STUDY ON THE RESIDUAL ION CONTENT FROM THE EMPLOYMENT OF PRECIPITATION METHOD FOR CATALYST SYNTHESIS

IVY WONG AI JIA

A project report submitted in partial fulfilment of the requirement for the award of Bachelor of Engineering (Honours) Chemical Engineering

Lee Kong Chian Faculty of Engineering and Science
Universiti Tunku Abdul Rahman

April 2019

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

Signature   : _____

Name   : Ivy Wong Ai Jia

ID No.   : 14UEB04121

Date   : 6 May 2019

I certify that this project report entitled **"STUDY ON THE RESIDUAL ION CONTENT FROM THE EMPLOYMENT OF PRECIPITATION METHOD FOR CATALYST SYNTHESIS"** was prepared by **IVY WONG AI JIA** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature   :

Supervisor   :   Dr. Yap Yeow Hong

Date   :   6 May 2019

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ABSTRACT

In this project, nickel alumina (Ni/Al_2O_3) and nickel-silica (Ni/SiO_2) catalysts were synthesized by employing coprecipitation method using different anionic salts and support precursors. In coprecipitation method, the resulting precipitates often contain impurities or residual ions which are deposited on the surface of the catalyst samples. It is crucial to determine the residual ion content on the catalyst as they could greatly affect the catalytic performance even though they present in very low concentration. The common poisons on catalyst include sulphur and chlorine. Thus, this project aims to investigate the effect of changing types of anionic salts and support precursors during coprecipitation on the characteristics of catalyst. The anionic salts that have been used in this project included nickel nitrate, nickel sulfate and nickel chloride. The support precursors used for the synthesis of Ni/Al_2O_3 comprised of aluminium nitrate, aluminium sulfate and aluminium chloride whereas sodium silicate was used as support precursor for the synthesis of Ni/SiO_2. In addition, this project aims to study the effect of different washing condition on the residual ion content present in the catalysts. Here, acetone and hot deionized water were used as solvent to wash off the impurities. Upon completion of catalyst synthesis, a series of catalyst characterization and properties are determined by employing various analytical techniques such as SEM-EDX, ICP-OES and VIS spectrophotometry. SEM-EDX and VIS spectrophotometry have shown a relatively low content of sulphur on acetone-washed samples, but the chloride ion was not successfully reduced. It is believed that acetone is more preferable in removing sulphur rather than chlorine. On the other hand, ICP-OES analysis have revealed significantly higher nickel concentration on Ni/SiO_2 samples rather than that on Ni/Al_2O_3 catalysts, which is likely to be caused by different level of supersaturation achieved during the coprecipitation. It is believed that nickel and aluminium were not fully precipitated during the synthesis of Ni/Al_2O_3 catalysts. Besides, there is trivial amount of sodium impurities found in both Ni/Al_2O_3 and Ni/SiO_2 catalyst samples where both have shown around the same level of sodium, which indicates significant of occlusion take place during the coprecipitation process.

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LIST OF SYMBOLS / ABBREVIATIONS

BET	Brunauer-Emmett-Teller
EDX	Energy-Dispersive X-Ray Spectroscopy
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
SEM	Scanning Electron Microscopy
TPDRO	Temperature-Programmed Desorption, Reduction, Oxidation
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
β	Pre-exponential term
A	Interfacial energy parameter
s	Supersaturation
L	Crystallite size, nm
λ	X-ray wavelength (1.54 Å)
β	Full Width of Half Maximum (FWHM)
θ	Angle (º)
K	Constant (often taken as 1)

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CHAPTER 1

INTRODUCTION

1.1 Synthesis of Heterogeneous Catalysts

Most of the catalysts used in industry are heterogeneous catalyst rather than homogeneous catalyst. This is because solid catalyst provides specific porosity and surface area to achieve high activity, good selectivity (multiple active sites) and thermal stability during the catalytic reaction. Besides that, the catalyst recovery is relatively effective and easier than the homogenous catalyst which is difficult and sometimes impossible to recover.

As mentioned by Bailie *et al.* (2001), most of the heterogeneous catalysts cannot be used without the aid of catalyst support. The support provides large surface area which helps to disperse the active catalyst. This is particularly important when it comes to expensive active agent like platinum, palladium and gold. The common catalyst support are alumina, silica, alumina-silica and carbon. The factors that should be taken into consideration when selecting the types of catalyst support include the porosity, specific surface area, chemical properties, acidity, and basicity. Support can either be inert or might interact with the active agent. Such interaction can lead to the change in surface structure of active agent and affect the activity and selectivity of the catalyst (NPTEL, n.d.).

Heterogeneous catalysts can be prepared via variety of methods such as impregnation, deposition-precipitation, coprecipitation, sol gel and so on. Coprecipitation can be carried out in several specific steps including preparation of specific solution of metal compound, mixing of solutions, drying and calcinations.

According to Noor Azeerah *et al.* (2012), the reasons that coprecipitation technique is preferred over other catalyst preparation methods are:

- ✓ require simpler steps and shorter time;
- ✓ easy to control particle size and composition;
- ✓ allow various possibilities to modify particle surface state and overall homogeneity;
- ✓ give high output and recovery;
- ✓ allow high metal loading.

The above factors lead to high consistency and low production cost and which is why it is favoured in the production of catalysts.

1.2   Problem Statement

When preparing supported catalysts using coprecipitation method, a highly soluble inorganic salts (metal precursor) such as sulfates, nitrates and chlorides are reacted with highly soluble basic reagent (precipitant) like sodium carbonates (Lok, 2009). As a result, an insoluble metal carbonates are formed as precipitates due to their lower solubility. However, the presence of impurities or residual ions on the surface of the precipitate can cause sintering and agglomeration of particle during further thermal treatment, leading to a loss of surface area (Munnik, de Jongh and de Jong, 2015). Furthermore, presence of impurities such as sulphur and chloride on the catalyst surface also lead to premature deactivation for some reactions.

1.3   Aim and Objectives

The aim of this final year project is to study the factors that lead to the presence of impurities (residual ions) in the coprecipitation process and to study the effect of different methods in reducing the impurities present in the precipitate. Here, nickel-alumina (Ni/Al_2O_3) and nickel-silica (Ni/SiO_2) catalysts will be synthesized by employing coprecipitation method using different anionic salts and support precursors. After that, we will look into the presence of residual ion content after the coprecipitation process.

The objectives of this project are:

I.   To investigate the effect of changing types of anionic salts and support precursors during coprecipitation on the characteristics of catalyst.

II.   To study the effect of washing condition on the residual ion present in the catalyst after coprecipitation.

1.4   Project Scope

Nickel-alumina (Ni/Al_2O_3) and nickel-silica (Ni/SiO_2) catalysts are prepared by using coprecipitation method. The types of anionic salts and support precursors are manipulated to produce each set of samples followed by heating at high temperature

to remove the solvent. After heating, washing and further calcination are required due to the presence of impurities or residual ion on the surface of the catalyst. Upon completion of catalyst synthesis, a series of catalyst characterisation and properties are determined by using the following analytical techniques:

- ➢ SEM-EDX
- ➢ ICP-OES
- ➢ VIS Spectrophotometry

CHAPTER 2

LITERATURE REVIEW

2.1   Synthesis of Heterogeneous Catalysts

Heterogeneous catalysts are employed in variety of industrial reactions, for example, ammonia synthesis, dehydrogenation and oxidation, Fischer-Tropsch synthesis, hydrodesulphurization and etc. (Munnik *et al*., 2015). A heterogeneous catalyst is a composite material that exists in different phase than the reactants so that it will not mix with the reactants during the catalytic reaction. Generally, heterogeneous catalysts work by adsorbing reactants onto the surface of the active site. The catalysts help to increase the rate of chemical reaction by lowering the activation energy. After the reaction, the product will detach from the catalyst, leaving it unaltered for the next reaction. Generally, a successful catalyst must fulfil certain requirements which are:

 - ➢ High activity;
 - ➢ High selectivity;
 - ➢ Sufficiently long life span;
 - ➢ Possibility to regenerate;
 - ➢ Sufficient thermal stability;
 - ➢ High mechanical strength; and
 - ➢ High attrition resistance

In industry, the catalyst manufacturers always aim to produce commercial catalysts that are active, selective and stable. As reported by Geus and Dillen (2008), the activity of a solid catalyst usually depends on the active sites available per unit volume of catalyst. An efficient catalyst with high activity implies that the active particles must be small. However, small particles alone are usually unstable and prone to sintering, especially at temperatures where typical catalytic reaction and thermal treatment are carried out. Hence, the support is particularly important which is highly thermostable, possess good mechanical strength and provides porous structure. With the support, the active phase can be deposited on the support to prevent sintering of small particles which can lead to low active surface area. The inert supports that are commonly used include silica, alumina, zinc oxide and carbon.
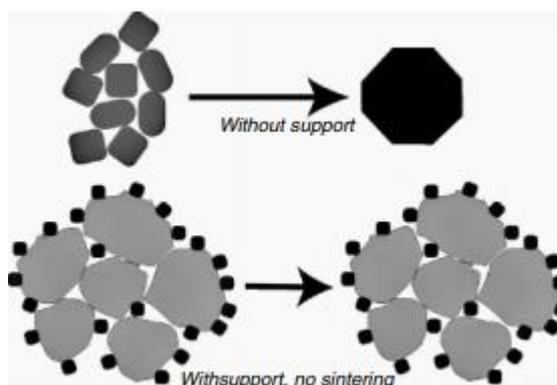
Figure 2.1: Top – sintering of unsupported active particles; Bottom- supported thermostable active particles. (Geus and Dillen, 2008)

According to Schwarz *et al*. (1995), the properties of a good catalyst can be classified into two categories: (1) properties used to determine the catalytic activity and selectivity, such as surface chemical composition, phase composition and local microstructure; and (2) properties that ensure successful implementation of catalysts in the catalytic reaction, for example, porosity, size and shape of catalyst particles, thermal and mechanical stability.

Heterogeneous catalysts can be prepared by several preparation methods which involves a combination of different stages such as: (i) introduction of metal precursors onto the support by coprecipitation, impregnation, deposition precipitation and sol-gel, (ii) drying and calcination, and (iii) reduction (Pinna, 1998). The principles of each catalyst preparation route will be explained further in more details in the following sections. Drying process is carried out at temperature between 80 °C and 200 °C to remove the excess solvent in the first stage. The rate of drying will influence the distribution of the active phase. If the drying rate is too slow, the salt will diffuse into the deeper pore, leading to higher solution concentration in the inner pore. In contrast, higher drying rate will create temperature gradients, forcing the solution towards the outer surface of the particles and results in precipitation since evaporation normally takes place at the external surface of the support particles (van Dillen *et al*., 2003).

Moreover, calcination of catalysts is usually conducted in an oxidizing air at a temperature higher than that of the operating reaction temperature. As referred to Al-Fatesh and Fakeeha (2012), calcination will bring several transformations that can change the catalyst such as: decomposition of dried precursor, solid state reactions of

supported oxide and support, transformation of amorphous into crystalline structure, sintering of different phases, and modification of pore structure and mechanical properties. Reduction process is carried out subsequently after calcination treatment. Through reduction, the metal oxide will transform into metal after going through thermal treatment in hydrogen. There must be enough hydrogen flow to eliminate the water from the support which is formed during the reduction process. This is because high water vapour in the support will cause detrimental effect on the metal dispersion (Pinna, 1998).

