CHAPTER 3

METHODOLOGY

3.1. Introduction

This chapter presents the methodology involved in this study. The chapter covers the steps in the material synthesis, the material characterization techniques and also the hydrogen adsorption experiments. The aim of this chapter is to illustrate the methods of this research so that it can act as a reference for future work on the subject.

3.2. Mg-Al HTlcs Synthesis by Coprecipitation

The Mg-Al HTlcs were synthesized using the coprecipitation method similar to a previous work however in this study magnesium nitrate were used instead of copper nitrate [64]. In this technique, the raw materials used were nitrate salts of the metals which are magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$) and aluminium nitrate nonahydrate ($Al(NO_3)_3.9H_2O$). The precipitating agent used in the synthesis was sodium carbonate (Na_2CO_3). Firstly, five metal salt solutions each containing 50±1g (magnesium nitrate hexahydrate + aluminium nitrate) in 500ml distilled water were prepared. The Mg/Al molar ratios of the solution were 0.5, 1, 2, 3 and 4. Next, each solution was added drop by drop into a 0.5M sodium carbonate solution maintained at 40°C (313K) under vigorous stirring. After addition was completed, the stirring was continued for another 15 minutes. Next, the precipitate was filtered and washed several times using distilled water to remove entrained Na^+ and NO_3^- ions. Then it was dried in an oven overnight (for about 20 hours) at a temperature of 110°C (383 K).

Afterwards the dried solid was ground in a ceramic mortar in order to obtain the final powder form. The resulting sample was calcined in air using a furnace at 450°C, 600, 750 and 900°C for two hours to obtain mixed oxides. The calculations for the amount of materials required for Mg-Al HTlcs synthesis is available in Appendix 1.1. The as-synthesized Mg-Al HTlcs were denoted as MA 2, MA 3 and MA 4 with the number being the Mg/Al molar ratio of the material. The specific molar ratios of the materials were used because the use of higher molar ratios will lead to the formation of other phases such as hydromagnesite which has been previously observed for Mg/Al ratio higher than 4 [67], [68]. Additionally, it was determined that the coprecipitation temperature has no influence on the BET specific surface area of the resulting mixed oxides therefore any suitable or proven synthesis temperature may be used [114].

3.3. Ni-Mg-Al HTlcs Synthesis by Coprecipitation

The preparation of the Ni-Mg-Al HTlcs was also conducted via coprecipitation with Na_2CO_3 as the precipitating agent and with metal nitrate precursors. The synthesis of Ni-Mg-Al HTlcs is similar to that of Mg-Al HTlcs with addition of nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$). Two salt solutions each containing 50±1g of the metal nitrate salts in 500ml distilled water were prepared. The Ni:Mg:Al molar ratios used in this study was 1:2:1 and 2:1:1. Next, the salt solution was added drop by drop into a 0.5M sodium carbonate solution maintained at 313K (40°C) and was subjected to vigorous stirring. After the addition step was completed, the stirring was continued for 15 minutes. Next, the precipitate was filtered and washed several times using distilled water to remove excess Na^+ and NO_3^- ions. Then it was dried in an oven overnight at a temperature of 383 K (110°C). The dried solid was then ground in a mortar pestle in order to obtain the final powder form. The resulting sample was calcined in air using a furnace at 450°C and 600°C for two hours respectively to obtain mixed oxides. The calculations for the amount of materials required for Mg-Al HTlcs synthesis is available in Appendix 1.2. The as-synthesized Ni-Mg-Al HTlcs were denoted as NiMA 1:2:1 or NiMA 2:1:1 with the number being the Ni/Mg/Al molar ratio of the material.

3.4. Material Characterization

The synthesized materials were characterized in order to determine the physical and chemical properties of the materials. In this study, the physical properties of HTlcs were determined using powder X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and N_2 adsorption. Meanwhile, Fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray (EDX) were used in determining the chemical properties of the HTlcs. Additionally, the reducibility of the materials were determined using Temperature Programmed Reduction (TPR).

3.4.1. Powder X-ray Diffraction (XRD)

X-ray powder diffraction or XRD is a rapid analytical technique which is used for phase identification of a crystalline material and can provide information on unit cell dimension (size and shape of unit cell). Apart from that, there are a number of other information that can be obtained from XRD data which include the structure solution (position of atoms in the crystal lattice) and also structure refinements [1].

