CHAPTER 2

LITERATURE REVIEW

2.1 Energy Demand versus Energy Storage

In 1990, the world population was 1.6 billion and the primary energy consumption was about 1000 million-Ton Equivalent of Petroleum (Mtep). In 1997, the population increased to 6.5 billion and the primary commercial energy consumption increased to 11,700 Mtep (Kayfeci & Keçebaş, 2019). This is a clear instance to show the increase of over eight times in primary energy consumption of the world within a century and an influence of population growth towards the energy demand. Report from International Energy Agency (IEA) stated that in 2020, global energy demand experienced falling by 4%, the largest absolute decline since World War II. This was the impact from the pandemic on global energy use. Surprisingly, the global energy demand is expected to be escalated by 4.6% in 2021 that will be surpassed pre-COVID-19 levels as the COVID restrictions are lifted and economies recover (IEA, 2020). Basically, the term “energy demand” is literally referring to any kind of energy required to meet individual or sectoral energy needs. This relates the relationship between the price and quantity of energy in the form of electricity or fuel. Globally, the energy demand refers not only to energy use but also location, exploitable energy sources and type and property of resources (Hasanuzzaman et al., 2019).

Besides, there is an observation of the impacts of income, carbon dioxide emissions and crude oil price on renewable energy consumption has been made in six major emerging economies (Brazil, China, India, Indonesia, Philippines, and Turkey). The crude oil price plays big role in reducing the adoption of clean energy in China and Indonesia. The carbon dioxide emission and per capita income allow the increase of renewable energy in Brazil, China, India, and Indonesia. This finding contributes to provide valuable perception for emerging economies to improve the share of renewable energy in the main energy mix to reduce carbon intensity (Shang et al., 2022). In Japan, the government is expected to apply hydrogen as an efficient and environmentally friendly alternative energy source in realising a low-carbon society. Currently, they have introduced approximately 150 hydrogen stations and over 3000 fuel cell vehicles (FCVs) into Japanese society and by 2030, they target 900 and 800,000 respectively (Hienuki et al., 2021).

Fossil fuels is the main source but there were enormous environmental impacts came from the combustion reaction of the fossil fuels that release harmful substances such as carbon dioxide (CO_2), carbon monoxide (CO), sulphur dioxide (SO_2) and nitrogen oxide (NOx). This can affect the increasing of CO_2 emissions and lead to the strengthening of the greenhouse effect in the atmosphere. Regarding to the high energy demand and limited reserves of primary energy resources, this the effects cause from the increases in fuel price, the population growth, industrialization, obligation to assess national resources, socioeconomic structuring of the 21st century, the negative effects of existing fuels on the environment including greenhouse effect, global warming, climate changes, rainfall abnormalities, acid rain and health problems (Kayfeci & Keçebaş, 2019). For future energy supply, hydrogen has been identified as an alternative energy and considered a regenerative and environmentally friendly fuel with high calorific value (Escobar-Alarcón et al., 2019). Thus, it becomes the best solution for this problem.

2.2 Hydrogen Energy

Hydrogen energy is the best option for energy sources in the next century due to it being abundant in nature and can be considered as a potential substitution for fuels from fossil sources. Hydrogen energy is high in calorific value and environmentally friendly (Escobar-Alarcón et al., 2019). Besides, one of the characteristics of hydrogen as an energy is that it does not contain toxic properties and cannot cause corrosion. Therefore, the use of hydrogen energy was safe and very simple whereby necessary precautions are taken into place (Kayfeci & Keçebaş, 2019). Hydrogen is the most abundant element in nature but hydrogen in gas form is hardly found on earth. Therefore, an investigation has been carried out to release the hydrogen contained in water (H_2O), which is the most abundant hydrogen compound on earth (Escobar-Alarcón et al., 2019). Water electrolysis method is used to separate water into oxygen and hydrogen via electrical energy.

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

(1.1)

The efficiency of hydrogen production with the electrolysis method is approximately 70%. Nowadays, there are several methods that are being studied to produce hydrogen, but water electrolysis method is the most efficient. For instance, steam-methane reform method where hydrogen is produced from fossil fuels by using thermal energy, but the production is only 40% - 45% approximately. Besides, the reaction between aluminum (Al) and water (H_2O) can produce hydrogen with addition of hydroxide (OH) to accelerate the reaction, but a problem arises because causing corrosion in the hydrogen equipment. The primary purpose of these studies is to obtain high rate of hydrogen at low cost (Tarhan & Çil, 2021).

Basically, hydrogen atoms are comprised of an electron and a proton. It is colourless and odorless. It is the lightest gas ever known (the density rate is 0.089 kg/m^3 at normal condition) which is lower density than density of air (Hassan et al., 2021). The gravimetric density of hydrogen energy is generally about seven times higher than the density of fossil fuels. It is undeniable that hydrogen energy is highly potential to become one of the main energy sources for the future but there are some improvements that need to be done such as in term of transportation and storage when hydrogen is successfully generated (Tarhan & Çil, 2021).

2.3 Hydrogen Storage

When hydrogen is successfully being produced, there are few ways that can be done to store hydrogen safely. Generally, hydrogen storage can be categorised into two main categories: physical based storage and material-based storage. Physical based hydrogen storage means that hydrogen can be stored as a compressed air, liquid, and cryo-compressed form (Kayfeci & Keçebaş, 2019). In state of compressed gas, hydrogen storage has limitation related to the high environment requirement due to the low specific gravity of hydrogen and materials of tank. Hydrogen can be liquefied at -253 °C that required 64% higher energy amount than high pressure hydrogen gas compression which is quite energy intensive process (Elberry, Thakur, Santasalo-Aarnio, et al., 2021). Besides, hydrogen can be stored in both parameters (pressure in compressed gas and temperature in liquid storage) as in cryo-compressed gas storage (Hassan et al., 2021).

Material based hydrogen storage means that hydrogen can be stored using materials such as sorbents, metal hydride and chemical hydrides (Kayfeci & Keçebaş, 2019). Hydrogen can be chemically stored by absorbing or reacting with other chemical compounds such as metals or organic substances (Elberry, Thakur, & Veysey, 2021). Metal hydrides are commonly used because they can store hydrogen at high densities that can exceed liquid hydrogen but there is challenge to store hydrogen in chemical form which is related to hydrogenation and dehydrogenation process considering high temperature and pressure demand (Huang et al., 2021). The categories of hydrogen storage can be referred to Figure 2.1.