2.1.1 Impregnation

Impregnation is a mostly used catalyst preparation technique compared to other methods due to its simple execution and low waste production. According to Schwarz *et al.* (1995), impregnation is a process whereby the dissolved aqueous metal precursor is adsorbed onto the surface of the oxide support, which is subsequently dried to remove the absorbed solvent. As stated by Munnik *et al.*, (2015), the liquid driven into the pores of the support is facilitated by the capillary pressure difference across the hemispherical meniscus of a pore.

Inorganic metal salts including metal chlorides, nitrates, sulfates, carbonates and acetates are the common precursors, whereas water is used as the common solvent for inorganic salts due to high solubility of most of the precursors. Concentrations below supersaturation are needed to avoid premature deposition of metal precursor in the solution (Munnik, 2015). Ion exchange reactions between the precursor ions in solution with the support surface is necessary to perform an effective interaction during impregnation (Hutchings and Védrine, 2004).

There are two methods of impregnation: wet impregnation and dry impregnation (incipient wetness). In wet impregnation, excess amount of solution is employed. The system is then left for a certain period of time to allow aging process under stirring, followed by filtration and drying process. After some time, the solid is separated and the excess solvent will be removed through drying. The amount of active precursor deposited on the porous support depends significantly on the concentration of impregnating solution, porous volume of the support as well as the adsorption isotherm (Schwarz *et al.*, 1995). The deposition process is relatively slow, leading to the loss of surface area. Nevertheless, it allows well control of species distribution and high dispersion can be achieved. (Haber, Block and Delmon, 1995).
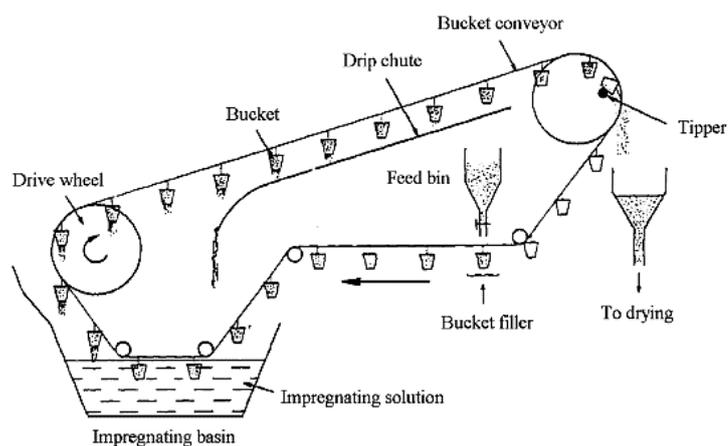
Figure 2.2: Supported catalyst preparation using wet impregnation method. (Campanati, Fornasari and Vaccari, 2003)

In dry impregnation, the amount of solution provided is just enough to fill the pore volume of the support (Munnik *et al*., 2015). This method is best applied when the interaction strength is weak between the active precursor and the support. Dry impregnation appears to be simple and economic when dealing with expensive active components and it is able to achieve high metal loading. This is because the precursor solution is sprayed onto the support to attain a more uniform distribution by removing the air trapped inside the inner pores of the support (Pinna, 1998). However, as claimed by Campanati *et al*. (2003), the maximum loading is controlled by the precursor solubility in the solution. Sequential impregnation steps can be carried out to overcome this limitation when higher metal concentration are required. Apart from that, drying process normally constitutes to serious redistribution of impregnated species, which results in the support being inhomogeneously covered by the active precursor (Schwarz *et al.*, 1995). Therefore, it requires precise operation control and repeated applications of solution is necessary.
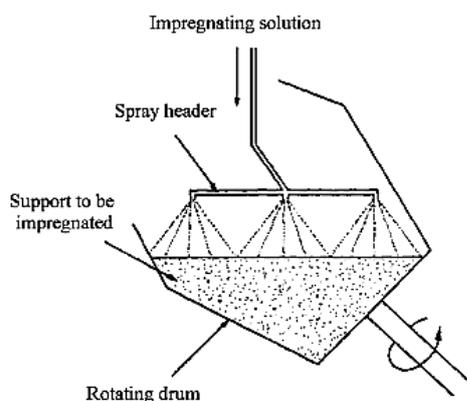
Figure 2.3: Supported catalyst preparation using dry impregnation method. (Campanati, Fornasari and Vaccari, 2003)

2.1.2 Deposition Precipitation

Deposition precipitation is a method whereby an active precursor is applied to a support through precipitation (Geus and Dillen, 2008). During the reaction, the catalyst precursor is transformed slowly into an insoluble form in the solution. Once the nucleation occurs, the precursor will adsorb onto the surface of the support suspended in the solution rather than in the bulk solution due to support-precursor interaction (Hutchings and Védrine, 2004).

Preferential precipitation on the support can be obtained through introduction of support in the solution. This is because it can reduce the energy barrier for nucleation, and thus nucleation can only happen on the support but not in the bulk solution (Munnik *et al*., 2015). It is necessary to ensure that the precursor particles precipitate inside the pores of the support so that the nucleation and growth of the particles will result in a uniform distribution over the support. Or else, the nucleation and growth in the bulk solution will lead to the formation of bigger crystallites and inhomogeneous distribution because the large particles cannot enter into the pores and tend to deposit on the external surface of the support (Pinna, 1998).

To ensure the homogeneity of the bulk solution, the uniform precipitation is achieved by the hydrolysis of urea as the source of OH^- ions instead of conventional alkali precipitating agent. Another method revealed by Schwarz *et al*. (1995) is through injection of precipitant below the surface of the suspension which contain the support and precursor, followed by vigorous agitation. As a result, the precipitant is distributed rapidly and precipitation occurs homogeneously.

Originally, deposition precipitation was developed to prepare catalysts with higher metal loadings than that obtained by impregnation which is limited by solubility. In recent years, this method has been employed to prepare low loadings of finely dispersed gold particles on the surface of the support (Geus and Dillen, 2008). Based on the work by Haber *et al*. (1995), deposition precipitation can ensure an excellent dispersion of active precursor despite the high metal content.

2.1.3   Coprecipitation

Coprecipitation is the process of precipitation of undesirable components with the desired precipitate (Sharma, 2006). Coprecipitation is mainly used to prepare catalysts based on more than one component through simultaneous precipitation. This precipitation method is employed to produce bulk catalysts and support material, for example Al_2O_3, SiO_2, ZrO_2 and TiO_2 (Guwahati, 2014).

In coprecipitation, metal hydroxide or carbonate is precipitated from precursor salt solution which is normally of low solubility, reacted with an alkaline precipitating agent and the support ions is often added and coprecipitated simultaneously in a single process step. When the mother liquor is stirred continuously at certain temperature for a period of time, the resulting precipitates will undergo ageing process, whereby the precipitate particles starts to sinter to form bigger particles, which transform the amorphous precipitates into crystalline form, leading to a change in catalytic performance (Hutchings and Védrine, 2004). After ageing, the process is followed by filtration, washing, drying and calcination to get the desired supported catalyst. The metal. Further details on coprecipitation will be discussed in Section 2.2.

2.1.4   Sol-gel

According to Campanati *et al*. (2003), sol-gel is a homogeneous process whereby a hydrated solid precursor (hydrogel) is transformed continuously from a solution. Several preparation steps via sol-gel method include: formation of hydrogel, ageing, solvent removal and lastly the heat treatment.
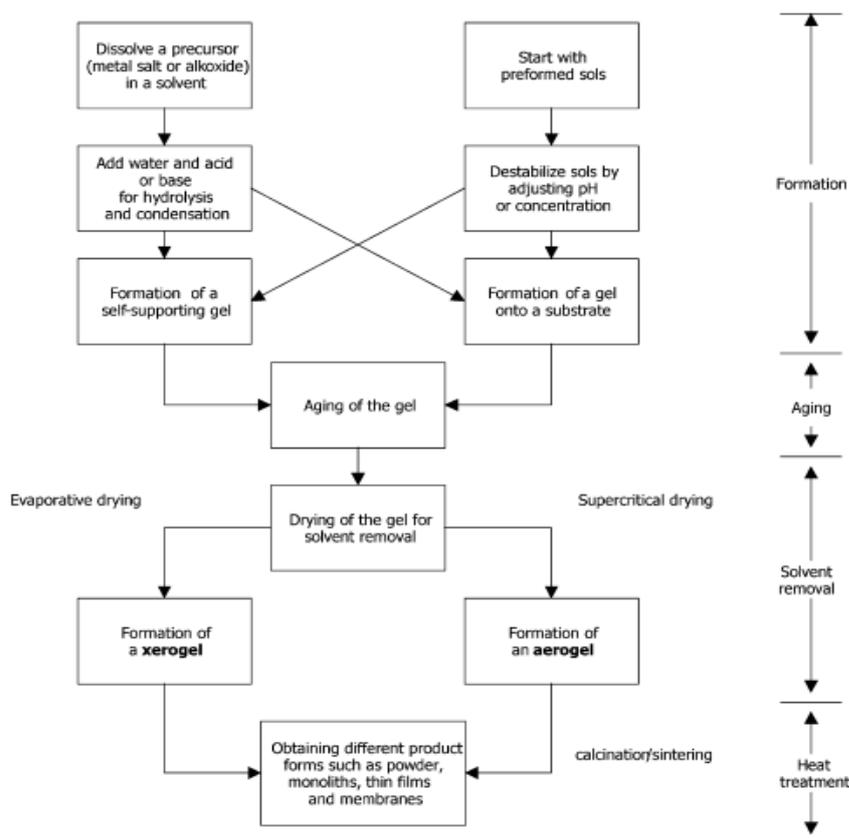
Figure 2.4: Schematic diagram of the sol-gel preparation. (Campanati *et al.*, 2015)

As stated by Guwahati (2014), in a sol-gel process, a colloidal solution known as sol is produced by hydrolysis and partial condensation of precursors such as metal alkoxides. The sol particles will then further condensed into 3D network, producing a gel in which the solids encapsulated the solvent. As illustrated in Figure 2.4, the encapsulated liquid can be removed from gel by both evaporative and supercritical drying. If the pore liquid is removed from the gel network through evaporative drying, shrinkage occurs and a xerogel is formed. In contrast, when the gels experience supercritical drying, the gel network does not collapse and a low density aerogel is produced either (Hench and West, 1990).

The porous gel is then heated at high temperature above its glass transition temperature to achieve the maximum density during the densification process. The composition and morphology will affect the densification rate and transition temperature (Hutchings and Védrine, 2004). Heat treatment at high temperature increase the density of monolith yet reducing the volume fraction of porosity due to

sintering. The densification temperature will decrease with the decreases in pore radius as well as increase in gels surface area (Hench and West, 1990).

Generally, sol-gel allows good control of the composition, texture, homogeneity and structural properties of the solids. It can be used to produce materials with different shapes, for instance, porous structures, dense powders, thin fibers and films. Since it is possible to prepare solids with high surface area through controlled porosity and homogeneous compositions, sol-gel method is widely used to synthesize micro and mesoporous materials, composite powders, mixed oxides and many more (Campanati *et al.*, 2003).