Atoms in crystals produce interference when they interact with X-ray waves and it can be imagined as the atoms are reflecting or scattering the waves. Figure 3.1 shows a beam of X-rays entering a crystal with the plane of atoms being at angle θ to the incoming beam of the monochromatic X-rays.

Ray 1 and Ray 2 (Figure 3.1) reflects off the respective planes at an angle θ equal to the angle of incidence. Ray 2 will travel a distance of 2a farther than Ray 1. Constructive interference occurs when the distance 2a is equal to an integral number of wavelengths ($n\lambda$) since both of the rays will be in phase when exiting the crystal. When the value of 2a is not an integral number of wavelengths destructive interference will occur.

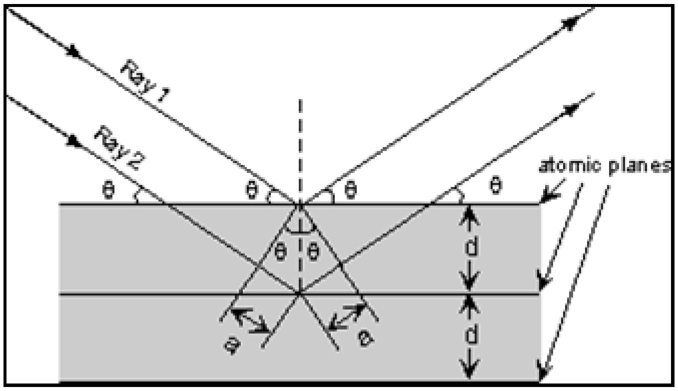

Figure 3.1: Paths of X-ray beams for Bragg's law

Therefore, the condition for constructive interference to occur is

$$n\lambda = 2a$$

then using trigonometry 2a can be written in terms od the spacing, d, between the atomic planes as in the following equations.

$$a = d \sin \theta$$

$$\text{or } 2a = 2\, d \sin \theta$$

$$\text{Thus} \qquad n\lambda = 2d'\sin \theta \qquad (3.1)$$

Equation 3.1 is Bragg's law which must be met for diffraction to occur. In equation 3.1, n is the order of diffraction and it can be any integral value consistent with sin θ not exceeding unity and is equal to the number of wavelengths in the path difference between rays scattered by adjacent planes. According to Bragg's law, if the wavelength , λ of the X-rays entering the crystal in known and the angle θ of the diffracted X-rays can be measured, then it is possible to find out the spacing or d-spacing between the atomic planes of the crystal.

X-ray diffraction, XRD may occur when Bragg's law is satisfied. This can be achieved by using three main diffraction methods which are Laue method, rotating crystal method and powder method. In each of the methods, the quantities either λ or θ are varied to satisfy Bragg's law. The XRD method that will be utilized in this study is the powder method. In this method, the crystal sample that is to be is already in the form of loose or consolidated microscopic grains or it is reduced to a very fine powder. The sample will be positioned in a suitable hold and is placed in a beam of monochromatic x-rays. The units that make up each particle is a tiny crystal, or assemblage of smaller crystals. The particles will be oriented randomly with respect to the incident beam. In a coincidence, some of the crystals will be correctly oriented so that their (100) planes, for example, can diffract the incident beam. Meanwhile, other crystals will be correctly oriented for the 110 reflections and so on. As a result, every set of lattice planes will be capable of diffraction. The mass of powder used in this method is equivalent to a single crystal rotated about all possible axes.

Whenever, a single crystal specimen is not available, the powder diffraction is the only method that can be used to characterize the sample by means of XRD. The method is most suitable for determining the lattice parameters with high precision and for the identification of phases both that occur alone and in mixtures for example polyphase alloys, corrosion products, refractories and rocks [115].

The XRD pattern consists of a series of peaks. The peak intensity is plotted on the ordinate (y axis) and the measured diffraction angle, 2θ, is plotted along the abscissa (x axis). Each peak or reflection corresponds to x-rays diffracted from a specific set of planes in the specimen and these peaks have different intensities. The information about atom position is provided by intensities of the reflection. The width of an individual peak, or the full width at half the maximum height (FHWM) can be used to determine the crystallite size and the presence of lattice distortions (strain) in the crystal [115].

