of 87K and pressure of 59atm [12].

The hydrogen storage on activated carbon is via physisorption and usually agrees with the Langmuir adsorption isotherm. Although the use of activated carbon was found and proven to be effective as a transportation storage medium for methane and natural gas at room temperature previous studies showed that only small quantities of stored hydrogen is achieved when room temperature and moderate pressures are used. This is because using activated carbon as hydrogen adsorbent requires low temperature operation and nanoporous (with high surface area and high bulk density) activated carbons in order to achieve acceptable excess of adsorbed hydrogen densities [1]. Furthermore, addition of the incorporation of surface groups and other reactive sites can be conducted to enhance the hydrogen adsorption-desorption. However these processes are not advantageous for promotion of hydrogen storage as they normally operate via chemisorptions [59].

2.4.3. Hydrogen Adsorption on Other Carbon materials

In addition to activated carbon, other carbon materials are also potential hydrogen adsorbents. The carbon materials give best adsorption of gases due to their ability of having different morphologies with a tailored and highly porous structure [9]. Among the studies that have been done on the hydrogen storage using carbon materials include a study on the comparison of the hydrogen capacities of different type of carbon material which was conducted by Xu et al. [7]. In this study, the hydrogen storage capacities of carbon materials at room temperature and liquid nitrogen temperature (77K) were investigated. It was found that at room temperature, the hydrogen storage capacities was less than 1wt% and a super activated carbon , Maxsorb exhibited the highest hydrogen storage capacity of 0.67wt%. Subsequently, lowering the temperature to 77K increased the hydrogen storage capacity of activated carbon, Maxsorb to 5.7wt% at a pressure of 3MPa. The hydrogen storage capacity of carbon materials was found to be proportional to their specific surface area and the volume of the micropores. The hydrogen storage capacities achieved were quite low even at 77K. However, other researchers have claimed to have achieved significant hydrogen storage capacity value when using materials such as multi wall carbon nanotubes (MWNT) with hydrogen storage capacity of 3.5wt% at 143K and 75.4 bar [60]. Meanwhile Fan et al. [61] reported a high hydrogen storage capacity of 10-13wt% obtained by using vapor grown carbon nanofibres.

2.4.4. Hydrogen Adsorption by Metal Oxides

Hydrogen storage by adsorption on metal oxides has previously been done since mixed metal oxides may become large catalytic hydrogen reservoirs called oxyhydrides once treated in hydrogen. Various metal oxides have been explored for hydrogen storage such as $CeM_zNi_xO_y$ mixed oxides [27], sodium oxides [29] and Ni/Ce composite oxide [28]. Furthermore, Jaloweicki-Duhamel [26] has studied the interaction of hydrogen with a series of mixed oxides CeM_xO_y ($M = Cu, Ni; 0 \leq x \leq 1$) in the 300 to 1073K temperature range. The results of the study showed that CeM_xO_y mixed oxides are large catalytic hydrogen reservoirs with marked diffusion properties for the hydrogen species. Additionally, the authors have also studied hydrogen adsorption on $CeNi_5$ oxide which was prepared by coprecipitation and then reduced under hydrogen. It was found that the $CeNi_5$ oxide could store hydrogen equal to that of the $CeNi_5$ intermetallic compound. The hydrogen adsorption using sodium oxides was also studied. In the study, sodium hydride (NaH) and sodium hydroxide (NaOH) are formed and the NaOH system could reversibly absorb and desorb hydrogen up to 3wt%. Furthermore, the addition of NaOH to NaH could also lower the desorption temperature by approximately 100°C [29].

The hydrogen storage by adsorption on mesoporous nickel oxide and magnesium oxide was also conducted by applying external electric field and also addition of platinum catalyst. It was found that the both the catalyst addition and the external electric field increased the hydrogen uptake with the latter increasing it by 37.5% and 25 % for nickel oxide and magnesium oxide respectively [30]. The usage of metal oxides for hydrogen physisorption is limited as it is difficult to synthesize highly porous metal oxides with unsaturated metal centres, which account for the strong interaction with hydrogen [30].