2.2   Coprecipitation

As mentioned earlier, coprecipitation is often used to prepare heterogeneous catalysts where one or more metals are precipitated in conjunction with the support or its precursor. This technique is usually carried out in aqueous media and it can be very attractive for a number of catalysts especially when it comes to large scale production. Commercial catalysts produced in this way are mostly used for catalytic reactions such as steam-reforming, methanol production, hydrogenation and water gas shift reaction. However, it requires precise control of conditions and more complicated equipment.

According to Lok (2009), the chemical phases, dispersion, surface area of the active phase, porous structure, particle size and shape are all strongly dependent on the process conditions throughout the precipitation process. Coprecipitation can achieve high metal loadings up to 80 % or higher and thus the catalysts are often referred to as bulk catalysts. Apart from that, this method has relatively high metal dispersion. Despite all these advantages, there are also several drawbacks. One of the main drawbacks of the coprecipitation process is that it will generate large amount of salt-containing solutions and require product separation after precipitation (Hutchings and Védrine, 2004).

The preparation of coprecipitated catalysts comprised of several steps which include precipitation, washing, shaping, drying, calcination and reduction. Among these steps, precipitation plays a vital role in determining the basic properties of the catalyst. This is because the catalyst performance can be greatly affected by the precipitation conditions. In the precipitation process, it consists of three major steps: liquid mixing, nucleation and crystal growth for the formation of primary particles, and agglomeration of primary particles. Nucleation always starts with the formation

of clusters which undergo spontaneous growth until they reach a critical size. Any clusters that are smaller than the critical size are likely to re-dissolve whereas a larger one will continue to grow. According to Schuth and Unger (1999), the nucleation rate is strongly dependent on temperature and concentration, which is usually described by the following equation:

$$\frac{dN}{dt} = \beta \ exp\left(\frac{-A}{ln^2 s}\right) \qquad\qquad (Eq.\ 1)$$

where β is the pre-exponential term, A is the interfacial energy parameter and s is the supersaturation.

It is essential to create certain degree of supersaturation for the crystallization to occur (Walton, 1967). Basically the nucleation is slow below the critical supersaturation concentration and above which nucleation is extremely fast. High supersaturation levels encourage nucleation instead of crystal growth and favour the precipitation of highly dispersed materials. The initial dispersion of precipitate can determine the final dispersion and activity of some catalysts, for example silica-supported nickel which desires high initial dispersion. However, due to high supersaturation during the precipitation process, homogeneous nucleation will occur spontaneously which limits the deposition of nuclei onto the internal surface of the preformed support and formed on the external surface instead (Lok, 2009). Thus, other methods are considered if a complete deposition onto a preformed support is crucial.

Other than nucleation and crystal growth, agglomeration is of paramount importance which result in fewer, larger but porous particles. Agglomeration or aggregation refers to the formation of nano-sized primary particles into micrometre-sized secondary particles. The ways in which the primary particles are stacked can determine the porosity of the particles.

In coprecipitation, highly dispersed coprecipitates can be obtained through rapid mixing of concentrated solutions to form insoluble materials. Suitable metal precursors are metal chlorides, nitrates and sulfate whereas metal carbonates or hydroxides are preferred as precipitates due to their low solubility. Support precursors such as sodium silicate or sodium aluminate are preferable than the preformed supports as the coprecipitates can achieve high metal content up to 90 % with only small amount

of the support precursors. Normally, around 20-30 % of alumina or silicate is enough to obtain high metal surface area after reduction (Lok, 2009).

Besides that, coprecipitation procedures may become difficult when it comes to scaling up at industrial level. For instance, the mixing efficiency of large amount of solution and uniform control along the catalyst bed during the thermal treatment such as temperature and water vapour pressure (Pinna, 1998). The commercial catalysts need to be shaped in the form of extrudates, pellets, tablets or spheres in order to be used in the industrial reactors to prevent build-up of pressure gradients over the catalyst bed. Regardless of the problem mentioned above, some of the important catalysts used in the industry are still preferable to be prepared by coprecipitation to achieve higher metal loading.

2.2.1　Parameters that Affect the Coprecipitation

As referred to Guwahati (2014), the initial mixing of components in the solution gives rise to a noticeable effect on the precipitation. In the case of coprecipitation, good mixing will result in a more homogeneous product. Stirring rate also plays an important part during the mixing as it affects the nucleation and aggregation of the particles. The aggregate size can also be affected by the manner of mixing as well as the stirring rate.

Apart from mixing condition, pH has to be well controlled as it can influence the precipitation especially when dealing with multicomponent system. As shown in Figure 2.5, the solubility curve will shift when the pH increases, whereby the point that was initially in the solution state becomes supersaturated. By increasing the pH value through addition of basic solution, the resulting compounds can be made insoluble and is easily precipitated from the solution. Lok (2009) concluded that it is very important to operate at high supersaturation condition to make sure the solubility of the products is exceeded to prevent the occurrence of undesired sequential precipitation.
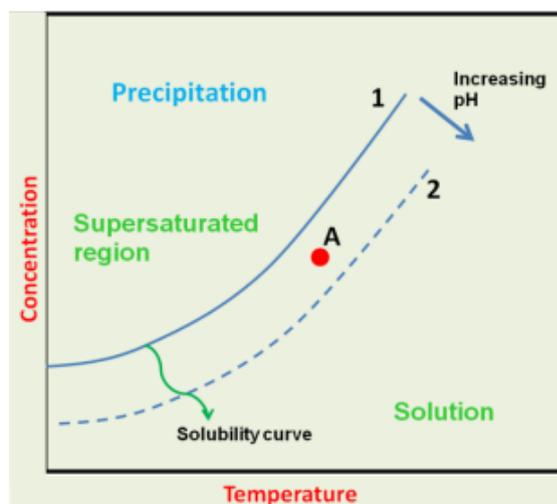
Figure 2.5: Parameters that affect supersaturation. (Guwahati, 2014)

In addition, supersaturation can be obtained by increasing concentration. It is preferable to precipitate at higher concentration of metal ions as it will lead to smaller particle size due to higher nucleation rates (Guwahati, 2014). In other words, high degree of supersaturation can produce smaller nanoparticles. This is because high supersaturation encourage nucleation rather than crystal growth. Small particles can be produced when nucleation rate is higher than the growth rate and vice versa. Besides, temperature has an obvious influence on the size of the particles as it alters the solubility of the particles in a solution (Feng *et al*., 2007). High temperature will lead to higher solubility, which in turn create lower supersaturation level. As a result, coarse particles are formed.

In summary, the mixing condition, pH level, concentration, and temperature are the main parameters that affects the particle size of the precipitates.

2.2.2   Examples of Catalyst Prepared by Coprecipitation

Coprecipitation is generally a very important method for the preparation of supported catalysts based on more than one component. It is a simultaneous precipitation of a soluble component with a macro-component from the same solution to form mixed crystals. Schuth and Unger (1999) in particular stated that coprecipitation is suitable in producing a homogeneous distribution of catalyst components and creating precursors with definite stoichiometry that can be easily converted into active catalyst. The calcination and reduction step to produce the final catalyst normally generates

very small crystallites of the components. Therefore, coprecipitation is undoubtedly an important and preferable technique in the manufacture of heterogeneous catalysts to achieve such a good catalyst dispersion which is hardly achieved by other means of preparation. Catalysts that are usually produced by coprecipitation include Ni/Al_2O_3 (steam reforming), Ni/SiO_2, $Cu/ZnO/Al_2O_3$ (methanol synthesis) and many more which are shown in Table 2.1 below.

Table 2.1: Examples of catalysts and supports obtained by precipitation or coprecipitation method. (Adapted from Schuth and Unger, 1999)

Material	Use	Important applications
Al_2O_3 (mostly γ, in special cases α or η)	support, catalyst	Claus process, dehydration of alcohols to alkenes and ethers, support of hydrotreating catalysts, support for three-way catalyst
SiO_2	support	Noble metal/SiO_2 for hydrogenation reactions, Ni/SiO_2 for hydrogenation reactions, V_2O_5/SiO_2 for sulfuric acid production
Al_2O_3/ SiO_2	catalyst	acid-catalyzed reactions such as isomerizations
Fe_2O_3	catalyst, catalyst component	Fischer-Tropsch reactions, major component of catalyst for ethylbenzene reaction to styrene
TiO_2	support, catalyst, catalyst component	major component of de-NOx catalyst
ZrO_2	catalyst	acid catalyst after sulfate modification
Cu/ZnO	catalyst	methanol synthesis
$(VO)_2P_2O_7$	catalyst	selective oxidation - for instance butane to maleic anhydride
Cu-Cr oxides	catalyst	combustion reactions, hydrogenations
$AlPO_4$	support, catalyst	polymerization, acid-catalyzed reactions
Sn-Sb oxide	catalyst	selective oxidation - for instance isobutene to methacrolein
Bi molybdates	catalyst	selective oxidation - for instance propene to anhydride acrolein (mostly supported)

2.2.3   Types of Impurities Produced during Coprecipitation

Basically, precipitation occurs in a solution that is rich in dissolved ions. Hence, the resulting precipitate often contains impurities either on the surface of the precipitate or within its lattice structure. As referred to Harvey (2017), the impurities are formed due to the physical and chemical interactions that occur on the surface of the precipitate. The precipitate formed is usually crystalline, in which the lattice is made up of cations and anions. Those ions on the precipitate's surface carry partial positive and negative charges that support the chemical and physical interactions, providing active sites for the formation of impurities.

For instance, as illustrated in Figure 2.6, each interior chloride ion (Cl^-) is surrounded and bounded to six silver ions (Ag^+) in AgCl precipitate. However, the chloride ion on the surface of the precipitate is only bounded to five silver ions, which means the chloride ion now carries a partial negative charge. It is due to the presence of these partial charges that cause the impurities to deposit on the surface of the precipitate.
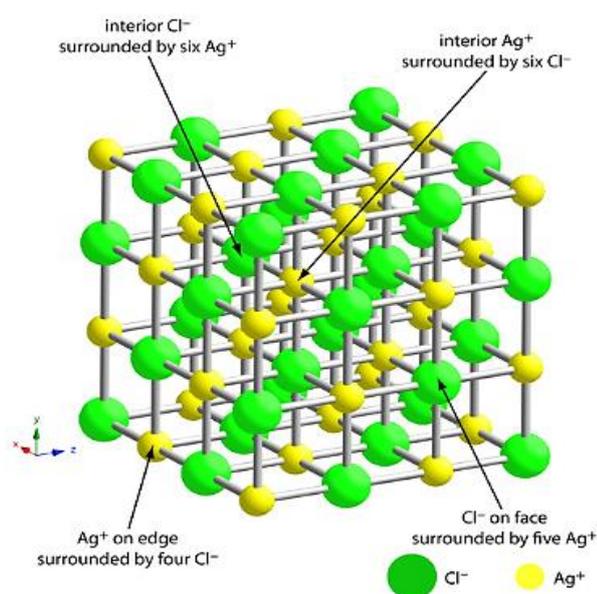
Figure 2.6: The lattice structure of AgCl. (Harvey, 2017)

In general, there are three types of impurities that may be formed during precipitation such as surface adsorbates, inclusions and occlusions.
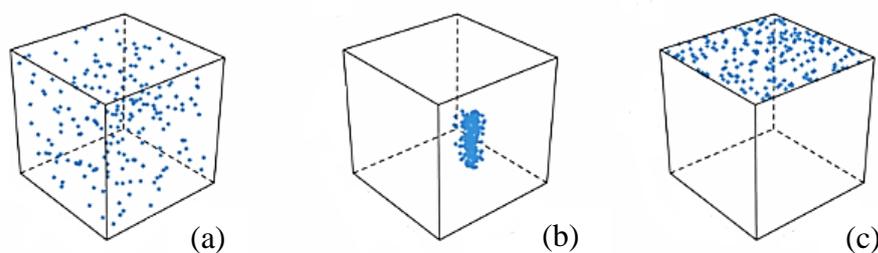
Figure 2.7: Types of impurities: (a) inclusions, (b) occlusions, and (c) surface adsorbates. (Harvey, 2017)

2.2.3.1 Surface Adsorbates

Surface adsorbates are impurities that are adsorbed onto the surface of a precipitate. After the precipitation process is completed, the active surface contains ions that are incompletely coordinated and free to attract oppositely charged ions from the solution (Terada, 2000) to form colloidal particles. The surface adsorption is greatly dependent on the surface area of the crystal. By reducing the available surface area of the precipitate, the surface adsorption can be minimized.