The factors that determine peak positions in an XRD pattern is the crystal structure (the shape and size of the unit cell) of the material (effects of texturing are ignored and the use of polycrystalline sample is assumed) and this will enable the determination of the structure and lattice parameter of the material. Additionally, the wavelength of the x-rays used also determines the peak positions. Symmetry of the crystal structure have to be considered because as the symmetry of the crystal structure decrease, the will be an increase in the number of peaks [115]. Another characteristic that can be obtained via XRD is the unit cell dimension or the lattice parameters. Lattice parameter a represents the mean cation-cation distance in the brucite-like layer may be calculated from the expression $a = 2d_{(110)}$, meanwhile, the parameter c which is three times the distance between adjacent brucite-like layers can be determined from the equation $c = 3\{d_{(003)} + 2d_{(006)}\}/2$ [19].

The advantages of diffraction analysis include the ability of this analytical technique to disclose the presence of a substance as it actually exists in the sample, and not in terms of its constituent chemical elements. Besides that, this technique also gives the phases present in a compound. Additionally, this can also be used to distinguish between different allotropic modifications of the same substance [116].

In the study, powder X-ray diffraction was used to characterize the materials in order to identify the species present and the crystallinity. This can be done using XRD since the powder diffraction pattern determined from the unit cell dimensions and atomic arrangement within the unit cell is unique to a specific crystalline phase. The comparison of measured XRD data with a diffraction diffractogram of a known phase in conducted to identify the phase present in the analysed sample. Comparison of the diffractograms may be done manually or by using a computer searchable crystallographic database [1]. The equipment used was Bruker D8 Advanced X-ray diffractometer with a Cu-Kα radiation source. The 2θ values were from 2° to 80° and the scanning speed used was 1° per second.

3.4.2. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared (FTIR) spectroscopy is a useful chemical analysis tool as this method is able to identify of the structure of an unknown molecule from the molecule's infrared spectrum. This analysis technique may be used for both organic and inorganic materials. This is mainly due to the correlation between the wavenumbers at which the molecules absorbs infrared radiation and its structure. FTIR has been used in a broad range of fields including material science, catalysis, biochemistry etc. [117].

Most FTIR spectrophotometer use the Fourier Transform technique with a Michelson interferometer (Figure 3.2). The infrared spectrum is obtained when interference in the radiation reaching the detector is generated when one mirror of the interferometer is moved. This will produce an interferogram (function of mirror movement, cm) with a complex pattern which then subjected to Fourier Transform in order to obtain the final adsorption spectrum which is a function of wavenumber (cm^{-1}) [117].

An infrared spectrum is a plot of measured infrared radiation intensity versus wavenumber (reciprocal of wavelength). The infrared spectra are traditionally plotted with high wavenumber on the left and low wavenumber on the right. The Y axis of the infrared spectra can be plotted as absorbance or transmittance. The former will give upward pointing peaks which represents wavenumbers at which the sample absorbed infrared radiation. Meanwhile, the latter will give peaks that point downwards which represents wavenumbers where sample transmitted less infrared radiation. Nonetheless, the molecular structure only depends on the X axis as it is in correlation with the wavenumber of the peaks. [118].