2.4.5. Hydrogen Adsorption by Metal Organic Frameworks (MOFs)

Metal organic frameworks (MOFs) are another potential adsorbent for hydrogen storage. MOFs consist of transition metals bridged by carbon ligands and are associated to carbon nanostructures. MOFs are attractive for physisorption-based applications since they possess large specific surface area (1000-6000m^2/g). This material may be modified by changing ligands, transition metals or by doping in order to fit certain storage applications [1].

The hydrogen adsorption via MOFs differs from metal hydrides because the adsorption process occurs through weak dispersion interactions and electrostatic potentials. The polarizability of MOF materials and the distance between hydrogen and potential surfaces determines the dispersion interactions. As a result, hydrogen are more preferentially adsorbed on MOFs possessing highly developed micropores. Additionally, adsorption occurs with higher potential interactions due to an overlap of potential fields from both sides of the pores [11]. Studies on hydrogen adsorption on MOFs include comparative studies involving a number of different MOF-5 synthesized with dimethylformamide (DMF). The study found that MOFs with higher order of crystallinity gives higher hydrogen adsorption capacity (0.5wt% hydrogen at 77K and 800mmHg) and faster hydrogen diffusion rate [62]. Luzan et al. [51] also studied the hydrogen adsorption near ambient temperature using Co- and Zn-based MOFs. A higher maximum hydrogen adsorption capacity of 0.75wt% was observed for the Zn-based hydride at 175 bar hydrogen pressure and temperature of -4°C. However, framework collapse of some MOFs was reported during degassing and also hydrogen adsorption due to their relatively low structural stability.

The advantages of hydrogen storage in MOFs materials include fast kinetics in charging and discharging and high adsorption capacity with the highest so far reaching 8.0wt%. The disadvantage of current MOFs is the low amount of hydrogen storage at ambient temperature since hydrogen adsorption is favoured at cryogenic temperature due to the weak dispersion interactions of hydrogen and the framework [11].

2.4.6. Hydrogen Adsorption by Zeolite

The earliest work on hydrogen adsorption by zeolite focuses on adsorption of the gas at high temperatures. This is because hydrogen molecules do not enter some zeolite cages at room temperature and lower temperatures. However, at higher temperature and pressures, hydrogen may be forced into the cages, with enhanced vibrational motion assisting access through the openings. Subsequently, reheating of the zeolite adsorbent is required to release the hydrogen which may remain trapped in the zeolite cages after ambient conditions are restored [1].

Hydrogen storage using zeolites are also investigated for on-board storage in fuel cell vehicles. The system will require conditions such as lower temperature and high hydrogen storage capacity [1]. For instance, Dong et al. [10] studied the hydrogen storage in several microporous zeolites at 77K and a pressure range of 0 to 1.6MPa. The maximum capacity obtained for one of the zeolites was 2.07wt%.

2.5 Hydrotalcite-like Compounds

Hydrotalcite materials or hydrotalcite-like compounds, HTlcs are also called mixed metal oxides, and also layered double hydroxides (LDHs). HTlcs and a large class of minerals with similar structures have been known for over 150 years since the discovery of the mineral hydrotalcite. These minerals are known as the sjőgrenite-hydrotalcite group by mineralogists. In 1915, Manasse was the first to determine the correct stoichiometry of hydrotalcite which is $[Mg_6Al_2(OH)_{16}].CO_3.4H_20$. However, the main structural features of the HTlcs were only understood after Allman and Taylor carried out pioneering studies on single crystal X-ray Diffraction (XRD) in the 1960s [63].

HTlcs are ionic and basic clays which are composed of positively charged brucite ($Mg(OH)_2$) layers with trivalent cations substituting divalent cations at the centres of octahedral sites of the hydroxide sheet. The vertex of the hydroxide sheet contains hydroxide ions where each –OH group is shared by three octahedral cations and points to the interlayer regions [15]. The structure of the HTlcs is illustrated in Figure 2.2.