The first layer of the adsorbed ions is called the primary layer, whereas the second layer is known as counter layer which is comprised of counter ions. When the counter ions completely neutralize the primary layer and stay very close to the layer, coagulation occurs whereby the colloidal particles tend to come together to form larger particles (Pietrzyk and Frank, 1979). The colloidal particles can be reverted back to its original dispersed state through a reversible process called peptization, which involves the breakdown of coagulated particles.
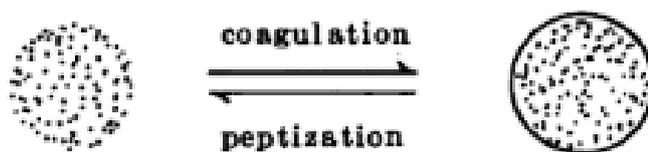
Figure 2.8: The reversible process of coagulation and peptization. (Pietrzyk and Frank, 1979)

2.2.3.2   Inclusion

Inclusion is also one of the common impurities found in coprecipitation. As stated by Sharma (2006), inclusion refers to mechanical trapping of solution and its solutes surrounding a growing crystal. The interfering ion which has the similar size and charge to the lattice ion will substitute and disperse randomly into the lattice structure as illustrated in Figure 2.7(a). When the concentration of the interfering precipitates is significantly higher than that of the lattice ions, there is higher probability that an inclusion will occur. Inclusion is relatively hard to remove as it is chemically part of the lattice (Harvey, 2017).

2.2.3.3   Occlusion

Occlusion happens when the foreign ions adsorbed on a crystal surface is trapped or occluded by subsequent crystal layers within growing precipitate during precipitate formation. It is the carrying down of impurities in the interior of the precipitate's particle. The ion is trapped in the middle of a crystalline matrix, preventing it from returning to the solution. Bard *et al.* (2012) claimed that the greatest amount of occluded ions can be found in the part of a crystal that was firstly formed. In addition, occlusion usually increases the precipitate's mass (Harvey, 2017) and gives poor yield of trace elements to be coprecipitated (Terada, 2000).

2.2.4   Ways to Reduce Impurities

There are various ways to reduce and remove impurities found on the precipitates and also within the crystal lattice. Methods such as washing, digestion and reprecipitation are employed for different types of impurities. For example, although there may be a potential loss of analyte, surface adsorbates can be removed by washing a filtered precipitate with a solution containing volatile electrolyte. According to Pietrzyk and Frank (1979), these electrolytes will replace the adsorbed impurities and are removed during the drying process.

However, washing the precipitates does not seem be an effective way to remove occluded impurities. Occlusion can be minimized by precipitation from dilute solution and employing a digestion period. During digestion, the precipitates are maintained in equilibrium with its supernatant solution for a certain period of time to encourage densification of nuclei. Upon digestion, the precipitates will dissolve and reform to make sure the occlusion is re-exposed to the solution (Harvey, 2017). There

is a small chance to form new occlusion due to slow dissolution and reprecipitation process.

On the other hand, inclusion can only be eliminated through reprecipitation. Based on Harvey (2017), the precipitate is initially isolated from its supernatant solution, followed by heating the precipitate in a suitable solvent. Hereafter, the solution is left to cool to reform the precipitate. Since the original precipitate's mass is larger, the reprecipitation process is repeated until the mass is insignificant. However, the loss of analyte will be the major source of error during this process.

It is crucial in terms of the selection of the salts because different salts will exhibit different solubility and different ability to decompose during calcination. The salts must be able to transform completely into oxides without leaving behind the side species that may affect the properties of the support (Marceau *et al.*, 2010). Thus, anions such as sulphate and chloride are to be avoided as they tend to occlude during precipitation which is difficult to remove afterwards. In contrast, nitrates can be removed easily during calcination which is why it is usually chosen as the salt precursors in coprecipitation process.

2.3   Catalyst Characterization and Testing

2.3.1   Brief Overview of Catalyst Characterisation and Reaction Studies

In general, both physical and chemical properties of the catalyst can determine its performance such as the activity and selectivity. The physical properties in this case refer to the particle size, surface area, pore size and pore volume, whereas the chemical properties includes composition, structure and nature of the carrier. These factors are crucial in governing the catalytic activity. Therefore, catalyst characterisation is important to measure these properties in order to obtain the catalyst with desired performance. The following subtopics review the characterization techniques that will be employed in this project.

2.3.2   Characterization of Catalyst

2.3.2.1 TPDRO

One of the useful techniques used for characterization of metal catalysts is TPDRO. Temperature-programmed reduction (TPR) experiment can help to decide the suitable reduction conditions of metal oxide precursor, identify their phases and oxidation state as well as their interaction with support. During the (TPR) experiment, reducing agent

such as H_2/Ar are flowed through the catalyst (where the active phase is in oxides form) in a reactor which is linearly heated (Pinna, 1998). A TPR profile is produced which shows several peaks for each reduction process. It provides useful information on the temperatures needed for the complete reduction of a catalyst (Leong, 2018). The area under the TPR curve indicates the total hydrogen consumption during the reaction. The amount of hydrogen used up is given by the difference between mixture concentration before and after the reduction process which is measured by a thermal conductivity detector (TCD).

2.3.2.2   BET

BET is an important analysis technique to measure the specific surface area of the catalyst. It is determined by physisorption of a gas on the solid surface resulted from weak van der Waals forces between the adsorbate gas molecules and adsorbent surface area of the powder being tested (Leong, 2018).

As mentioned in the research done by Hwang and Barron (2011), nitrogen is usually employed in BET surface area analysis to remove the physically bonded impurities from the powder surface due to its high purity and strong interaction with most solids. The amount of adsorbed gas is related to the total surface area of the particles including pores in the surface. Once the adsorption layer is formed, the sample is heated to release the adsorbed nitrogen from the material and quantified them. According to Haber (1991), the pore sizes can be classified accordingly:

1. Micropores   : < 2 nm
2. Mesopores   : $2 - 50$ nm
3. Macropores   : > 50 nm

2.3.2.3   Gas Adsorption

On the other hand, physisorption methods provide information on the total surface area of catalyst, surface area of active sites or the number of active sites. The relationship between the adsorbate and adsorbent can be described as chemisorption or physisorption (Haber *et al*., 1995). Adsorption involves the deposition of molecules such as hydrogen or nitrogen onto the surface of the support. It is directly proportional to the surface area whereby the adsorption increases with the increase in surface area of the active sites. Besides that, the pore volume and pore size distribution can be

measured by determining the incremental adsorption of gas in the internal pores (Ongari, 2017).

2.3.2.4 XRD

X-ray Diffraction (XRD) is a common technique used to characterize the crystallographic structure, crystallite size, and preferred orientation in polycrystalline or powdered solid samples. According to Leong (2018), XRD can also be used to determine the relative abundance of crystalline compounds and provide structural information on unknown materials. The effect of finite crystallite sizes are observed as a broadening peaks in XRD which can be expressed by Scherrer's Equation:

$$< L > = \frac{K\lambda}{\beta \cos \theta} \qquad (Eq.\,2)$$

where,

L = measure of dimension of the particle in the direction perpendicular to the reflecting plane

λ = X-ray wavelength

β = peak width

θ = angle between the beam and the normal to the reflecting plane

K = constant (often taken as 1)

2.3.3 Analysis on Ions Content after Precipitation

It is important to determine the ions content on the catalyst because they could greatly affect the catalytic performance even though they present in very low concentration. Catalytic systems are quite sensitive to these undesirable components since they result in rapid loss of activity. Common poisons on catalyst include sulphur and chlorine. Chemik (2012) claimed that these compounds can cause deactivation of catalyst which is why it is crucial to control their concentration during the synthesis of catalyst. However, it is mostly quite difficult and time-consuming to determine the sulphur content in the other materials especially when it presents in low concentration (Chemik, 2012).

One of the methods that has been employed is ion chromatography (IC). In one example employing this technique, the sample is decomposed by means of melting in

the presence of Na_2O_2 at 800 °C in zirconium crucible which is then dissolved in an acidic medium and the IC analysis will be performed on the liquid sample (Chemik, 2012). In another study conducted by Hall and Vaive (1989), a sample is heated in a furnace and the gases are collected in the solution which is later analyzed by IC. Apart from IC, the measurement of sulphur content can also be done by using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Czerewko *et al.*, 2003).

The ions content analysis can be divided into two categories: surface analysis and bulk analysis. Surface analysis is used to determine the elements present at the outer surface layers of the solid samples (Sykes, 2017) while the bulk analysis refers to the depth profile analysis of elements in the surface of material. The following subtopics will discuss the theory and capability of each type of analysis.

2.3.3.1   Surface Studies

➢ **Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDX)**

Scanning electron microscope (SEM) scans a focused beam of high-energy electrons on the specimen surface to reveal information such as surface topography, morphology and chemical composition (Nanoscience Instruments, 2019). Energy dispersive X-ray spectroscopy (EDX) is a surface analytical technique used in conjunction with SEM or TEM (Transmission Electron Microscopy) for performing elemental or chemical analysis.