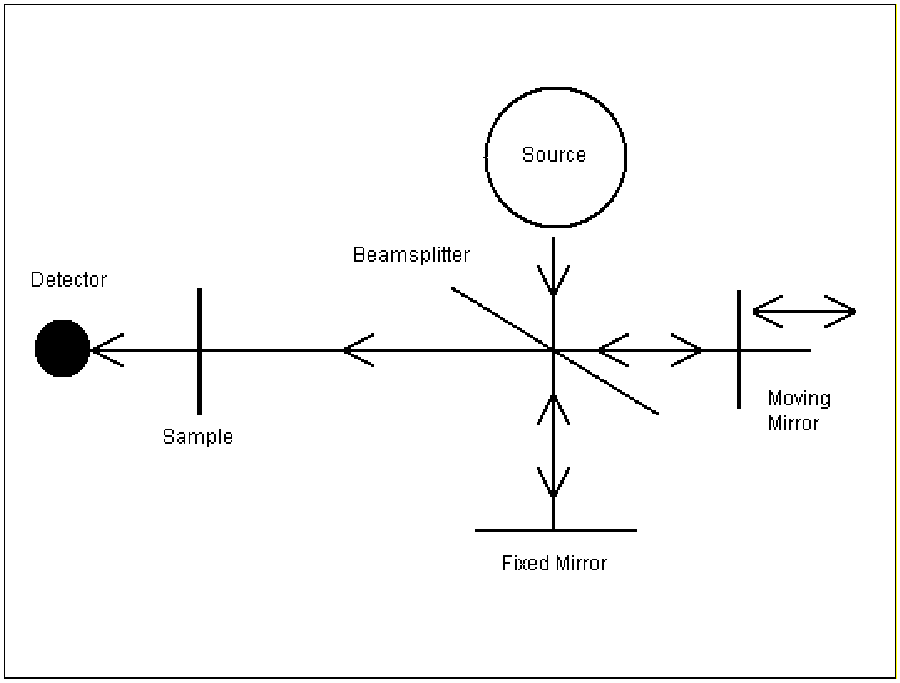

Figure 3.2: Diagram of Michelson Interferometer [83]

The Fourier Transform Infrared Spectroscopy (FTIR) is used in this study to characterize the materials as it can identify structural features of the anions that exists within the interlayer of the HTlcs [101]. This technique can also show the presence of impurity phases [107]. The FTIR analysis was conducted using a Shimadzu FTIR-8400S spectrometer. The samples were mixed with KBr to produce a pellet. The advantage of using the KBr pellet technique is KBr has no adsorption above 250cm^{-1} therefore it will not interfere (impede) the spectrum of the analyzed sample [117]. The spectra were recorded between 4000cm^{-1} and 400cm^{-1}. Twenty scans were recorded with a resolution of 1cm^{-1}.

3.4.3. Field Emission Scanning Electron Microscopy with Energy Dispersive X-ray (FESEM-EDX)

Field emission scanning electron microscopy (FESEM) is an analysis technique which can be used to investigate the morphology of a material and it is a variation of the scanning electron microscopy (SEM). In this technique, the scanning electron microscope which has a small electron probe is scanned on the surface of the specimen and by synchronizing the intensity of the resultant signal with the probe position one may obtain the intensity of the signals [119]. The use of an electron beam in SEM to produce images is possible by using an electron manipulation technique for the electron beam and operating it under vacuum conditions. The intensity of the final current and the diameter of the incident beam over the sample determine the final image resolution [120].

Energy dispersive X-ray (EDX) or energy dispersive spectroscopy (EDS) is used to determine the composition of materials. The EDX spectroscopy is the spectroscopy of characteristic X-rays resulting from inner-shell excitation [119]. EDX is usually used in conjunction with the scanning electron microscopy (SEM). The exposure of specimens to incident electrons during EDX results in the excitation of inner shell electrons in the surface atoms to higher energy levels. Consequently, the atom becomes unstable and causes a de-excitation which is followed by the emission of an X-ray [86]. The energy from the characteristic X-ray may be used to identify the elements present in the material since the X-ray peak is specific to each material. Although EDX is a useful characterization tool, it can only detect elements heavier than beryllium since the X-ray emission in this technique is more prominent for heavier elements compared to the lighter elements [119].

The morphologies of the HTlcs were determined using a Carls Zeiss Supra 35 Vp field emission scanning electron microscope. The magnification used in the study was 30000 and the voltage used was 5kV. The elemental analyses of the samples were investigated using energy dispersive X-ray manufactured by Oxford-INCA at a voltage of 20kV.

3.4.4. Specific Surface Area and Porosity Determination by N_2 Adsorption

The specific surface area and porosity are important characteristics of porous solid adsorbents. A widely used technique for the measurement of specific surface area is the basic BET method which was developed by Brunauer, Emmett and Teller (BET). The BET model shown in equation 3.2 accounts for multilayer adsorption and it can be used to extract the multilayer capacity and the specific surface area. This surface area is sometimes called the BET-surface and it is the surface of a monolayer adsorbate of N_2-molecules at boiling temperature of N_2 which is 77.3K at p_0 equals to 1 atm. The surface area measurements are usually determined by nitrogen adsorption at liquid N_2 temperatures (77.3K) for partial pressures up to 1 [42], [47]. The porosity of HTlcs has been characterized using this method in a number of previous researches [18], [24], [93].

$$\frac{p}{(p_0 - p)m^a} = \frac{C-1}{Cm_1}\left(\frac{p}{p_0}\right) + \frac{1}{Cm_1} \tag{3.2}$$

In the BET equation above, C and m_1 are parameters that are determined by a data fitting procedure which is preferably within the pressure range between $0 < p/p_0 < 0.3$. Meanwhile, the BET-surface A_{BET} of the monolayer can be calculated using equation 3.3. In the equation, the assumed cross section σ_{N2} is equal to 0.162 $(nm)^2$ per N_2 molecule and M_{N2} with the value of 28g/mol is the molar mass of nitrogen [42].

$$A_{BET} = \sigma_{N2} m_1 / M_{N2} \tag{3.3}$$

Apart from using nitrogen adsorption, the pore system of a solid adsorbent can also be characterized by various other methods which include mercury intrusion porosimetry, helium measurements and adsorption of other gases such as argon or carbon dioxide [42].