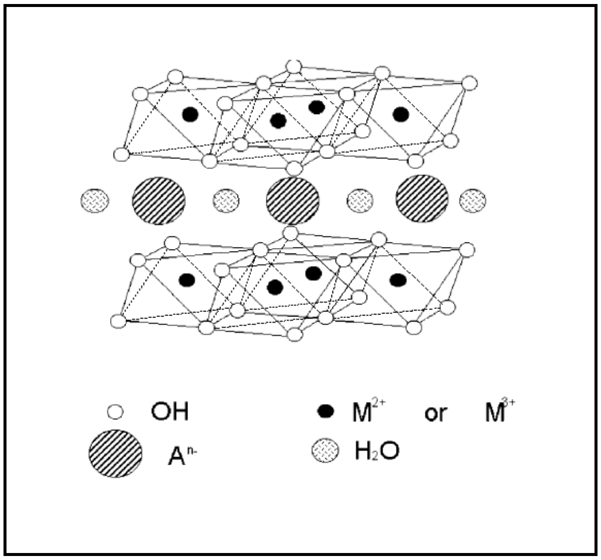

Figure 2.2: The structure of hydrotalcite-like compounds [15].

The general formula that can be used to represent HTlcs is $[(M^{2+}_{1-x}M^{3+}_{x}(OH)_2)^{x+}.(A^{n-}_{x/n}.mH_2O)^{x-}]$, where M^{2+} =Mg^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+} etc., M^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+} etc., A^{n-}= CO^{2-}_3 , SO^{2-}_4 ,NO^-_3 , Cl^-, OH^- etc. [15]. Meanwhile, x is the molar ratio of M^{3+}/ (M^{2+}+M^{3+}) [64] and the value of x is usually between 0.17 and 0.33 which corresponds to (M^{2+}/M^{3+} = 4) to (M^{2+}/M^{3+} = 2) in order to obtain single phase material [15], [65]. For instance in a previous study, when the value of Mg^{2+}/Al^{3+} is less than 1.5, bayerite will form as a byproduct [66]. Meanwhile, when high M^{2+}/M^{3+} or Mg^{2+}/Al^{3+} ratios are used, other phases may be formed such as hydromagnesite which has been previously observed for Mg/Al ratio higher than 4.4 [67], [68].

The various applications of HTlcs have made them a topic of interest for researchers. HTlcs can be used as anion exchange and adsorption materials, carriers for drugs, antacids in medicine, electrode modifiers, catalysts, precursors and supports of catalysts, decolorizing agents, polymer stabilizers, optical hosts and ceramic precursors. The features of HTlcs such as permanent ion-exchange and adsorption capacity, the mobility of their interlayer anions and water molecules, their large surface areas and the stability and homogeneity of the material formed by their thermal decomposition made their main applications possible [15].

2.5.1. HTlcs Preparation Methods

HTlcs are anionic clays that can be found in nature. However, for most applications they are usually synthesized [69]. There are various methods to synthesize HTlcs which was reviewed by He et al. [70]. The synthesis of HTlcs can be conducted using a wide range of compositions and a large number of materials with a wide variety of M(II)/M(III) cation combinations as well as M(I)/M(III) cation pairs (e.g. Li/Al) with different anions can be achieved. The HTlcs preparation methods available include coprecipitation, hydrothermal methods, urea hydrolysis method, sol-gel method and also a number of other different methods. For the different synthesis methods, the physicochemical properties of the product (such as crystallinity and surface area) and also the flexibility vary [63].

2.5.1.1. Coprecipitation Method

The coprecipitation method of HTlcs synthesis consists of mixing a solution containing the metal salts with a basic solution which cause a rapid precipitation of the HTlcs. In this technique, the both of the solutions may be added slowly into a third vessel where the precipitate solution is at a constant pH, or the metal salt solution may be added to the basic solution at changing pH [71]. The latter method is used in this study. The method of preparing HTlcs that is most commonly practiced is coprecipitation at a fixed pH since this method usually gives well crystalline materials [72], [73]. Additionally Kloprogge and Frost [74] also suggested that coprecipitation is probably the best method of HTlcs synthesis since homogeneous precursors are used as starting materials. This technique is extensively used for the one-pot direct synthesis of HTlcs containing various types of layer cations and interlayer anions [70].

Numerous studies on HTlc synthesis using constant pH coprecipitation were conducted which include production of Mg-Al HTlcs [Auxilio et al., 2007], Ni-Mg-Al HTlcs [Holgado et al., 2001] and Cu-Zn-Al HTlc [75]. Meanwhile the HTlc production by co-precipitation at variable pH was conducted for the synthesis of various HTlcs such as Mg-Fe HTlc [76], Mg-Fe-Al HTlcs [77] and also Mg-Al HTlcs [78], [79]. It was determined in a previous research that the use of fixed pH coprecipitation method produced HTlcs with higher crystallinity compared to the variable pH coprecipitation method [73]. Additionally, it has been found that solid crystallinity is enhanced with the use of high pH values for coprecipitation. The solid at pH 8.5 was determined to be less crystalline compared to solids obtained at higher pH values [80].