As shown in Figure 2.9 below, the sample is first bombarded by the SEM's electron beam, exciting an electron from the inner shell (e.g. K-shell) of the atoms while forming an electron hole. The vacancy is subsequently filled by an electron from an outer, higher energy shell (e.g. M-shell). The energy differences between the lower energy shell and higher energy shell is expelled in the form of X-rays.
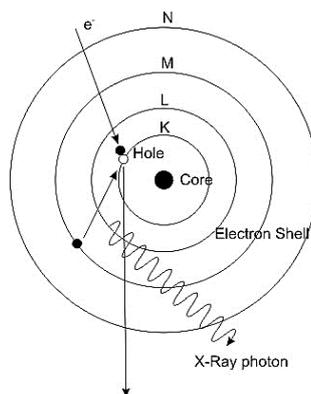
Figure 2.9: The schematic diagram of X-ray excitation. (Globalsino, 2006)

These emitted X-rays is subsequently strike on the EDX detector, producing signal that is proportional to the energy of the X-rays. The EDX detector can measure the relative abundance of emitted X-rays and their energy (Materials Evaluation and Engineering Inc., 2014). The X-ray spectrum is evaluated to determine the elemental composition of the sample. Even though this technique is more accessible and simpler than XPS, EDX possesses poor energy resolution in depth of about 1-2 μm. However, it can still provide useful information on the presence and distribution of various materials in nanofiber composites (Polini and Yang, 2017).
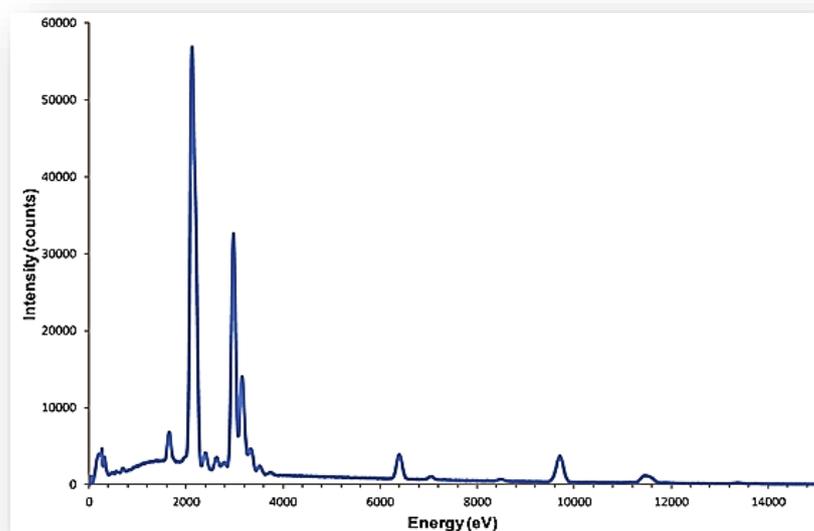
Figure 2.10: Sample of EDX spectrum. (My Scope Training, 2014)

2.3.3.2 Bulk Analysis

➢ **Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)**

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) is a powerful elemental analysis method used to determine the trace elements in aqueous solution. The working principle of ICP-OES is represented by a simple schematic diagram as shown in Figure 2.11.

In this technique, a sample solution to be analyzed is pumped by a peristaltic pump into a spray chamber through a nebulizer. The liquid sample will then converted into aerosol and transported into the central channel of the argon plasma. The ICP at its core withstands high temperature up to 10000 K where the aerosol is rapidly vaporized. Such high temperature results in substantial amounts of collisional excitation of the sample atoms within the plasma which impart energy to the atoms and convert them into ions, promoting the ions to the excited states (Hou and Jones, 2000).

Once the ions are in their excited states, they can relax to the ground states through photon emission. The grating will separate the emission radiation into wavelengths (Caruso *et al.*, 2017), followed by conversion of wavelengths into electrical signal by a detector. The signal is then amplified and displayed on the computer. In OES, the concentration of the elements can be determined by measuring the intensity of the light emitted at particular wavelengths (Boss and Fredeen, 2004). In other words, the total number of photons is directly proportional to the concentration of the elements in the sample.
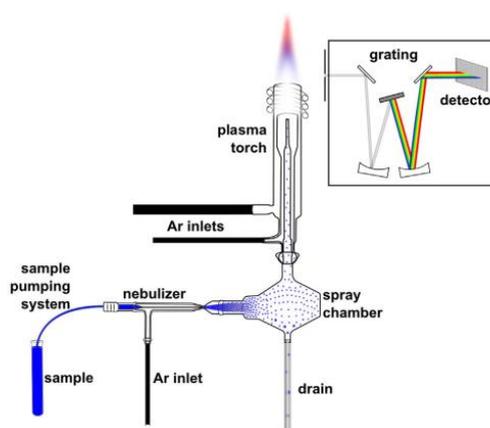
Figure 2.11: Schematic diagram of a typical ICP-OES instrument. (Caruso et al., 2017)

➢ **VIS Spectrophotometry**

VIS spectrophotometry, which is also known as visible spectrophotometry is a technique used to determine the anions concentration by measuring the light intensity when the beam of light passes through the sample solution. Generally, every chemical substances will absorb, transmit or reflect light over a certain range of wavelength. Spectrophotometry is to measure how much light the samples have absorbed or transmitted. According to Beer's law, the amount of light absorbed by a sample is proportional to its concentration in a solution. VIS spectrophotometry uses light over the visible range of 400 – 700 nm of electromagnetic radiation spectrum (Chemistry LibreTexts, 2018).

Figure 2.12 shows the basic structure of spectrophotometer. It is made up of two instruments: a spectrometer and a photometer. The spectrometer produce light of different wavelength whereas a photometer measures the light intensity. The spectrophotometer is designed in a way that the sample solution is placed between the spectrometer and photometer. The light beam is first transmitted by collimator which passes through monochromator to split the light beam into different wavelength. The wavelength selector then convey only the desired wavelength. After that, the light beam passes through the sample solution and photometer will measure the amount of photon absorbed which the signal is delivered to the digital display (Low, 2018).
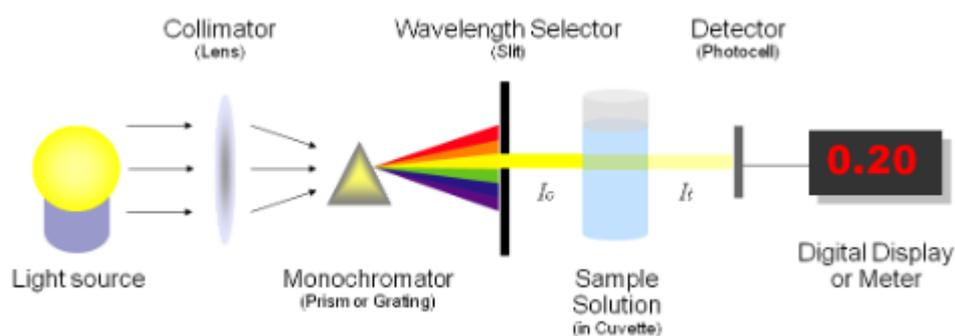
Figure 2.12: Schematic diagram of Spectrophotometer. (Chemistry LibreTexts, 2018)

CHAPTER 3

METHODOLOGY

3.1   Materials

For the synthesis of both nickel-alumina (Ni/Al_2O_3) and nickel-silica (Ni/SiO_2) catalysts through coprecipitation method, the materials used include:

Metal Precursors (Salts)
- Nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$
- Nickel sulphate, $NiSO_4 \cdot 6H_2O$
- Nickel chloride, $NiCl_2 \cdot 6H_2O$

Precipitants
- Sodium carbonate, Na_2CO_3

Support Precursor
- Aluminium nitrates, $Al(NO_3)_3 \cdot 9H_2O$
- Aluminium sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$
- Aluminium chloride, $AlCl_3 \cdot 6H_2O$
- Sodium silicate, $Na_2SiO_3 \cdot 5H_2O$

Solvent
- Deionized water, H_2O
- Acetone, C_3H_6O

Gases
- Nitrogen, N_2

3.2   Synthesis of Catalyst

Catalyst synthesis is performed to deposit the nickel catalyst onto the supports by coprecipitation. Precipitation of catalyst precursor is done through addition of sodium carbonate as precipitant. The types of precipitants, anionic salts and support ions are manipulated for the synthesis of Ni/Al_2O_3 and Ni/SiO_2 catalysts.

The synthesis begins with the simultaneous mixing of nickel nitrate and aluminium nitrate solutions, along with the addition of sodium carbonate to adjust the pH to form precipitate. The following steps outline the steps involved for the synthesis of Ni/Al$_2$O$_3$ catalyst using coprecipitation method:

1. 17.442 g of nickel nitrate, Ni(NO$_3$)$_2$·6H$_2$O was dissolved in 200 mL of deionized water to produce 0.3 M of nickel nitrate aqueous solution.

2. 47.7 g of sodium carbonate, Na$_2$CO$_3$ was dissolved in 100 mL of deionized water to produce 4.5 M of precipitating agent solution.

3. 7.5 g of aluminium nitrate, Al(NO$_3$)$_3$·9H$_2$O was dissolved in 20 mL of deionized water to form 1.0 M of aluminium nitrate aqueous solution.

4. The prepared Ni(NO$_3$)$_2$ solution and Na$_2$CO$_3$ solution were added simultaneously into a precipitating beaker at room temperature until the solution reached pH of 9.4.

5. The solution was then heated to 97 °C before adding the Al(NO$_3$)$_3$ solution. The temperature was maintained at 97 °C and Na$_2$CO$_3$ solution was added when necessary to maintain the pH at 9.

6. The slurry was aged at 97 °C and pH 9 for 90 minutes through vigorous stirring at 300 rpm.

7. After aging, the slurry was filtered with the aid of vacuum pump.

8. The precipitate retained is washed with 1 L of hot deionized water (80 °C) followed by 300 mL of acetone.

9. The washed precipitate was filtered and dried in an oven at 120 °C for 1.5 hours.

10. The dried precipitate was later calcined in a tube furnace at 400 °C for 4 hours with continuous nitrogen flow.

11. After calcination, the calcined precipitate was again washed with 100 mL of hot deionized water, dried and calcined.

12. The experiment is repeated by manipulating the metal precursor in Step 1 to nickel sulphate, NiSO$_4$·6H$_2$O and nickel chloride, NiCl$_2$·6H$_2$O

13. The experiment is repeated by changing the metal precursors in Step 3 to aluminium sulphate, Al$_2$(SO$_4$)$_3$ and aluminium chloride, AlCl$_3$·6H$_2$O.

Figure 3.1 illustrates the steps employed in the synthesis of Ni/Al$_2$O$_3$ catalyst.