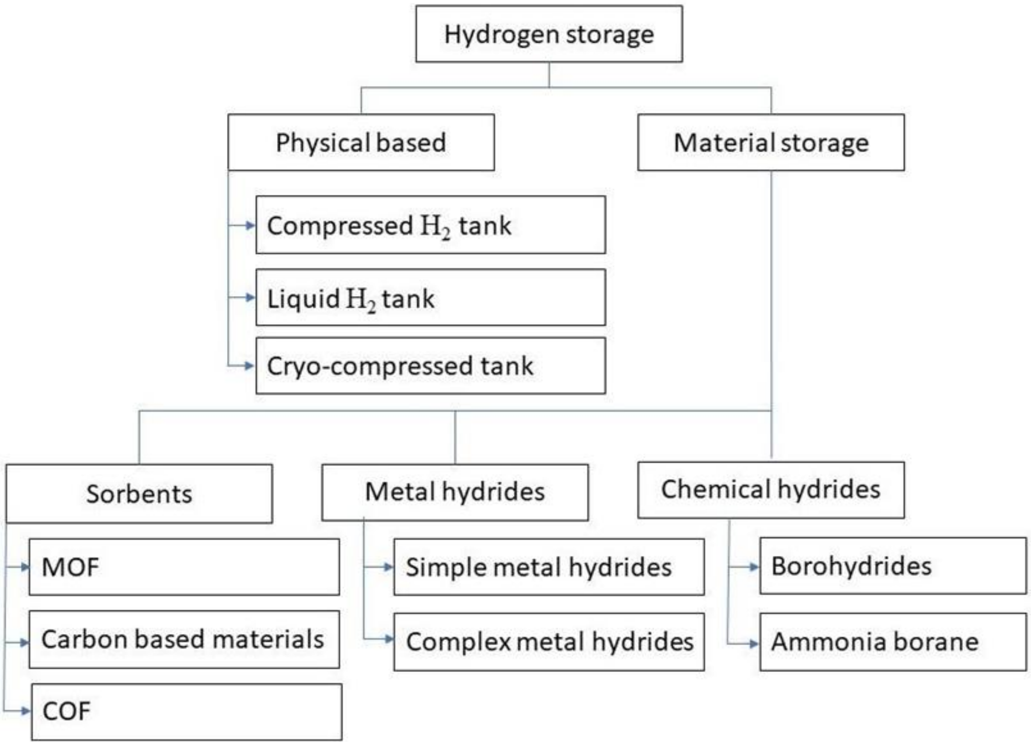


Figure 2.1: Categories of Hydrogen Storage

For large scale and long-term storage purposes, IEA has released a report in June 2019 stating that geological storage (salt caverns), depleted natural gas or oil reservoirs and aquifers are the best alternatives. Salt caverns have efficiency of 98% without any contamination towards the stored hydrogen while the depleted gas and oil reservoirs contain contaminant that must be eliminated first. For aquifers, there is possibility of hydrogen loss due to the reaction with rocks, fluid, and microorganisms (IEA, 2020). In selecting the best way for hydrogen storage, the determination of the storage purpose is crucial whether it is for small or large scale.

2.3.1 Physical-based Hydrogen Storage

Generally, hydrogen can be physically stored in a high-pressure tank, in the form of liquid and in a cryo-compressed tank. In high pressure resistant tank, hydrogen is stored depending on the type and weight of the tank (Elberry, Thakur, Santasalo-Aarnio, et al., 2021). Hydrogen gas needs to be compressed with pressures between 200 and 500 bar (Hassan et al., 2021). To store more hydrogen, the tanks are required to be lighter and more durable but it is considered as cost consuming (Olabi, Bahri, et al., 2021). This storage tanks are manufactured with well-defined safety guidelines especially in the aspects of their design, use and maintenance (Papadias & Ahluwalia, 2021). For instance, suitable materials are crucial for pressure tanks that can resist and oppose the effect of hydrogen at ambient temperatures such as austenitic stainless steel, aluminum, and copper alloys. If using other metals, some of them are prone to embrittlement caused by hydrogen adsorption and dissociation at the surface of the materials that can reduce the strength and durability of the tanks (Elberry, Thakur, Santasalo-Aarnio, et al., 2021). The compressed hydrogen gas storage tank is shown in Figure 2.2 below.

Source: (Kayfeci & Keçebaş, 2019)

Figure 2.2: Compressed Hydrogen Gas Storage Tank

To store hydrogen in the liquid form, the condition is required to be in a well-insulated tank with the temperature of -253 °C at atmospheric pressure. The liquid form of hydrogen consists of 3 times more energy than equivalent weight petrol and 2.7 times more volume was needed to equivalent the energy. This is the reason why the liquid form of hydrogen has a high volumetric energy density, making it easier to store and transport. The process of converting hydrogen gas into a liquid is known as the liquefaction process. This process uses multiple instruments such as compressors, heat exchanger, expansion engines and throttle valves to achieve desired cooling temperature (Kayfeci & Keçebaş, 2019). This method is more efficient and suitable for larger volumes and longer distances (Hassan et al., 2021).

2.3.2 Material Storage

Material storage can be considered as an alternative way to store hydrogen. In some extend, material storage has potential to compete with physical based storage of hydrogen (Rozzi et al., 2021). Material storage can be divided into sorbents, metal hydrides, and chemical hydrides. Among these three materials, only sorbents-based storage involves physical interaction towards hydrogen gas. To be exact, sorbents utilise Van Der Waal’s force to absorb hydrogen molecules (Clark et al., 2019). Metal hydrides consist of metal atoms with lattice imperfections and hydrogen molecules within lattice cavities. The hydration process through chemical adhesion and the electrochemical separation of water (Tarasov et al., 2021). Chemical hydrides such as sodium borohydrides, are liquid based hydrides. They release hydrogen in the form of solution and transform into sodium metaborate. However, the hydrogen obtained from the system is humid (Min et al., 2023). In conclusion, sorbent-based storage is more practical compared to the other methods because of its simple and safe storage mechanism, which involves fewer chemical processes.

2.3.2.1 Sorbents

Basically, sorbents are materials with high adsorptive capacity. In the process of adsorption, analysing the molecular structure of sorbents and understanding the chemical-physical mechanisms is promising due to its potential in the application of hydrogen storage (Clark et al., 2019). Sorbents are made up of synthetic or natural materials. They can be found in nature as raw materials or can be produced synthetically in the laboratory.

There are several microporous sorbent materials that have been investigated such as metal-organic frameworks (MOF), carbon-based materials and carbon organic frameworks (COF). The gas adsorption capacity of these materials needs to be studied for a few parameters including the surface area, the pore volume, the particle size distribution, thermal conductivity, and the packing density. Unfortunately, there are no materials yet success to achieve all these characteristics required for their purpose at room temperature (Rozzi et al., 2021).

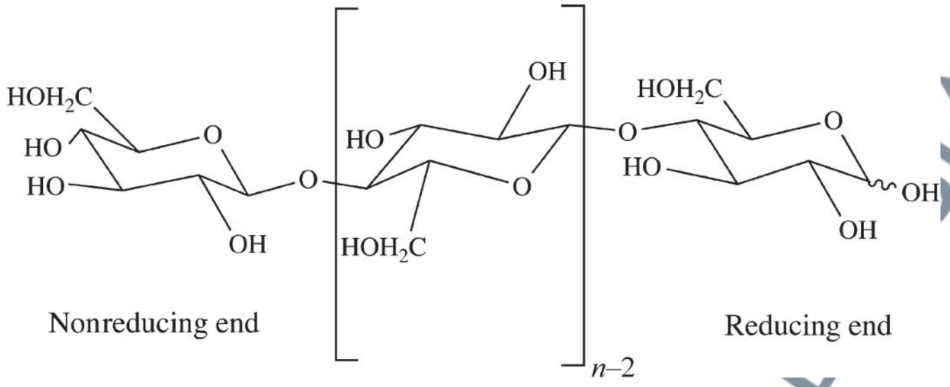
Carbon based materials are the most suitable candidate for gas storage, especially hydrogen gas. It is because it can be synthesised into very small particles with high porosity that can be a great contribution to adsorption process between the carbon atoms and the hydrogen molecules where Van Der Waal’s force is applied (Kayfeci & Keçebaş, 2019). CA is one of the examples of carbon-based materials. In the synthesis of CA, it is important to choose the right precursor because the variation of precursor materials can control the carbon’s pore structure. This is the benefits from the carbon’s high surface area and microporosity (Czarna-Juszkiewicz et al., 2020). Sorbents can exist in powder, granules, flakes, cylindrical pellets, spheres, and fibers. They can be categorised based on the pore sizes of the inner structure which are mesoporous and microporous (Clark et al., 2019).

CA can be synthesised from various carbon precursors, such as carbon nanotubes (CNT), which have been described by Wang et al. (2021) for the preparation of carbon nanotube/cellulose aerogel derived from biomass. The CNT suspension was first prepared and mixed with cellulose to form the CNT/cellulose suspension. Then, the suspension was freeze dried to form CNT/cellulose aerogel. Lastly, the aerogel was undergoing pyrolysis under a nitrogen (N_2) atmosphere to obtain the final CA (Wang et al., 2021). Besides, Yu et al. (2017) used sodium carboxymethyl cellulose (CMC) as a carbon source to prepare CA. Both researchers, demonstrate the synthesis process of CA by sol-gel, freeze-drying, and pyrolysis using carbon sources and succeed in obtaining CA with high porosity and high surface area, which contribute to the characteristics of a hydrogen storage material.