2.5.1.2. Hydrothermal Method

In the synthesis of materials that require intercalation of organic guests with low affinity for HTlcs, co-precipitation using soluble metal salts (e.g. nitrates and chlorides) cannot be applied. It has been found that hydrothermal methods are suitable in the above case because the inorganic sources in the form of insoluble hydroxides may be used to ensure that the desired anions occupy the interlayer space due to the absence of other competing anions apart from hydroxides. The temperatures used in hydrothermal synthesis also influence the crystal structure of the resulting material [63]. Previous studies were conducted by using hydrothermal methods to synthesize a number of HTlcs such as Ni/Al nitrate HTlc, Co/Ni/Al HTlcs and Zn/Al-CO_3 HTlcs [81]-[83].

In a previous work, Ni/Al nitrate form HTlcs were prepared using chemical precipitation and hydrothermal methods through pH control. It was found that at low pH values that nitrate HTlc was formed while at high pH carbonate HTlc is the product. This work provides an alternative way using hydrothermal method to produce nitrate hydrotalcite without a controlled environment to exclude CO_2 as the CO_2 in air is easily absorbed by high pH solutions thus forming carbonate ions in the interlayer. In this work, a highly crystalline HTlc is produced using the hydrothermal method at 180°C for 24 hours with the pH being 6. In contrast to the precipitation method, it was found that another compound (AlOOH) with boehmite structure phase appeared along with the nitrate HTlc when the hydrothermal method was used at other pH values [78].

Another work also investigated the hydrothermal synthesis of Mg-Al HTlcs using magnesium oxide and aluminium trioxide in order to overcome some limitations of the coprecipitation procedure. The study focuses of the pretreatment of the raw materials to obtain better product yield. The results form the study showed that crystalline brucite are formed during pretreatment and additional steps such as grinding MgO in organic solvent are required to overcome the problem [84]. Additionally, Mg-Al-CO_3 HTlcs have been synthesized using this method for use as adsorbent in tripolyphosphate adsorption in wastewater treatment [85].

2.5.1.3. Urea Hydrolysis Method

In the presence of a suitable anion, urea has been used to precipitate several metal ions as hydroxides or as insoluble salts. The use of urea hydrolysis method for precipitation of metal hydroxides is possible due to the suitable hydrolysis pH of about 9. The following equations show the hydrolysis of urea which occurs in two steps. The reactions will give ammonia and hydrogen carbonate [63].

$$CO(NH_2)_2 \rightarrow NH_4CNO \tag{2.8}$$

$$NH_4CNO + 2H_2O \rightarrow 2NH_4^+ + CO_3^{2-} \tag{2.9}$$

A number of investigations involve the use of urea hydrolysis method for HTlcs synthesis. For instance, Ogawa and Kaiho [86] used homogeneous precipitation with the utilization of urea hydrolysis to prepare HTlcs. It was found that the method produced well-defined hydrotalcite-like particles and the particle morphology of the HTlc was retained after thermal decomposition. However, the use of the urea hydrolysis method is limited to carbonate containing anions since the selectivity of carbonate to occupy HTlc interlayer is very high. Certain steps can be taken as possible solutions to overcome this shortcoming which is the use of other reagent for alkalinisation of solutions and use of the reconstruction method [86]. Another work investigated the Mg-Al HTlcs synthesis via urea hydrolysis and hydrothermal method. It was found that the products obtained via urea hydrolysis method possessed larger particle size compared to the latter method [16].

2.5.1.4. Sol-gel Method

Another HTlcs preparation method which is often used is the sol-gel method. In sol-gel technique, organic precursors are used and a gelling and crystallization step is conducted via thermal autoclave treatment. Examples of precursors used are alkoxides or acetylacetonate. This method produces HTlcs with lower crystallite dimension and higher BET specific surface areas compared to coprecipitated HTlcs [33], [87]. Another study involved the use of sol-gel method to produce Mg-Al hydrotalcite-derived mixed oxides as catalyst for transesterification of soybean oil with methanol. The mixed oxides produced were found to have high specific surface areas (120-266m^2/g) and narrow pore size distribution with a mesoporous structure. Addition of KI has increased the catalysts activity in transesterification compared to pure MgO or Al_2O_3 [88].