The full N_2 adsorption isotherms for specific surface area, pore size and pore volume were obtained using an adsorption instrument from Micromeritics ASAP 2000. Prior to the recording the isotherm, the samples were degassed at 400°C.

3.4.5. Temperature-Programmed Reduction (TPR)

Temperature Programmed Reduction (TPR) is a technique used for chemical characterization of solids whereby simultaneous reduction of the solid by gas and a predetermined temperature change of the system occurs. The records from the analysis of the gaseous products of a TPR experiment can be derived to give the chemical information of the solid tested.

Usually in a TPR apparatus, the solid is reduced by flowing hydrogen. The concentration of the hydrogen is monitored downstream of the reactor. The analysis record of TPR is the consumption and usually displayed as a function of temperature of the reactor, provided that reduction has taken place over the temperature excursion of the reactor. Figure 3.3 shows a typical reduction profile.

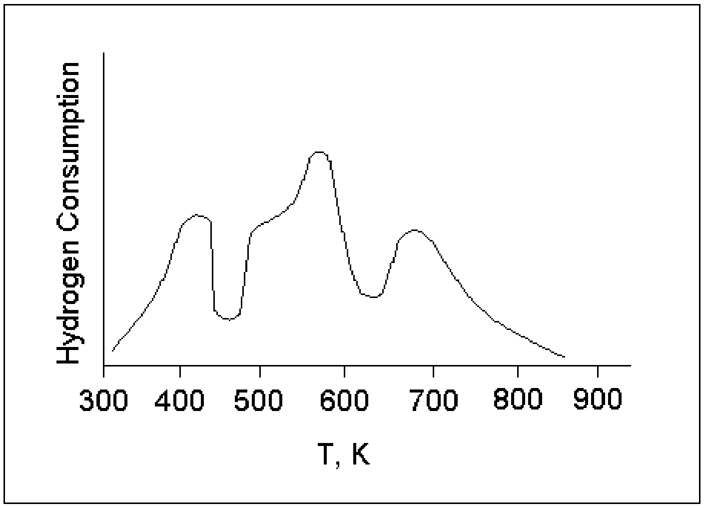

Figure 3.3: Reduction Profile [87].

In the reduction profile shown in Figure 3.3, the peaks represent a distinct reduction process involving a particular chemical component of the solid. The position of the peak reflects the chemical nature and environment of the chemical component while the area of the peak shows the concentration of that component present in the solid.

TPR is a highly sensitive technique of solid characterization and depends solely on the reducibility of the solid. Nonetheless, the condition that the solid must be reducible is not mandatory because the solids can be reduced by first mildly oxidizing the solids before initiating the TPR experiment. This conditions have made TPR attractive compared to other solid characterization technique as it can be used in a wider range of applications. TPR has many advantages, for instance in chemical analysis, the technique has the advantages of being sensitive and non destructive. Additionally, the solids do not have to be dissolved and it is particularly strong on the identification of the valence states of metallic components [121]. In the characterization of HTlcs, a number of studies involved the use of TPR to determine reducibility of the materials [17], [24].

The materials were calcined in air at 450°C, 600°C, 750°C and 900°C for two hours prior to the TPR experiment to provide mixed oxides for the following reduction process [122]. For the TPR experiments, a Thermo Finnigan TPDRO 1100 apparatus was used. The TPR of the materials were conducted using a mixture of H_2 (5%) and N_2 (95%) gas in order to investigate the HTlcs' reducibility and possible hydrogen uptake [123]. During the reducibility determination, a sample amount of about 0.15mg was placed in the sample holder and placed in the TPR apparatus. The sample was then heated from room temperature (28°C) at 20°C per minute until the temperature reaches 600°C with 5%H_2/N_2 gas flowing at 20ml/min. The temperature of 600°C is used since at this temperature it has been determined that the water, hydroxyl groups and interlayer carbonates have been eliminated and spinels are not yet formed at this temperature [124], [125]. Then at 600°C, the temperature is kept constant for 10 minutes during which all reducible components are expected to be reduced to metals. Afterwards, the temperature is lowered until it reaches room temperature to see the possible adsorption of H_2. The reduced samples were then characterized by XRD to identify the species present.