2.4 Cellulose

Cellulose is the main polymer constituent of plant walls that can be extracted directly from biomass and agricultural waste such as oil palm mesocarp fiber, oil palm, rice straw, corn, sugarcane bagasse and starch (Thi Thuy Van et al., 2022). Cellulose is the first candidate for green synthesis because it is biodegradable, biocompatible, sustainable, renewable, nontoxic, and inexpensive (Ajayi et al., 2022). For instance, banana tree wastes can be chosen as one of the main sources of cellulose as banana is planted worldwide and one of the main export products of many countries. Banana tree wastes need to be fully used and benefitted because more than 50% of total banana stem are made up from cellulose (Thi Thuy Van et al., 2022).

Besides, it existed in some lower plants including algae and mosses and can be produced by fungi and bacteria. The chemical structure of cellulose remained the same even though coming from different sources. Generally, β-D-anhydro glucopyranose was the basic monomer unit of cellulose. These units were joined together covalently by acetal functions between the equatorial group of the C4 carbon atom and the C1 carbon atom (β-1, 4-glycosidic bonds). These linkages put up cellulose that represented the structure of cellulose as shown in Figure 2.3.



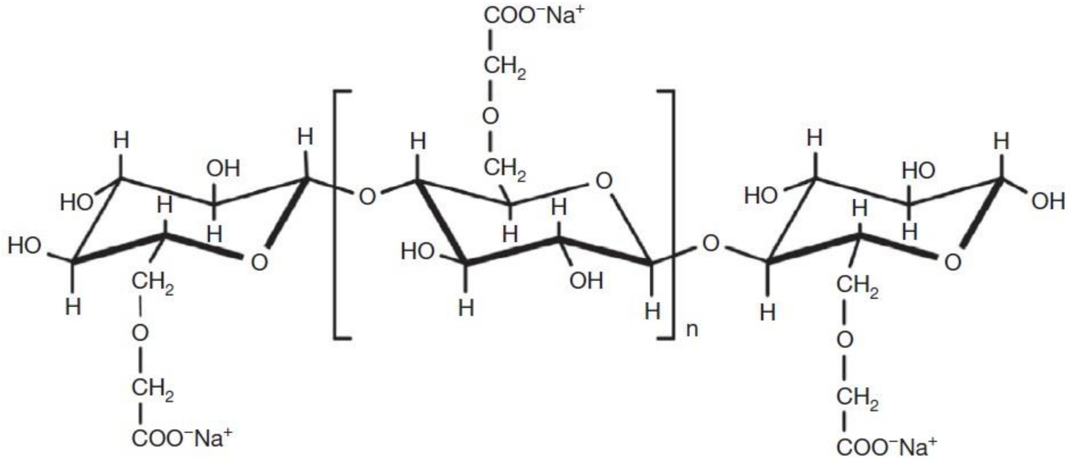
Source: (Ergun et al., 2016)

Figure 2.3: Structure of Cellulose

A building block of cellulose was made up from beta linkage which caused the formation of extended and rigid conformation with each glucose ring 180° from its neighbour. Lots of cellulose chains are aggregated together in parallel by hydrogen bonds to form a highly compact, fully extended sheet structure. Van der Waals interactions assembled these sheet structures. Each cellulose chain was composed of one reducing end terminated with C1-OH group, which is in equilibrium with the aldehyde structure while the other end was non-reducing end with C4-OH group. This had led to the stable property of cellulose and its aqueous insolubility. Then, imparted cellulose with its characteristic properties of hydrophilicity, crystallinity, and chemical modifying variability due to the abundant presence of hydroxyl groups. These hydroxyl groups were basis for extensive hydrogen bond network, which formed the highly rigid and ordered cellulose molecular structure (Aravamudhan et al., 2014).

2.5 Carboxymethyl Cellulose (CMC)

CMC is an anionic, water-soluble cellulose derivative and major cellulose ether (Dürig & Karan, 2019). In production of CMC, the concept of reactive structure fraction was applied by activating the non-crystalline region of cellulose and the selective regions of alkylating reagents can attack the cellulose. Besides, the same reaction can be done by derivatisation of cellulose in reactive microstructure, formed by induced phase separation. The usage of sodium hydroxide (NaOH) in anhydrous state and solvents such as dimethylacetamide/lithium chloride (DMA/LiCl) were involved in this process. Solubility of CMC depended on the degree of polymerisation (DP), the degree of substitution and the uniformity of the substitution distribution. Water solubility of CMC was increased as the DP decreased, carboxymethyl substitution uniformity increased. The viscosity of the solution was increased as the DP and concentration increased. CMC can dissolve in water at any temperature. CMC hydrated rapidly due to its highly hygroscopic nature. Thus, it may cause agglomeration and lump formation when CMC powder was added into water. This can be avoided by applying high agitation as the powder was added into the water. Due to its high solubility and clarity of its solution (Ergun et al., 2016). The structure of CMC is shown in Figure 2.4.



Source : (Ergun et al., 2016)

Figure 2.4: Structure of Carboxymethyl Cellulose (CMC)

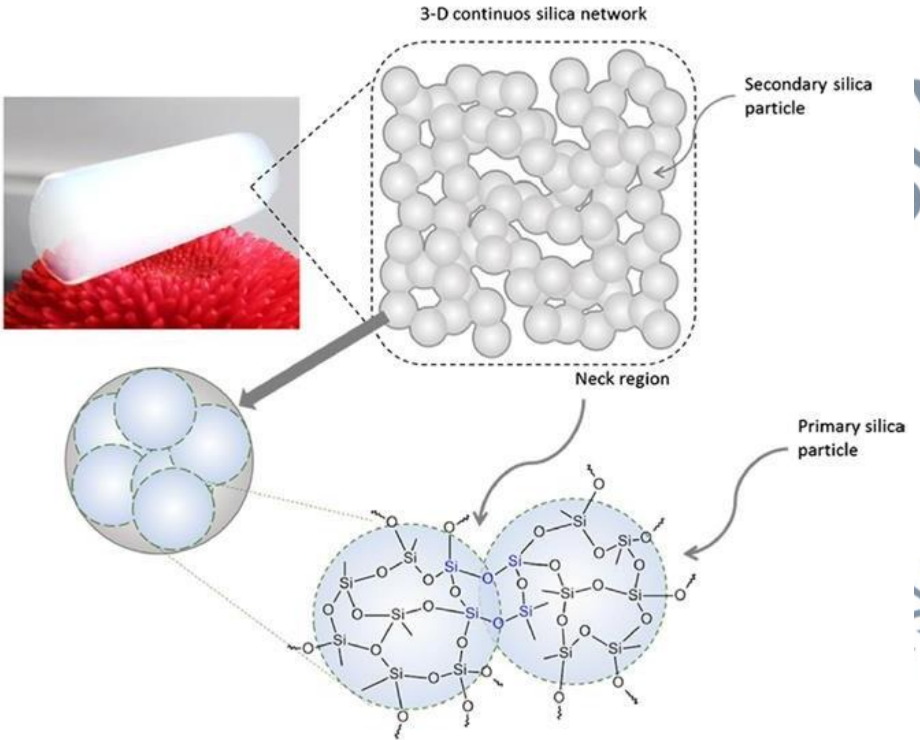
CMC was used as an additive for beverages, drug delivery system for mucosal tissue and scaffold in tissue engineering. Besides, CMC can act as carbon source in the process of preparing CA. Yu et al. (2017) used CMC as a carbon source to obtain CA, but they mixed the CMC solution with nickel sulphate ($NiSO_4$) which acts as a nickel (Ni) source, to form CMC-Ni hydrogel via the sol-gel process for the enhancement of CA (Yu et al., 2017). Then, the CMC-Ni hydrogel was freeze-dried followed by pyrolysis to obtain CA-Ni composites. In addition, Yu et.al. (2018a) used CMC as carbon sources and collagen as nitrogen (N) sources to prepare N-doped CA (Yu et al., 2018b). The preparation process was the same as previous research, starting with sol-gel, freeze-drying and finally, pyrolysis. For both studies, the obtained CA exhibited developed pore structures and high surface areas, which were the main characteristics of hydrogen storage materials owing to the presence of foreign substances in its structure. The CMC can be crosslinked with foreign substances to form a crosslinked network structure due to the presence of carboxyl groups, as shown in Figure 2.4. Thus, the properties of CMC-based CA can be enhanced for hydrogen storage materials.