Recently, microwave irradiation technique has been used in sol-gel synthesis in place of the conventional thermal autoclave treatment. The use of this technique has enabled the production of HTlcs with controlled high specific surface areas. Additionally, the use of microwave treatment as a gelling and crystallization method produced HTlcs with high purity in short preparation times [89].

2.5.2. Applications of Hydrotalcite-like Compounds

2.5.2.1. Applications in Gas Adsorption

Hydrotalcite-like compounds have been used to adsorb gases such as carbon dioxide, CO_2. Hutson and Attwood [90] have studied the adsorption of CO_2 on various HTlcs at an elevated temperature of 603K. The results of the study showed that the naturally occurring hydrotalcite material, $[Mg_{0.73}Al_{0.27}(OH)_2](CO_3)_{0.13}.x\ H_2O$ had the best overall adsorption capacity and kinetics. Apart from that, when compared to activated carbon, HTlcs give high CO_2 adsorption capacity at high temperature while activated carbon presented stability problems at high temperature [91].

Additionally, it was also found that the hydrotalcite material prepared by high supersaturation method showed high gas adsorption compared to other adsorbent such as Al_2O_3 and MgO due to its high surface area and basicity [92]. Meanwhile, Miyata and Hirose [31] used dehydrated Mg^{2+}-Al^{3+}-$(Fe\ (CN)_6)^{4-}$ to adsorb N_2, CO_2 and hydrogen. However, no hydrogen adsorption was observed. HTlcs have also been studyed for NO_x adsorption using CoMg/Al HTlc with varying Co and Mg composition. It was described that the for mixed oxides derived from an M-Mg-Al hydrotalcite compound, Al_2O_3 acts as the support; MgO acts as a NOx adsorbent; and the metal can act as the active component for enhancing NOx storage. [24].

2.5.2.2. Other Applications of HTlcs

Hydrotalcite-like compounds are very useful in catalysis. It has been applied as catalyst for a vast number of reactions. For example, Li-Al, Mg-Al and Mg-Fe HTlcs have been studied for the role of catalyst in biodiesel synthesis and it was found that Li-Al HTlcs showed highest catalytic activity due to the existence of higher concentration of medium and strong basic sites compared to the other two HTlcs [93]. Besides that, Mg/Al HTlcs have also been utilized in the ketonisation of acetic acid with the highest conversion of acetic acid being 86.5 percent [18]. HTlcs have also been used as catalyst precursor in hydrogen production via autohermal reforming of methane, CH_4 [94] with encouraging results. The features that make this material an attractive catalyst for this reaction are its appreciable number of basic sites, high thermal resistance and high specific surface area [18].

Another important application of HTlcs is in the area of wastewater treatment. Hexavalent chromium, Cr (IV) which is a common toxic metal in industrial wastewater has been removed and recovered using Li/Al HTlcs. This procedure is possible as the Cr (IV) is adsorbed by replacing the Cl^- anion initially present in the interlayer of the adsorbent [22]. Furthermore, calcined Mg-Al HTlcs were also successfully used for adsorption of dyes such as C.I. Acid Blue 9 and indigo carmine from water. This application was possible since the dyes may be intercalated within the interlayer of the calcined HTlcs [95]. Additionally, calcined and uncalcined Mg-Al HTlcs have also been used in the defluoridation of drinking water with promising results where the F^- ion content of the aqueous solution was reduced from 5mg/l to below 1mg/l [96].

2.5.3. Thermal Decomposition of Hydrotalcite-like Compounds

The thermal decomposition of hydrotalcites depends highly on the nature of the layer cations, (whether they are oxidisable or unoxidisable) and the nature of the interlayer anions. Another aspect that influences the decomposition of hydrotalcites is the conditions during heating (oxidation, inert or reducing conditions) [17]. Heating causes the highly ordered HTlcs to produce an amorphous mixture of mixed metal oxides with very small crystal size that are thermally stable. Interesting properties exhibited by these mixed oxides include high specific surface area, high active metal dispersion, a strong interaction between different metals in mixed oxides and a controllable basic character of the calcined mixed oxides [97].