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(9)

(10)
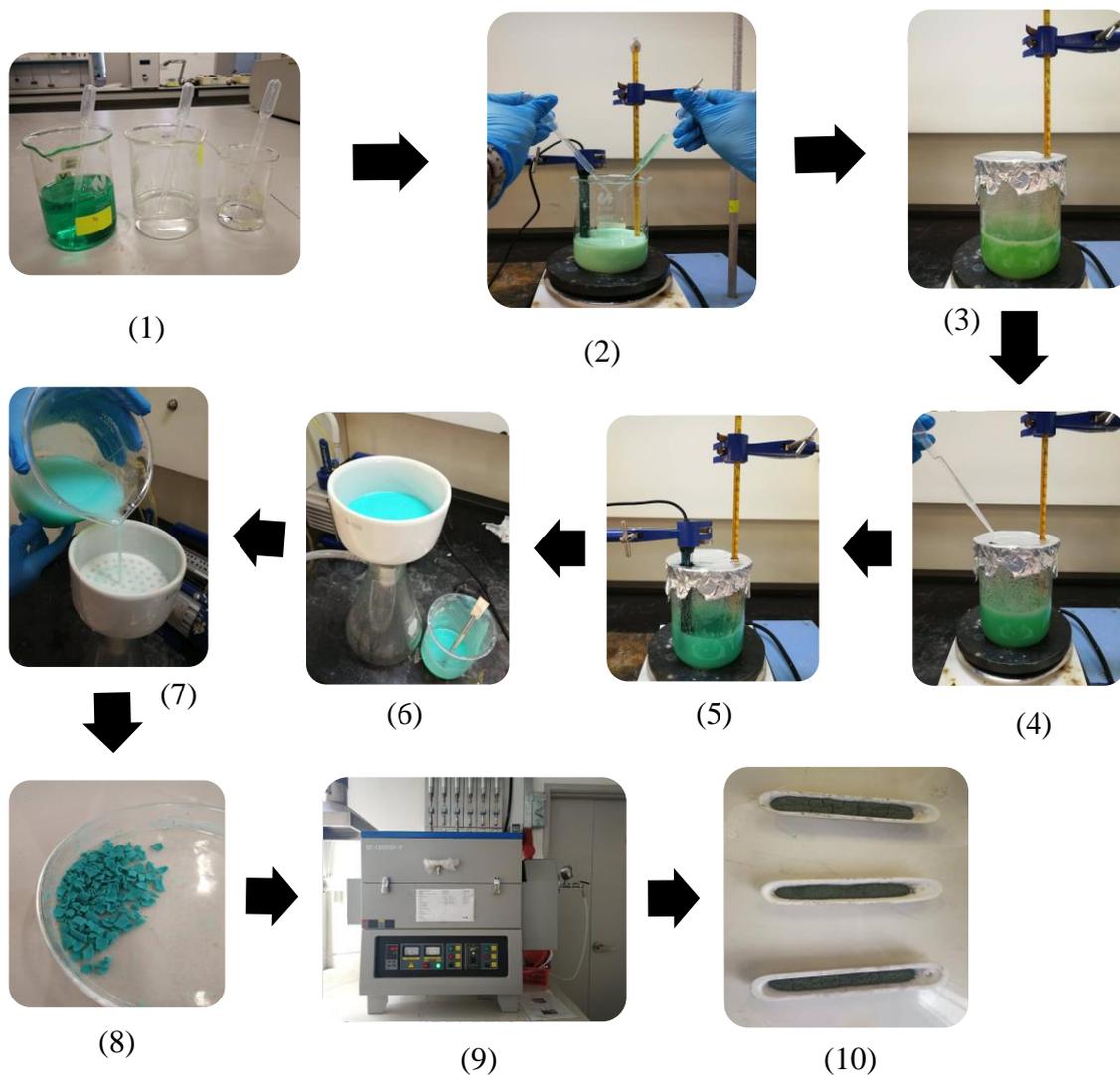
Figure 3.1: Major Steps Involved during the Synthesis of Ni/Al₂O₃ Catalyst by Coprecipitation: (1) Dissolving, (2) Simultaneous Addition of Solutions, (3) Heating, (4) Addition of metal precursor solution, (5) Aging, (6) Filtration, (7) Washing and Filtration, (8) Drying in Oven, (9) Calcination, (10) Formation of Catalyst

On the other hand, the following steps outlined the steps involved in synthesizing Ni/SiO_2 catalysts:

1. 17.442 g of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 100 mL of deionized water to produce 0.6 M of nickel nitrate aqueous solution.

2. 10 g of sodium carbonate, Na_2CO_3 was dissolved in 100 mL of deionized water to produce 10 wt % of precipitating agent solution.

3. 3 g of sodium silicate, $Na_2SiO_3 \cdot 5H_2O$ was dissolved in 150 mL of deionized water to form 2 wt % of sodium silicate solution.

4. The $Ni(NO_3)_2$ solution was preheated to 50 °C at 300 rpm.

5. Na_2CO_3 solution was then added dropwise to the $Ni(NO_3)_2$ solution to obtain pH of 8.8.

6. The solution was heated to 90 °C upon adding the Na_2SiO_3 solution.

7. The slurry was aged at 90 °C for 30 minutes.

8. After aging, the slurry was filtered using vacuum pump and washed with 1 L of hot deionized water (80 °C).

9. The washed precipitate was filtered and dried in an oven at 120 °C for 1.5 hours.

10. The dried precipitate was later calcined in a tube furnace at 400 °C for 4 hours with continuous nitrogen flow.

11. After calcination, the calcined precipitate was again washed with 100 mL of hot deionized water, dried and calcined.

12. The experiment is repeated by manipulating the metal precursor in Step 1 to nickel sulphate, $NiSO_4 \cdot 6H_2O$ and nickel chloride, $NiCl_2 \cdot 6H_2O$.

3.2.1   Changing Types of Anionic Salts

The anionic salts which are the metal precursors used in coprecipitation are manipulated in order to observe the effect of corresponding ions on the final catalysts. In this case, nickel nitrate, $Ni(NO_3)_2$, nickel sulphate, $NiSO_4$ and nickel chloride, $NiCl_2$ are employed to see the effect of nitrate, sulphate and chloride on the catalyst performance.

3.2.2   Changing Types of Support Ions

A good support establishes high dispersion of active phase and high thermal stability of the catalytic components. Therefore, the support should have the ability to prevent

the small crystal of active phase from sintering by separating them with the support components. Therefore, aluminium nitrates, $Al(NO_3)_3$, aluminium sulphate, $Al_2(SO_4)_3$ and sodium silicate, Na_2SiO_3 are used as support in this study to produce alumina and silica supported catalysts.

3.2.3   Effect of Washing Condition and Heat Treatment after Precipitation

After the precipitates are filtered out from the solution, several washing steps are carried out to remove residual or unwanted compounds to avoid sintering and aggregation of particles during thermal treatment. This is followed by drying and calcination of precipitates. After that, the calcined precipitates are washed again with deionized water. This is because after the precipitates undergo calcination process, the forces between the adsorbed ions and the precipitates will become weak. Thus, the ions will be easily desorbed from the precipitates and removed through washing. This washing process is repeated until the impurity level decreases to the desired purity. Usually, deionized water is used as the solvent in the washing of precipitates. However, Wong *et al*. (2018) in their research, reported that acetone can also be used for washing precipitate as it acts as good solvent for sodium ions.

3.3   Characterisation

Succeeding the synthesis of catalyst, different characterisation techniques and instrumentations were performed on the prepared catalyst samples to determine the performance, catalytic activity and help in the investigation of the catalyst preparation method. In this topic, the methods used to characterize the prepared catalysts are described. SEM was applied for the study of physical properties, whereas EDX, ICP-OES and VIS spectrophotometry were utilized for the chemical characterisation.

3.3.1   Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

Perkin Elmer Optical Emission Spectrometer Optima 7000 DV is employed to perform analysis on the bulk composition of the catalyst samples with argon gas as plasma. Since the samples introduced into ICP-OES should be in liquid form, the catalyst samples were completely dissolved in 1 M nitric acid at room temperature for 1 day prior to ICP-OES analysis in order to release the metal elements into the solution. The synthesized catalysts were analysed for the presence of Ni, Al and Na. The standard solution for nickel, aluminium and sodium was prepared at concentration of 10, 50,

100 and 500 ppm while the blank solution used in this analysis was nitric acid. The actual concentration of Ni, Al and Na present in the catalyst samples were determined from this range of standard using the calibration curve obtained.

Three replications of measurement were taken for each sample to obtain results of better accuracy. A wash time of 2 minutes was allocated between each analysis. For analysis of Na content, 50 ppm of potassium was added into the calibration standards and samples by using potassium chloride, KCl_2 in order to prevent ionisation interference. Calibration standards were prepared by using $Ni(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and Na_2CO_3 dissolved in 2 M nitric acid respectively. Calculations involved in preparation of standards an d samples for ICP-OES analysis are presented in Appendix B.

Figure 3.2: Perkin Elmer Optical Emission Spectrometer Optima 7000 DV

3.3.2 Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

The SEM was carried out to determine the surface morphology and topography of the catalyst samples, whereas EDX analysis was carried out in conjunction with SEM to

investigate the sub-surface (1 μm depth) elemental composition of the sample. Hitachi S-3400N was employed with electron beam of 20 kV energy and various magnification was used for the measurements. A small amount of samples was placed on the multi sample holder and coated with a layer of palladium and gold with Emitech Sputter Coater to increase their conductivity.

Figure 3.3: Hitachi S-3400N Scanning Electron Microscopy

3.3.3 VIS Spectrophotometry

VIS Spectrophotometry was conducted using HACH DR3900 VIS Spectrophotometer to measure the concentration of the residual anions such as nitrates, sulfates, and chlorides present in the catalyst samples. Each of the ions required different sample preparation before carrying out the analysis.

To test for the nitrate ions concentration, cadmium reduction method was being applied by using the NitraVer 5 Nitrate Reagent powder pillow which contains all the necessary reagents. The reagent powder was then added into the sample solution filled in a clean and clear sample cell, while taking a 10 mL of sample solution as blank having 0 mg/L of NO_3^- . A mixing reaction time of 6 minutes was required before the

sample cell is inserted into the cell holder of the spectrophotometer. It is measured at the wavelength of 500 nm using the built-in photometric programme with reference to the standard nitrate solution.

On the other hand, sulfate ions were estimated by USEPA SulfaVer 4 Method. In this method, a SulfaVer 4 reagent powder pillow was added to the sample cell and it was swirled to mix the prepared sample. A 5 minutes reaction time was then started. Another sample cell was filled with 10 mL of sample solution and the sample cell was wiped and placed into the cell holder. The zeroing program was selected and the screen will display 0 mg/L of SO_4^{2-}. After the 5 minutes reaction, the prepared sample was inserted into the cell holder. The read program was selected to obtain the concentration of the sulfate ions. It is measured at the wavelength of 450 nm using the built-in photometric programme with reference to the standard sulfate solution.

In addition, chloride ions were determined by Mercuric Thiocyanate Method at wavelength of 455 nm. 0.8 mL of Mercuric Thiocyanate solution was pipetted into each sample cell (prepared sample and blank solution), followed by addition of 0.4 mL of Ferric Ion solution. The blank solution used in this test was deionized water having 0 mg/L of Cl^-. After thorough mixing, orange colour developed, indicating the presence of chloride ions in the sample. The concentration was recorded after 2 minutes reaction time.

Figure 3.4: HACH DR3900 VIS Spectrophotometer

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Observation from Synthesis of Catalysts

Both Ni/Al_2O_3 and Ni/SiO_2 catalysts were synthesized by coprecipitation method. There are a total of 5 samples for alumina-supported catalysts and 3 samples for silica-supported catalysts which were prepared by different combination of anionic salts and metal precursors.

For alumina-supported catalysts, a number of samples were selectively washed with acetone to study the effectiveness of acetone in removing the impurities or residual ions on the surface of the catalysts. As shown in Table 4.1, the first 3 samples labelled with 1a, 2a and 3a were washed with hot deionized water whereas part of the samples (1b, 2b and 3b) were further washed with acetone at room temperature.