2.6 Aerogel

Aerogel is a gel composed of a microporous solid in which the dispersed phase was a gas. When light was dispersed through them, they became translucent and smoked. If the aerogel were derived from biopolymers, they would appear as soft and thin foams compared to the others carbon-based aerogel, they looked like crunchy black bodies. The term aerogel was used for sol-gel materials which is during preparation process, the liquid component of the gel was substituted by gas, leaving only a solid nanostructure without pore collapse. The volume of the gel was made up of 90%-99%

of air (Reyhani et al., 2021b). The composition and nano structure of aerogel were controlled based on the preparation steps and chemical reaction parameter to obtain a dry porous body in monolithic form or granules. The microstructure of aerogel was formed by solid continuous network of primary and secondary colloidal particles connected to each other by condensation or cross-linking or by the formation and aggregation of fibrils because of the arrangement of polymer chains on macromolecules as shown in Figure 2.5 (Montes & Maleki, 2020). Liquid from the solid wet gel was extracted through techniques that can make the gel dry with low to minimal structural deformations. Aerogel showed promising physical properties that made it attractive to scientists or technology researchers because of its low density. The typical densities value of stable silica aerogel was between 0.02 and 0.2 gcm^{-3}.

Aerogel had a very high specific surface area of around 300-1500 m^2g^{-1} due to its low weight/volume ratio. Thus, made it the best candidate materials for light weight applications. Besides, aerogels had high specific surface area and highly porous solid with nanometer pores. Any materials with a pore size of 2-50 nm were called mesoporous materials which aerogels were one of them. This feature made aerogels the best reinforcement for polymer composites where aerogels can be used as mesoporous fillers. The aerogels can induce the high interaction between the polymer and the filler. Aerogels had different types and CA was one of them. CA were very light because they consisted of carbon element (Reyhani et al., 2021b). Thus, made them to have a high specific area and contributed to superior physical properties in aerogel. Aerogel can be categorised based on its composition such as inorganic aerogel, organic aerogel, hybrid aerogel and carbon aerogel.



Source: (Montes & Maleki, 2020)

Figure 2.5: Microstructure of Aerogel

2.7 Carbon Aerogel (CA)

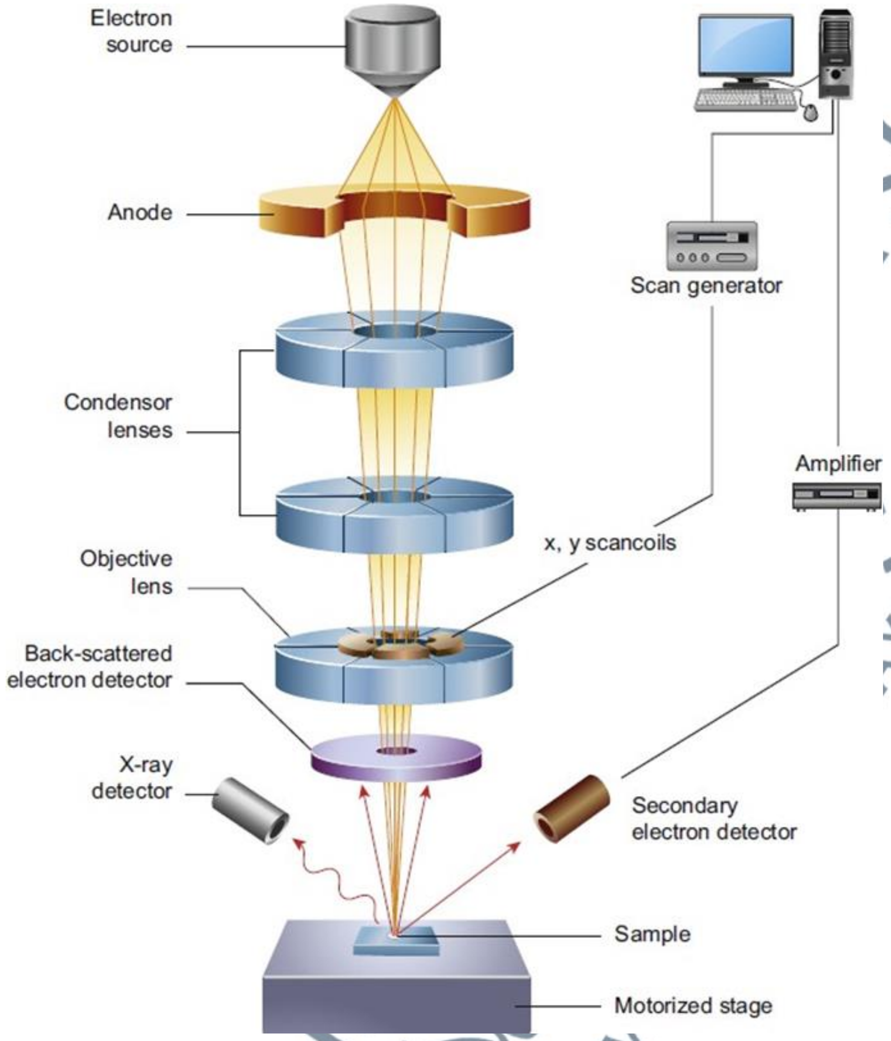
Carbon Aerogel (CA) is a promising type of carbon material due to its merits such as high porosity, large surface area, low density, corrosion resistance and high electrical conductivity. CA was conventionally prepared by carbonisation of organic aerogels such as resorcinol/formaldehyde aerogels, cresol/formaldehyde aerogels and phenol/formaldehyde aerogels. However, this type of CA were high costs, utilising toxic precursors and involved complicated synthesis process that hinder their mass production and commercialisation (Yu et al., 2017). Generally, CA was synthesised from pyrolysis of organic polymers in an inert atmosphere. The agglomerate of uniform spherical carbon particles was made up of the structure of CA as it contained interlaced meshes of microcrystalline platelets with micropores of about 0.6 nm. The thermal treatment was performed to increase the structural order of the CA. The changes in the pore structure of CA were at high temperature and can be up to 2800 °C. At temperatures up to 2000 °C, the micro porosity of CA disappeared while the meso porosity remained even after heat treatment up to 2800 °C. However, half of the volume of mesopores will be lost from the fusion of carbon particles. Besides, CA was fragile after pyrolysis because there will be a substantial collapse of their structure that later affected the application of CA (Montes & Maleki, 2020).

In the fabrication of CA as hydrogen storage material, there are several methods that can be applied, but at the present time, most researchers choose to use a simple, direct, and safe method such as pyrolysis. They derived CA from various carbon sources, such as CMC, CNT, graphene, and resorcinol/formaldehyde (R/F) via pyrolysis. Because of its ability to crosslink with foreign materials and contribute to the enhancement of CA, CMC is a highly promising candidate as the best carbon source to prepare. Yu et al. (2017) used nickel sulphate ($NiSO_4$) as a crosslinking agent. They mixed $NiSO_4$ with CMC to initiate the crosslinking reaction via the sol-gel process to form the CMC-Ni hydrogel. Then, the hydrogel was freeze-dried to form CMC-Ni aerogel. Lastly, the CMC-Ni aerogel was pyrolysed to obtain CA. The obtained CA was high in porosity and surface area and consisted of mesopore, which are the main characteristic of hydrogen storage materials. This method is recommended for this research because it is simple, safe, and environmentally friendly. Besides, there was another researcher who prepared CA-Pt to enhance the hydrogen uptake capacity of CA. Zhong et al. (2018) fabricated Pt-doped CA (CA-Pt) for hydrogen storage. They prepared pristine CA first and then mixed it with a platinum chloride ($PtCl_2$) solution at room temperature to irradiate the mixture. After irradiation, CA was washed with ethanol and deionized water. Pt-doped CA was derived from the drying of the resultant monoliths in a vacuum drying oven. The CA showed increased hydrogen storage capacity when doped with metal (Zhong et al., 2018). In this research, CMC crosslinked with metal ions is a potential candidate as carbon precursor to synthesis CA as hydrogen storage materials.