The decomposition of HTlcs occurs in a number of steps. A number of authors have discussed the decomposition of hydrotalcites. For instance, according to the review by Rives [17], there are four decomposition steps that take place when no oxidation or reduction process exists. They are:

1. Removal of water physically adsorbed on the external surface of the crystallites
2. Removal of interlayer water
3. Removal of hydroxyl groups from the layers as water vapour
4. Removal of the interlayer anion (in some cases only)

Meanwhile, Vagvolgyi et al. [98] studied the mechanism of hydrotalcite decomposition using a controlled rate thermal analysis method and obtained the following results. First of all, from ambient temperature to 300°C, the evolution of bound water occurs. Next at temperatures between 300 to 400°C, the decomposition process occurs due to the dehydroxylation and decarbonation of the mineral. Finally at 800 to 1000°C a slow mass loss step is observed due to the degradation of the hydrotalcite mineral. High calcination temperature degrades HTlcs into mixed oxides and also spinels with destruction of the hydrotalcite structure.

On the other hand, Othman et al. [33] also reported that the decomposition of Mg-Al HTlcs occurs in three stages where the first stage is the loss of interlayer water, second stage is the removal of carbonate from the interlayer and removal of hydroxyls from brucite-like layer. Finally is the sustained release of residual or physically adsorbed water. The decomposition of the materials was found to complete at 660°C. Palmer et al. [77] also reported a three stage thermal decomposition of HTlcs. However, order of evolution is different where it starts with the removal of adsorbed water (<100°C), the elimination of interlayer structural water (100-200°C) and the simultaneous dehydroxylation and decarbonation of the hydrotalcite structure (300-400°C).

Besides that, the HTlcs decomposition can also be described in only two steps. The first step that occurs between 100-250°C was ascribed to the removal of interlayer and adsorbed water molecules. The second step occurring between 250-500°C is the dehydroxylation of the interlayer hydroxyl group and decomposition of interlayer anion (carbonate and nitrate) which cause the collapse of the layered structure. It has also been stated that the decomposition of carbonate takes place in the temperature range of 250-600°C [24]. Another study that was conducted on HTlc decomposition showed mass loss steps which consist of dehydration, dehydroxylation and also loss of carbonate from the interlayer. The final dehydration product is dependent on the interlayer anion [14].

2.5.4. Calcination Effects on HTlcs

In order to obtain the mixed oxides for further applications, the HTlcs has to be calcined. Upon calcination, various changes occur to the HTlc sample such as, loss in sample mass (ca. 45%), significant increase of surface areas and pore volumes caused by the formation of micro and mesopores due to the expulsion of CO_2 and water from the HTlcs. The loss of CO_2 and water can be indicated by the increment of Al and Li content in calcined samples relative to the uncalcined sample from the XPS measurement [93]. However, when the calcination temperature was increased to 600°C it was found that the specific surface area decreased which is probably due to the sintering of crystallites [19]. Besides that, calcination of HTlcs causes decrement of the interlayer spacing due to the removal of CO_3^{2-} groups. This however, can be recovered by rehydration to give the initial spacing [99].

2.6 Properties of Hydrotalcite-like Compounds

HTlcs has been characterized in order to determine the properties of the synthesized materials. The properties of the HTlcs such as specific surface area, morphology, reducibility determines the suitability of the HTlcs for certain applications. Additionally, it is also important to determine the type of phase in the material, the amounts of elements and also the ions present in the HTlcs. Numerous characterization techniques has been used on HTlcs such as X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX), N_2 adsorption for textural properties determination, Temperature Programmed Reduction (TPR).

2.6.1. Phase Determination using X-ray Powder Diffraction

The use of X-ray diffraction spectroscopy has been utilized in numerous studies for the determination of the existence of hydrotalcite phase in the synthesized products. The characteristic HTlcs peaks obtained from XRD which are at 2θ angles of 11°, 22°, 35°, 38° and 46° corresponding to the (003), (006), (009), (015) and (018) crystal planes. In addition, two peaks just over 60° may correspond to the (110) and (113) crystal planes of hydrotalcite are also observed for HTlcs [20], [24]. It was found that the peaks for HTlcs were found to decrease as the Mg-Al is increased [18].