Table 4.1: List of synthesized Ni/Al_2O_3 and Ni/SiO_2 catalysts

Label	Anionic Salts	Support Precursors	Precipitant	Washing Condition
1a	$Ni(NO_3)_2 \cdot 6H_2O$	$Al(NO_3)_3 \cdot 9H_2O$		Hot water
2a	$NiSO_4 \cdot 6H_2O$	$Al_2(SO_4)_3 \cdot 18H_2O$		Hot water
3a	$NiCl_2 \cdot 6H_2O$	$AlCl_3 \cdot 6H_2O$		Hot water
1b	$Ni(NO_3)_2 \cdot 6H_2O$	$Al(NO_3)_3 \cdot 9H_2O$		Acetone
2b	$NiSO_4 \cdot 6H_2O$	$Al_2(SO_4)_3 \cdot 18H_2O$		Acetone
3b	$NiCl_2 \cdot 6H_2O$	$AlCl_3 \cdot 6H_2O$	Na_2CO_3	Acetone
4	$Ni(NO_3)_2 \cdot 6H_2O$	$Al_2(SO_4)_3 \cdot 18H_2O$		Hot water
5		$AlCl_3 \cdot 6H_2O$		Hot water
6	$Ni(NO_3)_2 \cdot 6H_2O$			Hot water
7	$NiSO_4 \cdot 6H_2O$	$Na_2SiO_3 \cdot 5H_2O$		Hot water
8	$NiCl_2 \cdot 6H_2O$			Hot water

4.1.1 Physical Appearance and Colour

In the experiment, the simultaneous addition of nickel salts and sodium carbonate solutions, followed by metal precursor solution produced precipitates with different colour. Ni/Al_2O_3 catalyst shown bluish-green precipitates while Ni/SiO_2 catalyst shown greenish precipitates. The physical appearances of Ni/Al_2O_3 and Ni/SiO_2 catalysts during the precipitation were illustrated in Figure 4.1.

(a)   (b)
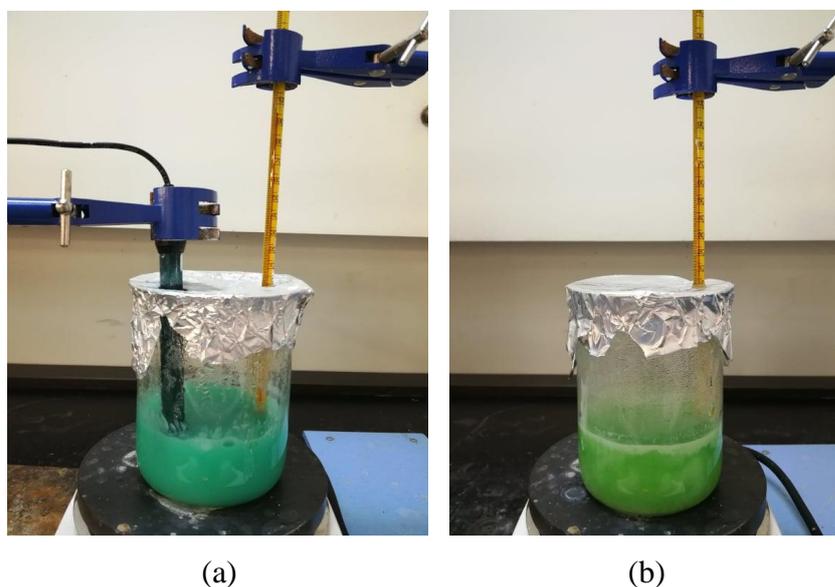
Figure 4.1: (a) Bluish-green precipitate of Ni/Al_2O_3 catalyst; (b) Greenish precipitate of Ni/SiO_2 catalyst

After the precipitation process, the resulting slurry was filtered, washed, dried and finally grinded into powder form prior to calcination. The colour of dried, powdered Ni/Al_2O_3 and Ni/SiO_2 catalysts are same as the colours shown during precipitation which is shown in Figure 4.2.

(a)   (b)

Figure 4.2: (a) Powdered Ni/Al$_2$O$_3$ catalyst; (b) Powdered Ni/SiO$_2$ catalyst

Subsequently, the powdered catalysts were calcined in a tube furnace with continuous flow of nitrogen gas under 400 ℃ for 4 hours. As shown in Figure 4.3, the appearance of Ni/Al$_2$O$_3$ and Ni/SiO$_2$ catalysts after the calcination were slightly different with the former shown dark greenish powder (which probably indicates the reduction was incomplete), and the latter shown black colour powders.

(a)   (b)
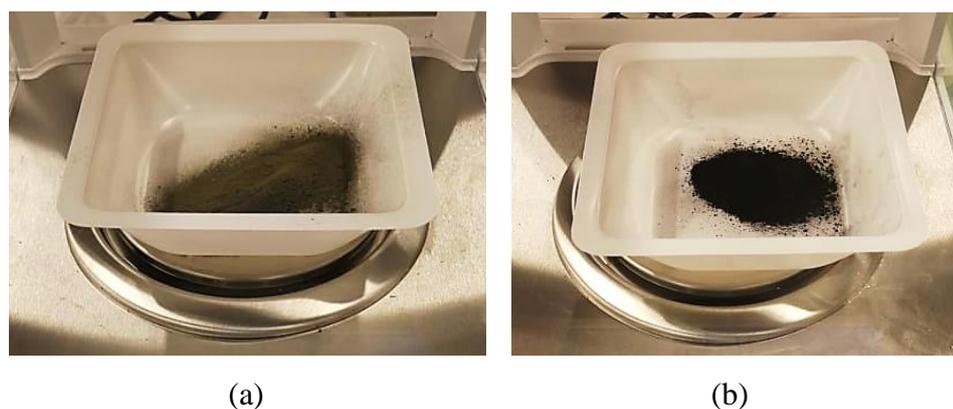
Figure 4.3: (a) Dark-greenish Ni/Al$_2$O$_3$ catalyst powder; (b) Black Ni/SiO$_2$ catalyst powder

4.2   Characterization of Catalyst

The synthesized Ni/Al$_2$O$_3$ and Ni/SiO$_2$ catalysts were subjected to various characterization techniques to study the surface analysis and bulk analysis of the catalysts. The characterization techniques employed were Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDX), Inductively

Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and VIS Spectrophotometry. The results obtained from these analyses are presented in the following sections.

4.3   Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

The surface morphology of synthesized Ni/Al_2O_3 and Ni/SiO_2 catalysts were observed using SEM. Concurrently, EDX was employed to determine the elemental composition on the surface of the catalyst samples. The SEM images of all the synthesized catalyst samples were shown in Figure 4.4 to Figure 4.14. These SEM images illustrate that all catalyst samples have rough coarse surfaces and have very similar morphology between the samples.

Figure 4.4: SEM image of Ni/Al_2O_3 catalyst (Sample 1a) – Magnification ×2000

Figure 4.5: SEM image of Ni/Al_2O_3 catalyst (Sample 1b) – Magnification ×1800
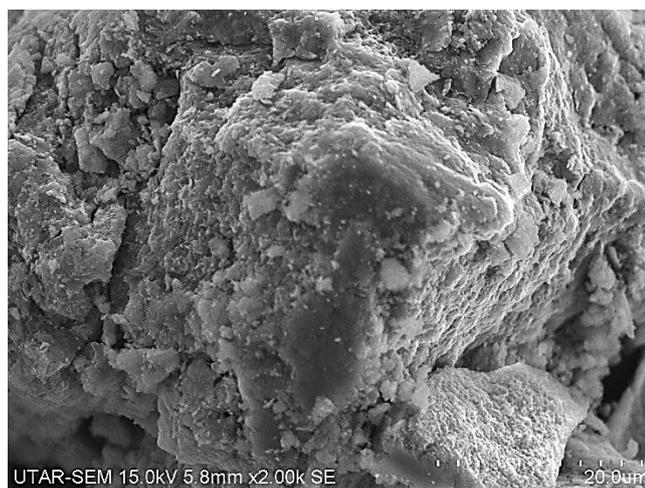
Figure 4.6: SEM image of Ni/Al$_2$O$_3$ catalyst (Sample 2a) – Magnification ×2000

Figure 4.7: SEM image of Ni/Al$_2$O$_3$ catalyst (Sample 2b) – Magnification ×1600
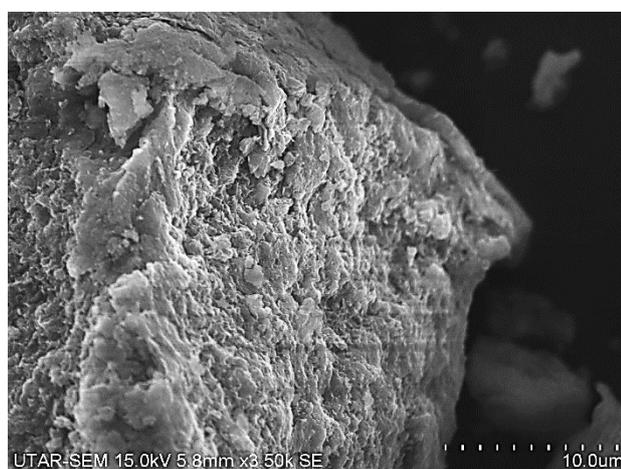
Figure 4.8: SEM image of Ni/Al$_2$O$_3$ catalyst (Sample 3a) – Magnification ×3500
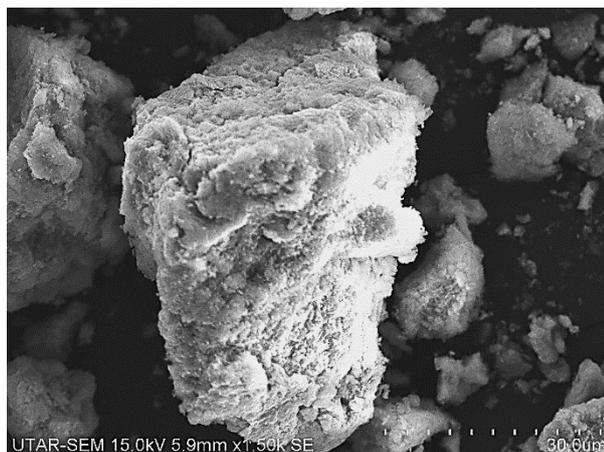
Figure 4.9: SEM image of Ni/Al₂O₃ catalyst (Sample 3b) – Magnification ×1500