2.8 Analysis of Carbon Aerogel (CA)

2.8.1 Field Emission Scanning Electron Microscopy (FESEM)

Field emission scanning electron microscope (FESEM) was a type of electron microscope that analyse sample surface morphology. Figure 2.6 shows the schematic diagram of the core components of FESEM microscope which consisted of electron gun, electromagnetic lenses, vacuum chamber, sample stage and detector.



Source : (Inkson, 2016)

Figure 2.6: Schematic Diagram of The Core Components of FESEM

Basically, electrons generated from electron guns in FESEM where it accelerates electrons through 1-30kV accelerating voltage. Electromagnetic lenses act to focus the electrons into a beam, adjust beam astigmatism, move the beam across the specimen and the beam raster to generate images. The pressure of the chamber is usually in a high vacuum at 0.1-10-4 Pa, but the vacuum can be reduced to inhibit evaporation of volatile components for any specific specimen. The detectors determine the imaging modes and application range of SEM.

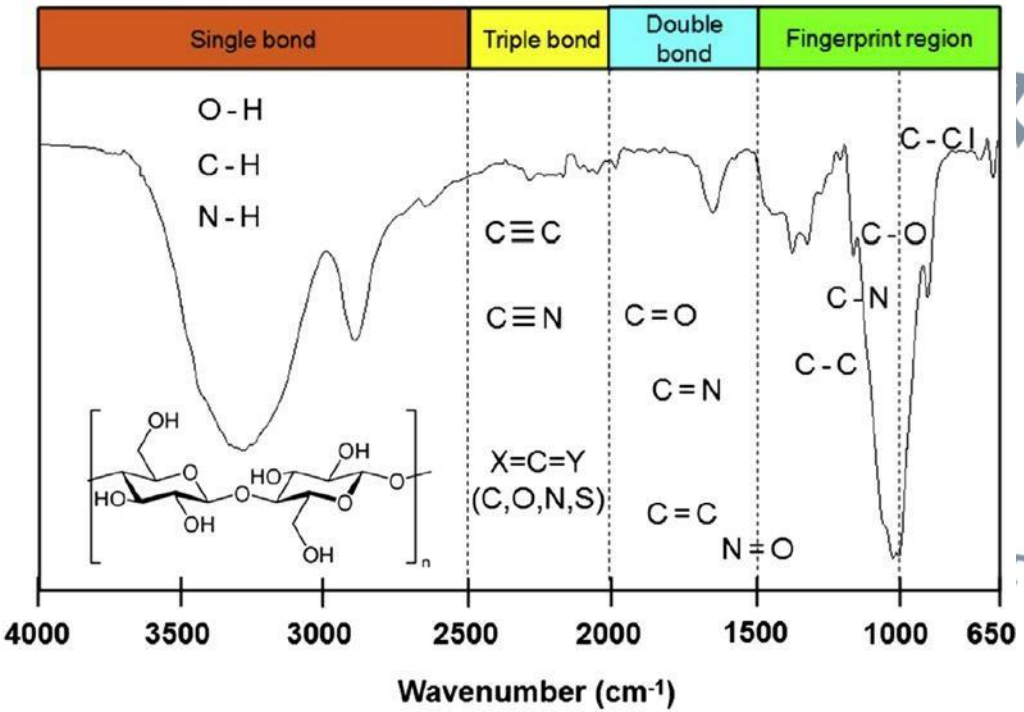
For FESEM analysis, most researchers used FESEM to record the surface morphology of samples. In a research of synthesising carbon aerogel through ambient pressure drying method where R/F gel was prepared and carbonised to obtain carbon aerogel. The sample parameters were varied in terms of catalyst concentration to promote the gel growth. From the FESEM micrograph of the sample, it can be said that CA morphology is dominated by pearl-like particles and clearly visible. All the prepared CA samples showed the microstructure with the configuration of particles and intervening pore structure. The particles were seen as nearly spherical geometry and can be categorised as large particles (>1 µm). Macropores were formed from the interparticle spaces. This was expected to happen due to the low catalyst concentration and lead to the formation of large particles (Pandey et al., 2020).

Compared to the other research, CA samples were derived from CMC through gelation, freeze-drying and pyrolysis process. In this research, CMC was crosslinked with nickel ions, Ni^{2+} to improve the CA structure. The metal ions were varied in terms of concentration. The FESEM images represented the morphology of the as-prepared CA and CA-x samples. From the images, the CA obtained from pyrolysis of pure CMC aerogels exhibited a lamellar structure while CA-x samples showed an interconnected three-dimensional (3D) network structure with the addition of Nickle ions, Ni^{2+}. This may be attributed to the cross-linking reaction between Ni^{2+} and CMC during the aerogel preparation process and formed crosslinked network structure. The porous network structure became denser with increasing Ni^{2+} addition and resulting in a more homogenous pore structure (Yu et al., 2017). Furthermore, previous research used metal ions such as platinum (Pt) which is one of noble metal as a doping purpose in fabricating CA for hydrogen storage. They prepared pristine CA first using R/F aerogel as carbon precursor after sol-gel and freeze-drying process. The R/F aerogel was pyrolysed to obtain pristine CA, and then the pristine CA was doped with a Pt by mixing CA with $PtCl_2$ solution until Pt ions were well dispersed into CA. The SEM images of CA-Pt showed a large amount of metal Pt particles that were well distributed in the framework of CA. The Pt particle was about 300 nm spherical in shape and was called Pt nanospheres. Due to the doping of Pt to CA, the maximum hydrogen storage capacity of CA was increased, even with doping at low content of CA (Zhong et al., 2018). The addition of metal ions to CA structures, whether by crosslinking or doping, has contributed to a promising enhancement of CA structures especially as hydrogen storage materials. Most research used various parameters to enhance the morphology of CA and investigated the changes using FESEM analysis.

2.8.2 Fourier transform infrared (FTIR) Spectroscopy

Membranes were characterised based on surface charge, hydrophilicity and chemical structure and these characteristics can affect their performance significantly. FTIR spectroscopy was the main tool to determine functional groups in the membrane and possible molecular bonds between chemical compounds of membrane. In this analysis, spectrophotometer determined the absorption spectrum for a compound.

FTIR spectroscopy is one of tools for determination of functional group in a membrane together with possible molecular bonds between chemical compounds of membrane. Basically, the IR spectrum obtained lies in the mid-IR region 2.5-15 µm between 4000 and 666 cm^{-1} where many functional groups are in this region (4000-400 cm^{-1}) and the existence of an absorption band in this region can be used to determine specific functional group that presence within the molecule. There were four regions of types of bonds that can be analysed from the FTIR spectra as shown in Figure 2.7.

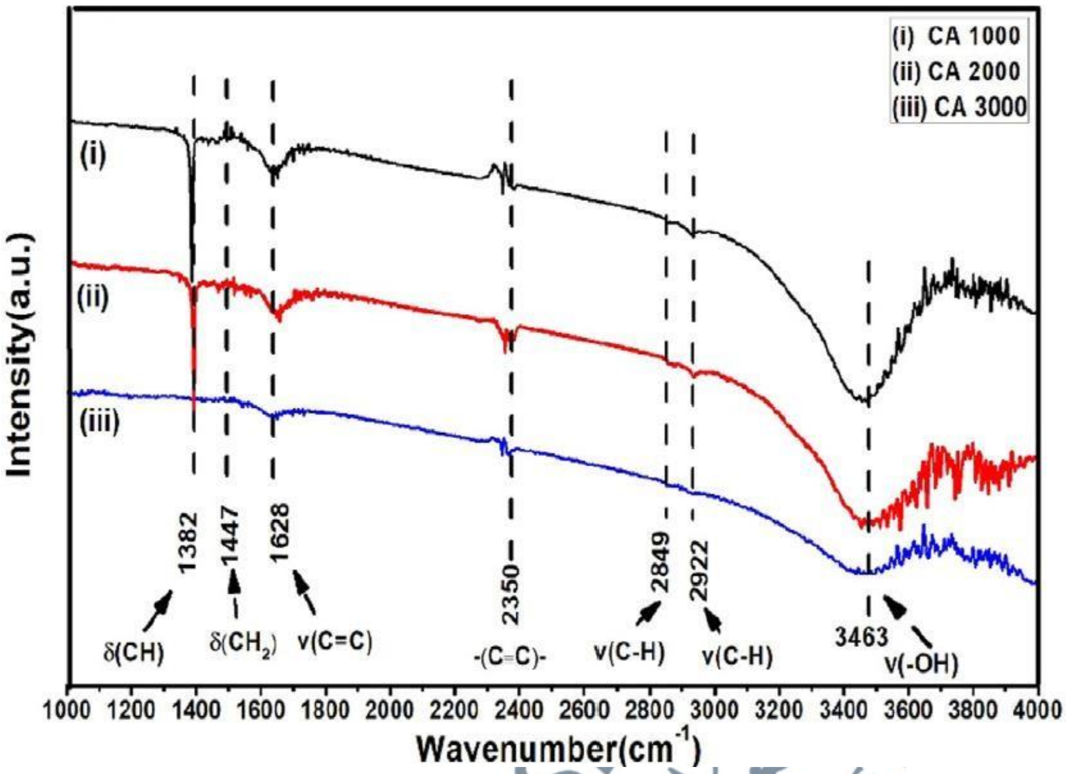


Source : (Mohamed et al., 2017)