Additionally, XRD is also used to determine the formation of mixed oxides as a result of calcination. In previous studies, the formation of mixed oxides is indicated by the disappearance of the characteristics HTlc peaks and the appearance of broad peaks at lower 2θ angles 37°, 43° and 62 ° which can be attributed to the mixed magnesium oxide MgO [24], [100]. However, in certain cases the hydrotalcite structure is preserved in the calcined samples due to the rehydration of the materials prior to testing [100].

Meanwhile for Ni-Mg-Al HTlcs, the characteristic hydrotalcite peaks are also observed after subjecting the material to XRD [73], [101]. As with the Mg-Al HTlcs, previous literature on XRD characterizations of Ni-Mg-Al HTlcs also showed new peaks after calcination with subsequent disappearance of characteristic hydrotalcite peaks. It was found that the new peaks existing at 2θ angles 37°, 43° and 62 ° can be attributed to presence of MgO and NiO [102].

Nonetheless it was previously found that these two oxides cannot be differentiated as the peaks overlaps [103]. Moreover, the calcination temperature was found to affect the crystallinity of the samples since higher calcination temperature has produced materials with sharper peaks indicating improved crystallinity with increasing calcination temperature [104].

Additionally, XRD may also be used to determine the basal spacing of the HTlcs. The basal spacing is the distance from the centre of one layer to that in the adjacent layer or the distance between two hydroxyl groups in adjacent layers [105].

2.6.2. Characterization by Fourier Transform Infrared Spectroscopy

The use of FTIR spectroscopy is useful to determine the presence of interlayer anions, layer ions and also impurities in the hydrotalcite-like compounds. The investigation by Tsyganok and Sayari [101] showed that for Mg-Al HTlcs containing transition metals (Co, Ni, Cu) an intense peak was observed at around 1360-1366cm^{-1} due to the asymmetric stretching mode of interlayer carbonate and nitrate, while the symmetrical stretching vibration of carbonate is observable as a weak peak around 1039-1043 cm^{-1}. However, Othman et al. [33] attributed the peak at around 1300cm^{-1} due to only carbonate since no nitrate is observed in the EDX results. Meanwhile, the broadband at around 1614-1634 cm^{-1} are due to the bending mode of water molecules. The observation of the carbonate stretching mode at 1300cm^{-1} is shifted from the value of the free CO_3^{2-} ion (1450cm^{-1}) probably due to the restrictions experience by the carbonate in the interlayer caused by the strong hydrogen bonding with hydroxyl sheets and interlayer water molecules [106], [107].

Meanwhile, peaks in the low wavenumber range also play a role in HTlc characterization. As an example, Kloprogge and Frost [74] studied the It has been investigated that for Mg-Al HTlcs samples, peaks at 637, 704 and 506 cm^{-1} can be attributed to existence of Mg-O and Al-O bands in the calcined samples [33].

2.6.3. Morphology Determination by Field Emission Scanning Electron Microscopy

Previous HTlcs that has been examined using Field Emission Scanning Electron Microscopy (FESEM) showed that the HTlcs exhibited various types of morphologies. For instance, numerous authors observed hexagonal plate-like morphologies [69], [108]. Apart from that, a number of studies exhibited HTlcs with coral-like morphologies [109], [110]. It was previous;ly found that the synthesis steps influences the morphology of HTlcs. Nonetheless, the morphologies of the as-synthesized HTlcs are not altered by thermal treatment [105].

2.6.4. Elemental Analysis via Energy Dispersive X-ray

In a previous work it was stated that any differences between metal M^{2+}/M^{3} ratios of starting solution and final synthesized material were usually ascribed to a prefential precipitation of either one cation as hydroxide [107]. A work by Othman et al. [33] showed that the HTlcs contained high carbon content and it was suggested that this is caused by the remnants of K_2CO_3 in the sample. Additionally the high amount of oxygen was suggested to be indicative of the presence of mixed oxides in the calcined samples. Finally the increment of calcination temperature was found to cause an increase in oxygen content and a decrease in the Na content of Mg-Al HTlcs.