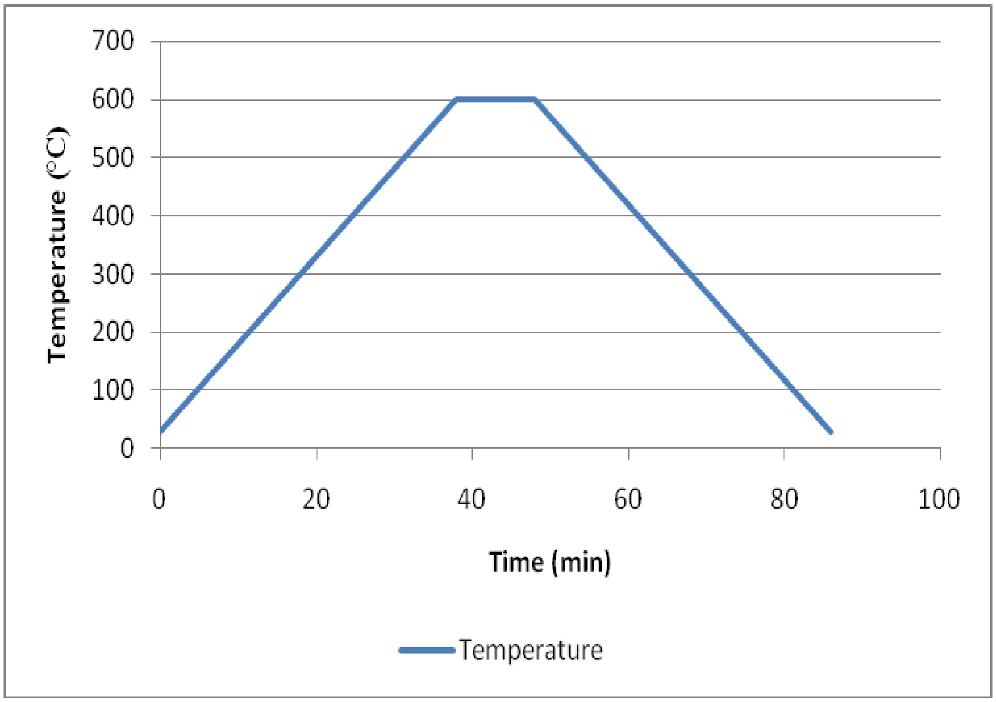

Figure 3.4: The temperature profile for Temperature-Programmed Reduction experiments

3.5. Thermogravimetric Analysis (TGA)

The term thermogravimetric analysis (TGA) refers to the study of weight changes of a specimen as a function of temperature. The technique is useful strictly for transformations involving the absorption or evaluation of gases from a sample which consists of a condensed phase. TGA devices have balances which are highly sensitive with resolutions as small as 1mg and these TGA can be applied in various investigations such as the decomposition of clays to high temperature oxygen uptake in the processing of superconducting materials [91]. The difference between TGA behavior compared to Differential Thermal Analysis or Differential Scannning Calorimetry (DTA/DSC) is mass loss or gained in this technique will not be reversed. Therefore, the use of slow heating rate in TGA does not influence its sensitivity. In TGA, highly sensitive balance which allows the use of small specimens is preferable in order to avoid temperature gradient and gaseous compositional gradient within a granulated specimen.

The thermogravimetric analysis (TGA) in this study was conducted using a Perkin-Elmer Pyris 1 thermal gravimetri analyzer and samples used in the experiments were 10mg. The experiments were carried out according to the temperature profile shown in Figure 3.5. The temperature profile can be divided into two parts. The first part is the pretreatment part where the temperature of the system was heated under H_2-N_2 (5% H_2/95%N_2) atmosphere at a rate of 15°C per minute until the temperature reached 600°C. Then the system temperature is kept constant at 600°C for 15 minutes. The purpose of conducting the pretreatment is to remove adsorbed water, interlayer water, bonded hydroxyls and interlayer carbonate and to obtain fresh adsorbent for the gas adsorption process. Additionally, pretreatment of the material also intend to produce mixed oxides with hydrotalcite skeletal structure for the subsequent H_2 storage [122].