Figure 2.7: FTIR Spectra of Regenerated Cellulose Membrane with The Various Common Types of Bonds Absorb in The Estimate Regions (Inset Correspond to Cellulose Molecular Structure).

In the middle wavenumber region 2000 – 2500 cm^{-1} and 1500 – 2000 cm^{-1}, the triple and double bond were detected. In the low wavenumber region 650 – 1500 cm^{-1}, the molecule showed vibration as a whole and can be considered as identification of the molecule. FTIR spectrophotometer gives out the IR spectrum much more efficient compared to the traditional spectrophotometer.

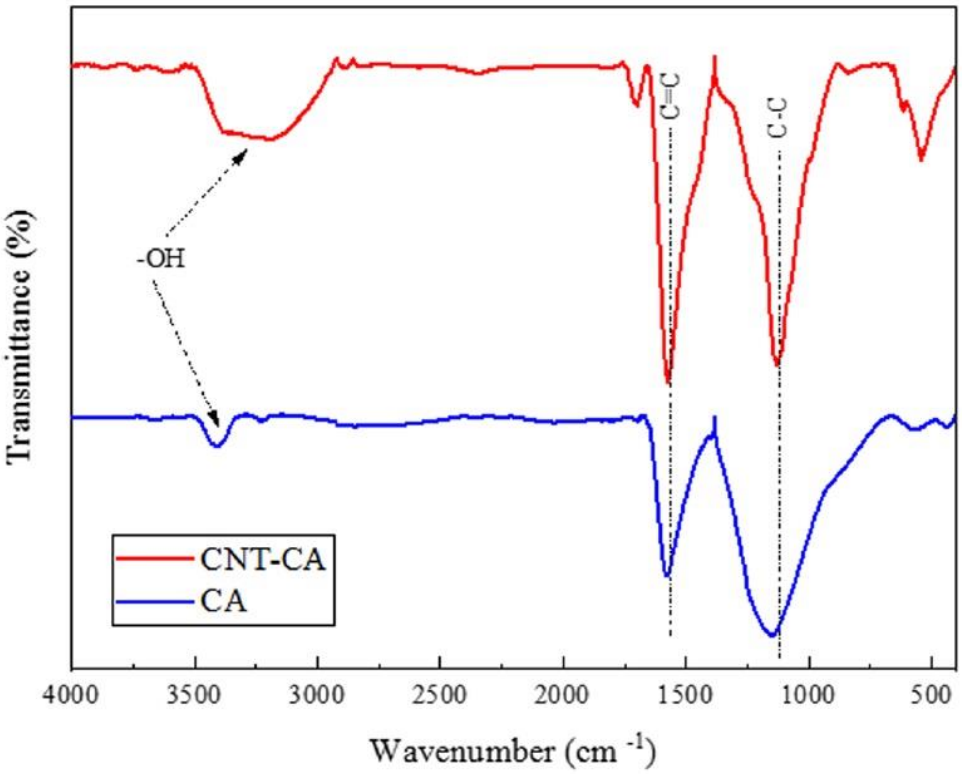
In analysing CA samples, FTIR spectroscopy was used to characterise molecular vibration of different CA samples. In research where CA samples were derived from R/F gel with different concentration of catalyst to promote gel growth, FTIR spectra of the CA samples consisted of many peaks and the molecular vibration was labelled as shown in Figure 2.8 (Pandey et al., 2020).



Source: (Pandey et al., 2020)

Figure 2.8: FTIR Spectra of (i) CA 1000, (ii) CA 2000, and (iii) CA 3000

Compared to the previous reported studies, it can be said that the FTIR spectra of different CA samples were similar. There were changes in intensity and slight shifting in wavenumber representing molecular vibration may have been caused by the different catalyst concentration. This can be explained by other researchers where they were synthesised powdered CNT-doped CA. In this research, they prepared CA and CNT-CA by sol-gel conventional method. They analysed both samples using FTIR analysis to investigate the chemical structure of the samples. They stated that the presence of OH, C-C and C=C in both samples as shown in Figure 2.9 (Reyhani et al., 2021a).



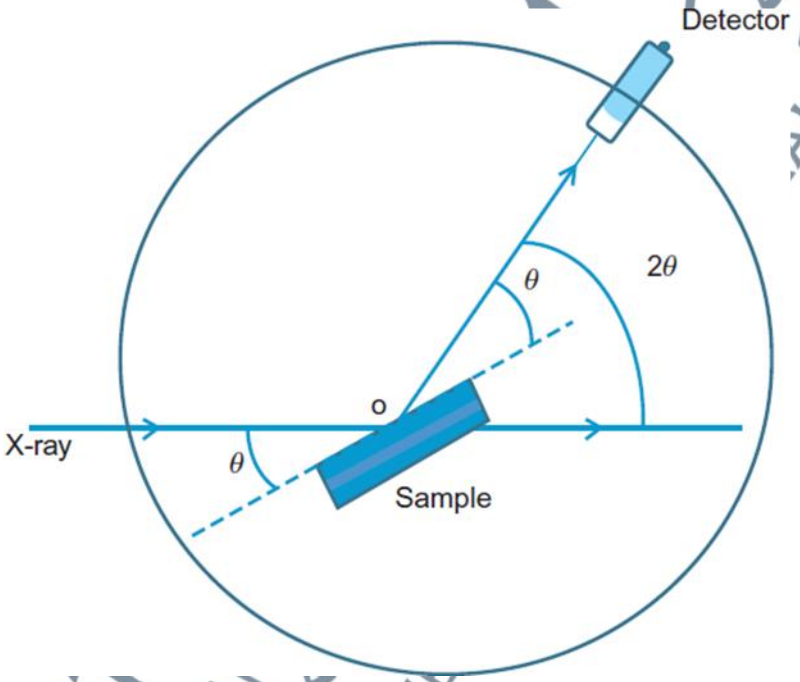
Source: (Reyhani et al., 2021a)

Figure 2.9: FTIR Spectra of CA and CNT-CA

Based on Figure 2.8 and Figure 2.9, both figures represented FTIR spectra of CA but with different parameters during synthesis process. CA from both research identified the presence of OH, C-C and C=C but with different intensity as explained before. FTIR analysis is crucial to study the changes in chemical structure of CA when added with other substances. Then, a comparison can be made.