2.6.5. Textural Properties Determination by Nitrogen Adsorption

The textural property of a material plays an important role in determining its performance as an adsorbent. Therefore the specific surface area and porosity of HTlcs has been investigated in numerous investigations. For instance, Yu et al. [24] used the BET method to calculate the specific surface area and the BJH method was used to acquire the pore volume and size distribution from the adsorption isotherm of the HTlcs. In another investigation by Parida and Das [18], it was found that Mg-Al HTlcs (synthesized via coprecipitation) characterized using N_2 adsorption was mesoporous with pore diameter ranging from 40 to 70Å. Meanwhile, the specific surface areas of the Mg-Al HTlcs were determined to be in the range of 186-230 m^2/g. In the work by Auxilio et al. [95] the specific surface area of Mg-Al HTlcs increased with higher carbonate content due to the formation of many small pores resulting from the release of CO_2 from the HTlcs.

The use of different metals for HTlcs synthesis also influences its specific surface area. For instance, it was found that the amount of Ni in Ni-Mg-Al HTlcs (formed via coprecipitation) does not significantly affect the specific surface area but the property is more dependent on the aluminium content as the specific surface area decreases with increment of aluminium [103]. Apart from that, the surface area and pore volume of the oxide catalyst decreases with increasing Co content while the average pore size between the crystallites increases. This is in agreement with another study which states that the addition of nickel metal into the HTlcs reduced the crystallite size [105]. Besides that, the work by Olsbye et al. [71] also found that the increment of gallium metal content in the Mg-Ga-Al HTlcs lowers the surface area of the calcined material resulting in a less attractive catalyst carrier.

2.6.6. Material Reducibility Determination using Temperature Programmed Reduction

In order to improve the properties of Mg-Al HTlcs for certain applications, other metals are sometimes added into this compound. For instance, Yu et al. [24] used CoMg/Al HTlc as storage catalyst for the adsorption of nitrogen oxides (NOx). It was found that the reduction of the catalyst was influenced by the cobalt content as no reduction was detected when cobalt was not present. Another study also used TPR to investigate the reduction behaviour of Mg/Fe/Al hydrotalcite-derived mixed oxides. Two reduction peaks were observed at 433°C and 907°C [111].

On the other hand, the TPR of Ni-Mg-Al HTlcs with Mg-rich catalyst gives two reduction peaks. Two peaks exists are caused by the segregation of both MgO and NiO phases that exists in the HTlcs. It was also found in the previous investigation that the calcination temperature cause a decrease in the Ni reducibility due to the enhanced thermal stability of the mixed oxides [94], [103]. Furthermore it was also found in another work that the reducibility of Ni-Mg-Al HTlcs decreases with increment of Mg/Al molar ratio and also calcination temperature [112].

2.7 Hydrogen Adsorption using Thermogravimetric Analysis

Thermogravimetric analysis can be defined as a technique where the mass change of a substance is measured as a function of temperature whilst the substance is subjected to controlled temperature programme. This method is used for the adsorption of gases such as hydrogen because it allows the determination of the mass loss steps, its temperature and also the mechanism involved during the mass loss. Besides that, thermogravimetric analysis can also give thermal stability for HTlcs [98].

The hydrogen adsorption has been conducted using thermogravimetric analysis (TGA) in many previous researches. As an example, Langmi et al. [113] studied the hydrogen storage on zeolites using this method. In the study, a constant pressure thermogravimetric analyzer was used and the hydrogen gas used was of 99.995% purity. Firstly, the sample was heated to 400°C in order to dry it. Afterwards, the sample was cooled to the required temperature which was between -196 and 300°C.

Aside from that, it has been found that for Mg-Al HTlcs and Ni-Mg-Al HTlcs shows a two step weight decrease during the heat treatment stage at the beginning of the TGA experiment. It has been stated that the first weight loss at below 500K corresponds to removal of interlayer water. Next, the second weight decrement has been attributed to dehydroxylation which overlaps with the first weight loss at about 500K. It has been reported that at 573K (300°C) CO_2 is evolved from Mg-Al and Mg-Al-Ni HTlcs samples [105]. It was also found in a previous research that the decomposition of the HTlc sample is completed at 660°C after samples experienced a three stage weight loss [33].

Summary

With reference to the literature review conducted, it is apparent that the hydrotalcite-like compounds (HTlcs) possess features that make it attractive for a number of applications including adsorption. The formation of mixed oxides as a result of HTlcs calcinations may make this material a potential hydrogen storage media since the hydrogen adsorption on mixed oxides has given encouraging results according to previous works.