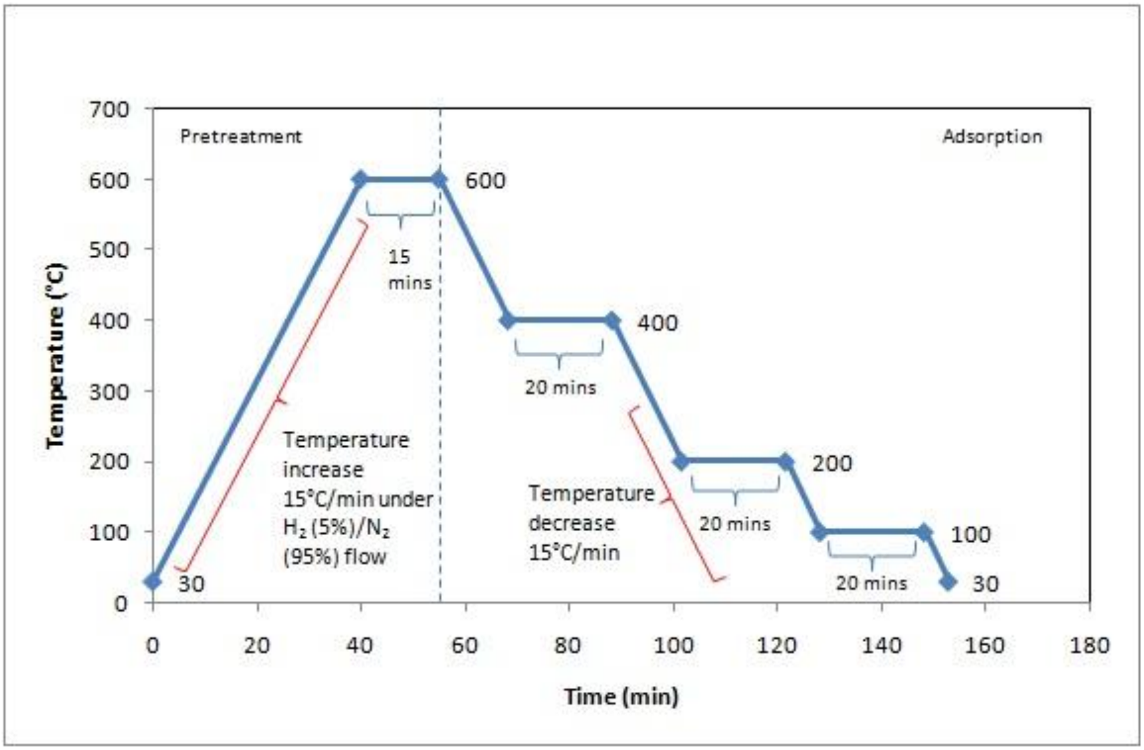

Figure 3.5 : Temperature Profile for Thermogravimetric Analysis of HTlcs

The second stage is the reduction of mixed oxides at 600°C. During this stage, all reducible mixed oxides are expected to totally or partially reduce. The third stage is the adsorption stage where the temperature of the system is lowered to 400°C and the temperature is kept constant at this value for 20 minutes. Subsequently, the temperature is then lowered and kept constant for 20 minutes at holding temperatures of 200°C and 100°C until it is finally lowered to the room temperature. The system temperature is kept constant at the selected holding temperature in order to investigate the total adsorption capacity that occurs at each temperature. The holding temperatures were applied in this study in order to allow the system to reach steady state where no appreciable change of mass occurred. The system temperature is kept constant at the selected holding temperatures in order to investigate the equilibrium adsorption that occurs at each temperature [122].

In the hydrogen adsorption experiments using thermogravimetric analysis the temperature 600°C is chosen because at this temperature the water, hydroxyl groups and interlayer carbonates have been eliminated and the mixed oxides are formed [111], [125]. The temperature is held at 600°C to allow reduction of the mixed oxides. Next, the first holding temperature is at 400°C as this is in the temperature range for hydrogen production by steam methane reforming (400-600°C) [38], [35]. A significant hydrogen adsorption capacity at this temperature will make the adsorbents applicable as hydrogen storage material at high temperature after production. Meanwhile, the holding temperatures of 200°C and 100°C are chosen since these are within the common temperature range chosen in a number of previous studies on hydrogen storage using metal oxides and metal hydrides [26], [126]-[129].