2.8.3 X-ray Diffraction (XRD)

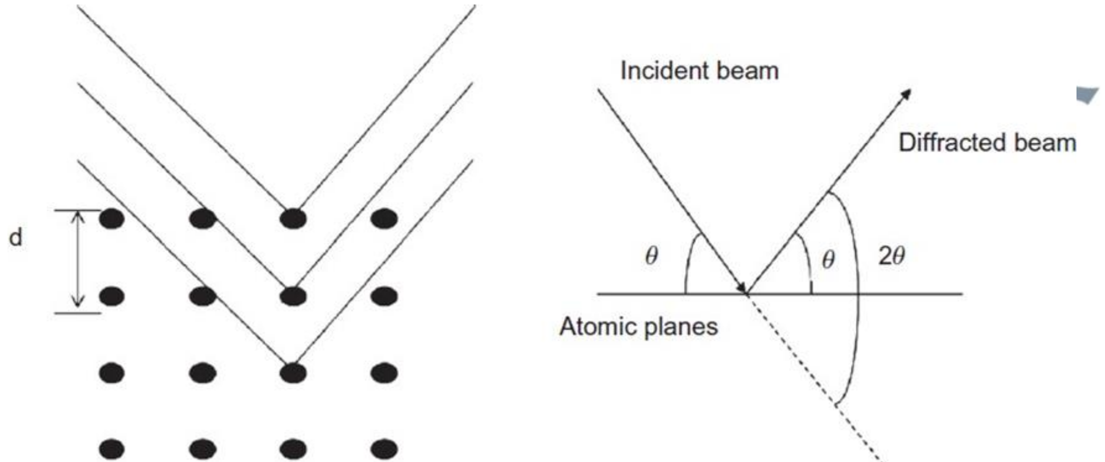
Generally, XRD is a basic tool for material characterization and analysing crystallographic materials such as polymers. XRD was conventionally used in analysing the crystalline and amorphous structure of polymers, composite, and fillers. The characterisations of crystalline materials were based on a periodic arrangement of atoms. Figure 2.10. shows typical experimental setup for XRD spectroscopy measurements.



Source : (Abhilash et al., 2016)

Figure 2.10: Typical Experimental Setup of XRD Spectroscopy

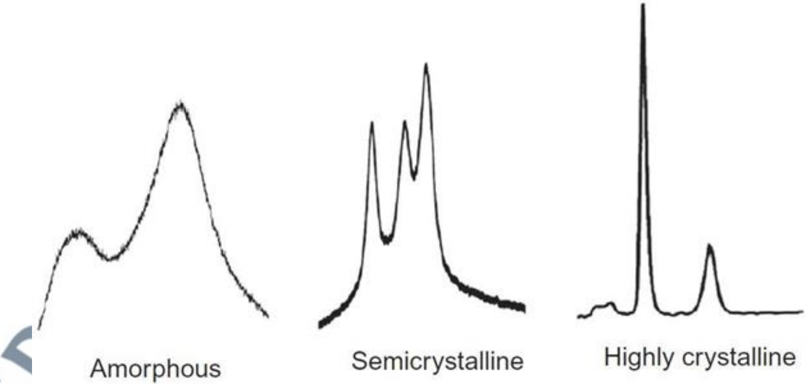
Figure 2.11 shows the schematic of the process where the sample was exposed to a X-ray beam of wavelength (λ) at an angle θ with the tangential surface, and the beam is diffracted at an angle of 2θ.



Source : (Abhilash et al., 2016)

Figure 2.11: X-ray Diffraction Principle

In crystalline materials, the pattern obtained shows sharp maxima, called peaks, at their respective diffraction angle, and in amorphous solids, the orderly structure was absent, which showed broad maxima called a hump as shown in Figure 2.12.

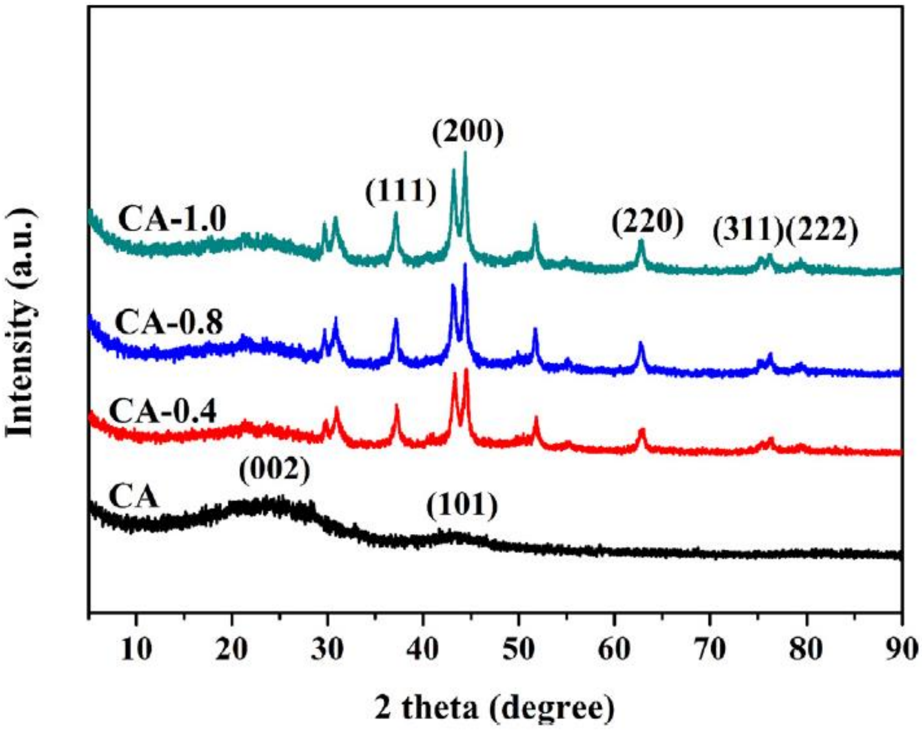


Source : (Abhilash et al., 2016)

Figure 2.12. Peak Characteristics of Different Polymer Phases

XRD spectroscopy became popular due to its simplicity, reliability, the quantitative information it provided, and its non-destructive nature. The high potential of XRD had made it used to explore the structure of bulk and thin film crystalline or polycrystalline materials on the atomic scale.

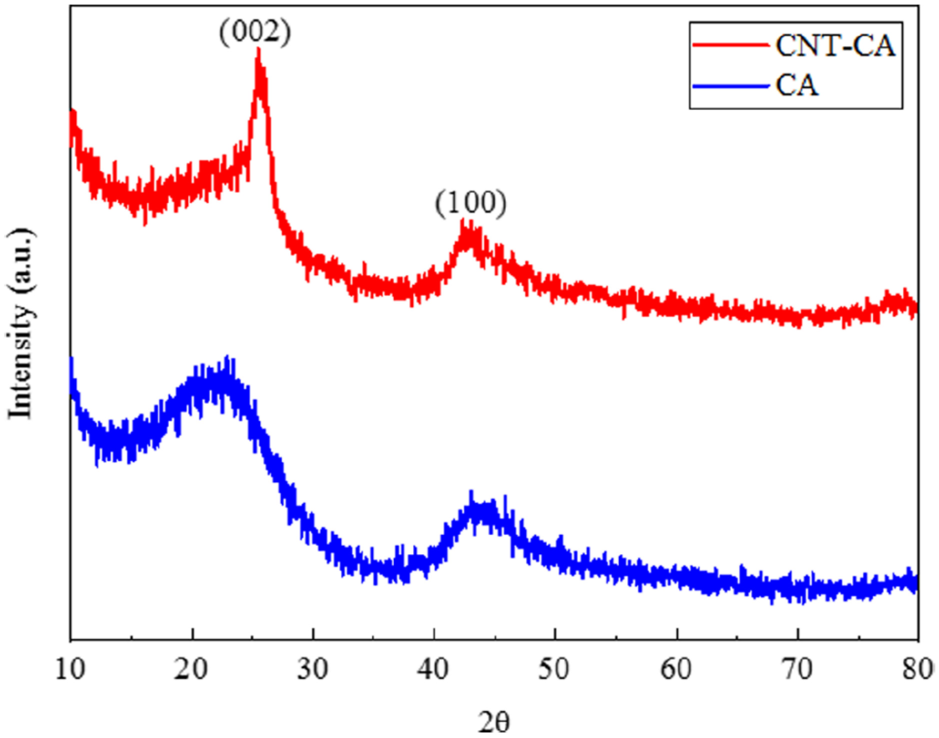
Yu et al. (2017) derived CA from CMC by pyrolysis of CMC aerogels via sol-gel and freeze-drying process. They used different concentration of Nickle Sulphate ($NiSO_4$) as an enhancer and the XRD patterns of the samples were shown in Figure 2.13 below. The pure CA showed two diffraction peaks at 2θ correspond to the peak (002) and (101) which represented the characteristic peaks of amorphous carbon. In the pattern of CA-x samples, they showed the characteristic peaks of graphite-type carbon. These diffraction peaks illustrated the crystalline phase of NiO at lattice planes of (111), (200), (220), (331) and (222). The XRD patterns for both samples indicated the characteristic features of CA (Yu et al., 2017).



Source: (Yu et al., 2017)

Figure 2.13: XRD Patterns of CA and CA-x Samples

Reyhani et al. (2021) prepared CA and CNT-CA using sol-gel conventional method. They used CNT to be doped to CA and studied the changes. Based on XRD pattern of CA and CNT-CA (Figure 2.14), they identified two wide peaks at 2θ for both samples correspond to the peak (002) of graphitic carbon and the peak (100) of the crystalline plane diffraction. These patterns represented characteristic peaks of CA. The presence of CNT caused the peak (002) of CNT-CA sample to be sharper and thinner compared to CA. Thus, indicated CA had more amorphous and disordered characteristics while CNT-CA has higher crystallised carbon (Reyhani et al., 2021a).



Sources: (Reyhani et al., 2021a)

Figure 2.14: XRD Patterns of CA and CNT-CA Samples

Based on XRD patterns from both research, we can conclude that most of the CA samples doped or added with any materials possessed characteristics features of CA.

Besides, XRD analysis can show the crystalline phase of any metal oxide if CA was doped with any metal.

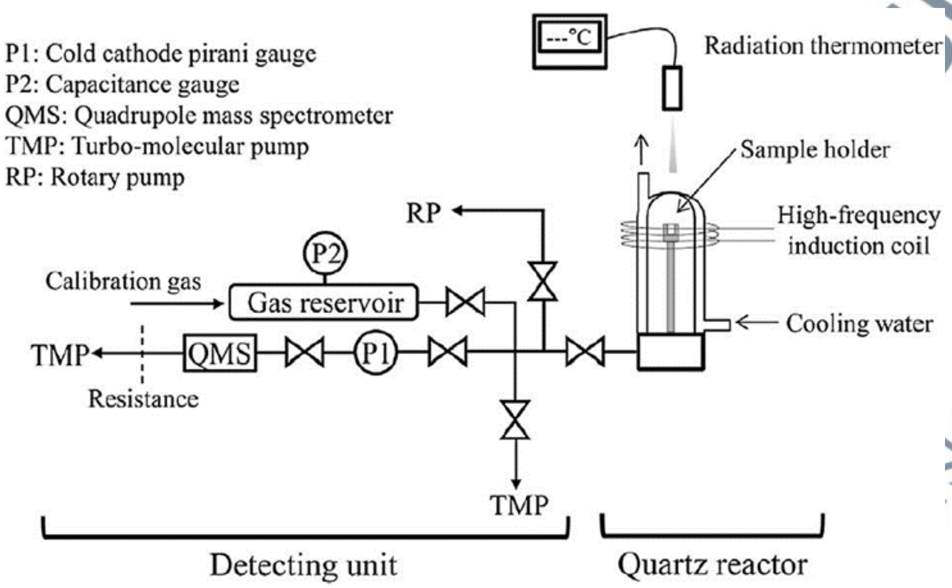
2.8.4 Brunauer–Emmett–Teller (BET) Method

BET method was surface area measurement for gas adsorption onto a solid surface. In surface adsorption, there were two possible mechanisms that could occur which were physisorption and chemisorption. The concept of these mechanisms was the intermolecular attractions between the molecule and the surface, where starting with physical interaction and then following with chemical bonding. From physisorption, several pieces of information can be obtained including surface area, pore size and pore size distribution of the material. Chemisorption can provide information of characterisation of catalyst surface and was the main key mechanism of heterogeneous catalysis of chemical reactions. This method is to determine the specific surface area and pore size distribution of certain materials. Surface area means the interaction of solid to its surroundings such as liquids and gases. This can be obtained by reduction of particle size via grinding and milling to ensure the porosity of the materials. However, these properties can be destroyed by high temperatures. As gases adsorb on the surface of a solid, the surface area of the solid can be determined by calculating the amount of adsorbate gas corresponding to the monomolecular layer on the surface (Naderi, 2015).

In research where CA samples were synthesised through ambient pressure drying method with different concentration of catalyst. BET analysis was important in investigating the porosity of the as-prepared CA samples. Based on BET curve, the samples gave out different total surface area, pore size and pore volume due to the different catalyst concentration of each sample. The sample with the lowest concentration of catalyst had the highest surface area, low pore size and low pore volume. This research was aimed to obtain CA microstructure (<2 nm) but otherwise (Pandey et al., 2020). Other researchers derived CA from Na-CMC doped with Nickel Sulphate (NiSO4). Based on BET curve, the specific surface area, pore size and pore volume were already determined and tabulated in the table. Each sample contained a distinct hysteresis loop in the relative pressure region of $0.4 < P/P_0 < 1.0$ which indicated the existence of mesopores. This can be said that CA doped or added with any materials had different pore volume where pure CA had small pore volume while doped CA had larger pore volume (Yu et al., 2017). However, since BET analysis used nitrogen adsorption, all micropores may not be easily accessible for nitrogen because nitrogen molecule had size of ~3.6 Å unlike hydrogen has smaller size (~ 2 Å). Thus, making hydrogen will get adsorbed in micropores (Pandey et al., 2020). The present research needs to focus more on the synthesis of CA having abundance of micropores which lead to high hydrogen adsorption.

2.8.5 Temperature Programmed Desorption (TPD) Technique

Generally, TPD had been used in the study of catalysis because the technique able to study the interaction of reaction gases with solid surfaces. Hence, allowed the evaluation of active sites on catalyst surfaces and the understanding of the mechanisms of catalytic reactions including adsorption, surface reaction and desorption. The story was different in carbon materials, TPD was used to analyse oxygen-containing functional group formed on carbon surfaces because the functional groups act as intermediates in carbon oxidation reaction with O_2, H_2O and CO_2 and play important role in governing the surface chemistry of carbon materials. During TPD analysis, these functional groups were thermally decomposed to give out CO_2, CO, and H_2O at different temperatures. This was depending on the thermal stability of the groups.



Source: (Ishii & Kyotani, 2016)

Figure 2.15: Experimental Setup for TPD Analysis

Based on Figure 2.15, the illustration showed TPD apparatuses which consisted of two major parts: quartz reactor unit and a high vacuum detecting unit. Inside quartz reactor, there was a sample holder made of pyrolytic carbon-coated graphite that can be heated under high vacuum by a high-frequency induction method. With the presence of graphite sample holder and the induction heating system, the TPD temperature can reach as high as 1800 °C. While in detecting unit, there were quadrupole mass spectrometer (QMS), a gas reservoir and a stainless-steel high vacuum line pumped by two turbomolecular pumps (TMP) to maintain a base pressure of about 1 x 10^{-5} Pa. The amount of CO_2, CO, and H_2O can be quantitatively determined with a sensitivity of about 0.1 pmol/s from this setup as shown in Figure 2.15 (Ishii & Kyotani, 2016).

TPD was the best way to investigate the desorption behaviour of hydrogen storage materials in a wide temperature range as CA was one of them. Huang et al. (2021) used Ni/$CoMoO_4$ as an addition to MgH_2 to improve its hydrogen storage properties. After MgH_2 doped with Ni/$CoMoO_4$, the initial dehydrogenation temperature of MgH_2 was substantially reduced based on TPD curve of the sample. Zhou et al. (2020) studied the isothermal dehydrogenation properties of pure MgH_2 sample and MgH_2-Pr_3Al_{11} composite at first. Then, they studied the growth characteristics of Mg crystallites during the hydrogenation desorption process. The presence of Pr_3Al_{11} promoted the growth rate of Mg crystallites due to the catalytic effects. This occurred because of the defect on the MgH_2-Pr_3Al_{11} interface that can act as nucleation site for Mg. These findings can provide improvement for hydrogen storage materials especially in this research where CA was enhanced with several metal ions to obtain better surface feature for hydrogen desorption.