Figure 4.10: SEM image of Ni/Al₂O₃ catalyst (Sample 4) – Magnification ×1900
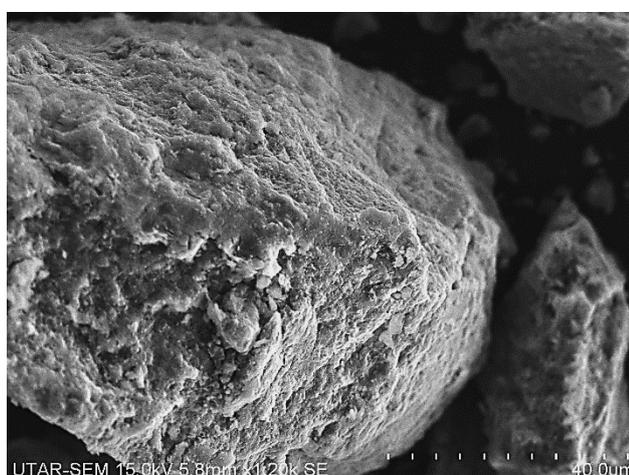
Figure 4.11: SEM image of Ni/Al₂O₃ catalyst (Sample 5) – Magnification ×1200
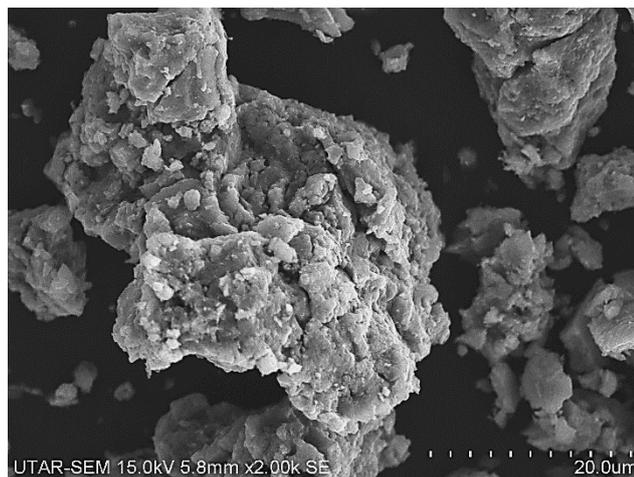
Figure 4.12: SEM image of Ni/SiO₂ catalyst (Sample 6) – Magnification ×2000
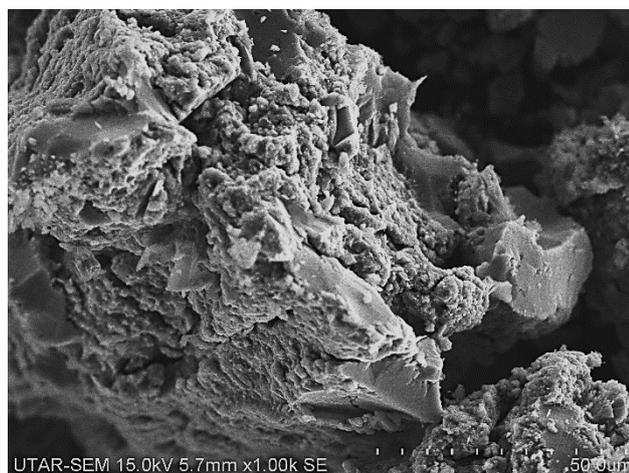
Figure 4.13: SEM image of Ni/SiO₂ catalyst (Sample 7) – Magnification ×1000
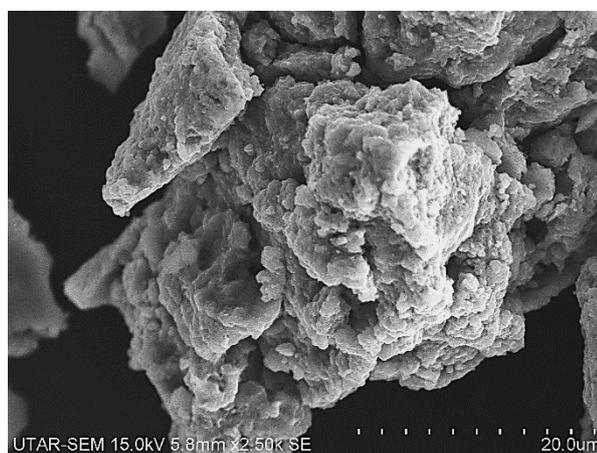
Figure 4.14: SEM image of Ni/SiO₂ catalyst (Sample 8) – Magnification ×2500

For EDX analysis, the information of the nickel, sodium and aluminium loading on the catalysts are tabulated in Table 4.2 in terms of weight percentage with the raw data of EDX attached in Appendix C.

Looking at Table 4.2, the nickel loading on Ni/SiO$_2$ catalysts are relatively higher than Ni/Al$_2$O$_3$ catalysts, where the loading of around 60 to 70 wt% came very close to the intended nickel loading of 65.1 wt%. This showed that nickel metals are well precipitated on the surface of the silica and are uniformly distributed. On the contrary, Ni/Al$_2$O$_3$ samples showed lower nickel loading ranging from 38 to 62 wt%, which is somewhat lower than the originally intended 64 wt%. This probably shows a non-uniform distribution of nickel metals. In addition, too low nickel content could also indicate that significant amount of nickel are not precipitated to form the takovite as most of them have been washed away during the synthesizing process. Since EDX can only provide surface elemental composition of the samples rather than bulk compositions, therefore, the nickel loading of Ni/Al$_2$O$_3$ and Ni/SiO$_2$ samples should not rely solely on EDX analysis, but further clarification was conducted by ICP-OES as discussed in the following section.

Furthermore, the amount of sulphur and chlorine on the surface of the samples are of main concern. It is expected that the sulphur content will be higher for takovite samples prepared from sulfate anion and chlorine content will be higher for takovite samples prepared from chloride anion, which are in fact true for most of the samples. Theoretically, the acetone-washed catalysts labelled with 1b, 2b and 3b as shown in Table 4.2 should exhibit a lower weight percentage of sulphur and chlorine content compared to the other samples that were washed with purely hot deionized water. However, the results obtained from EDX analysis reflect otherwise, especially chlorine, which show higher weight percentage on acetone-washed samples. This might take into account the fact that acetone is comparatively better solvent for sulphur than chlorine. On the other hand, among the acetone-washed catalysts, it can be seen that sample 3b has slightly higher sulphur content than sample 3a, which is washed with hot deionized water. This might be due to the usage of acetone at room temperature which affects the solubility of sulphur in the solvent. According to Isoflex (2015), sulphur is moderately soluble in acetone, with its solubility increasing with temperature.

Table 4.2: EDX elemental composition

Label	Weight Percentage of Elements (Wt %)							
	C	O	Ni	Na	Al	S	Cl	Si
1a	17.50	20.15	53.99	0.46	6.58	0.25	0.30	0.77
2a	8.14	20.64	61.80	0.37	7.17	0.92	0.16	0.81
3a	22.02	20.84	50.17	0.28	5.66	0.22	0.33	0.46
1b	29.20	25.50	38.65	0.19	5.56	0.00	0.31	0.58
2b	11.09	22.52	57.22	0.37	7.24	0.61	0.35	0.61
3b	13.39	20.11	57.55	0.00	7.74	0.23	0.38	0.61
4	18.17	20.76	52.32	0.36	6.58	0.61	0.46	0.74
5	27.72	21.25	45.82	0.00	4.76	0.13	0.17	0.15
6	16.58	18.51	59.20	0.50	0.57	0.00	0.21	4.43
7	8.92	18.69	65.53	0.43	0.82	0.19	0.32	5.09
8	5.35	18.25	69.79	0.24	0.62	0.22	0.00	5.53

4.4 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

The results obtained from ICP-OES analysis are presented in Figure 4.15. It is observed that the Ni/SiO_2 samples contain high Ni concentration as compared to Ni/Al_2O_3 samples, in which the results are mostly in agreement with that obtained from EDX analysis. Comparison is done by comparing the trends of ICP-OES and EDX. It is realised that the graphs have shown different trend for samples 3a and 5. The nickel content in ICP-OES shows an increasing trend for both of the samples but the trend turns out opposite in EDX. As discussed in the previous section, it might be due to the nickel content that has been washed away from the surface of the samples, and most of the nickel were deposited in the internal surface of the catalysts, resulting in lower nickel surface distribution observed by EDX and higher bulk composition of nickel.

The comparison between nickel and aluminium content with their corresponding theoretical values have been carried out and plotted in graphs as shown in Figure 4.16 and Figure 4.17 respectively. The theoretical values for nickel and aluminium are included in the figures and they represent the starting amount of nickel and aluminium content that were used and assumed fully precipitated during the coprecipitation process. From Figures 4.16 and 4.17, it can be seen that both the nickel and aluminium content that are present in the Ni/Al_2O_3 catalysts are much lower than

their theoretical values. The fact that both nickel and aluminium concentration from ICP-OES are consistently lower than the theoretical nickel and aluminium concentration probably implies that supersaturation has not been fully achieved to precipitate out all the nickel and aluminium during the coprecipitation of Ni/Al_2O_3 based catalysts.

In contrast, the measured nickel and aluminium concentration for Ni/SiO_2 has revealed that both metal content are higher than the theoretical value. There are several possible reasons for this: (i) lower silica is precipitated which result in higher relative nickel percentage, however this requires further studies on the residual silicon content in water; (ii) sampling error that resulted from selecting samples that have high nickel content. The second reason looks unlikely given that three Ni/SiO_2 samples consistently show higher nickel content compared to theoretical values. For the Ni/SiO_2 catalysts, the higher value of measured nickel compared to theoretical value also indicates that full supersaturation most likely has been achieved for nickel precipitation.

In addition to the reason stated above, the discrepancy between measured and theoretical concentration of nickel and aluminium could be due to the fact that during the sample preparation upon the ICP-OES analysis, especially during the weighing process of samples because the weighing scale has inconsistent negative Zero Error.

Figure 4.18 shows the sodium content of the synthesized catalyst samples. The theoretical concentration for sodium should be zero, as the chemistry (Eq. 4 and Eq. 6 shown in Appendix A) indicates that all the sodium should be soluble during the coprecipitation process. As can be seen from Figure 4.18, significant (although low) amount of sodium can be observed on the catalyst samples, and it implies that significant occlusion take place during the coprecipitation. In addition, it can also be seen that generally acetone washed samples exhibit lower sodium content and there is no significant difference between the sodium content for alumina-based and silicate-based samples, where both show around the same level of sodium.
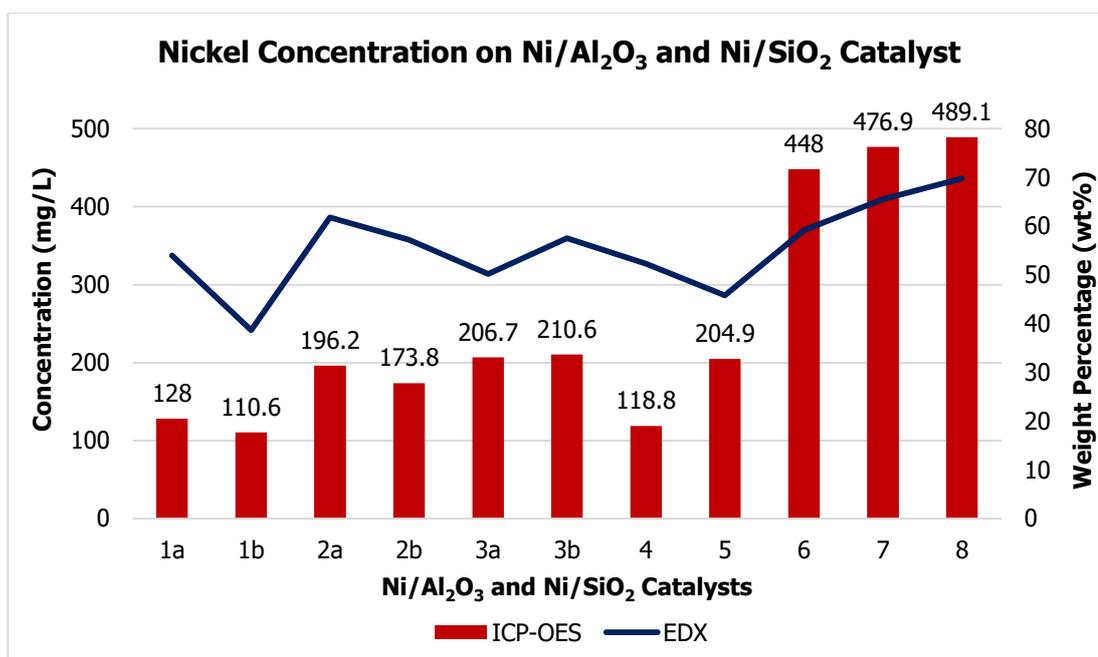
Figure 4.15: Comparison of results obtained from ICP-OES and EDX on Ni concentration
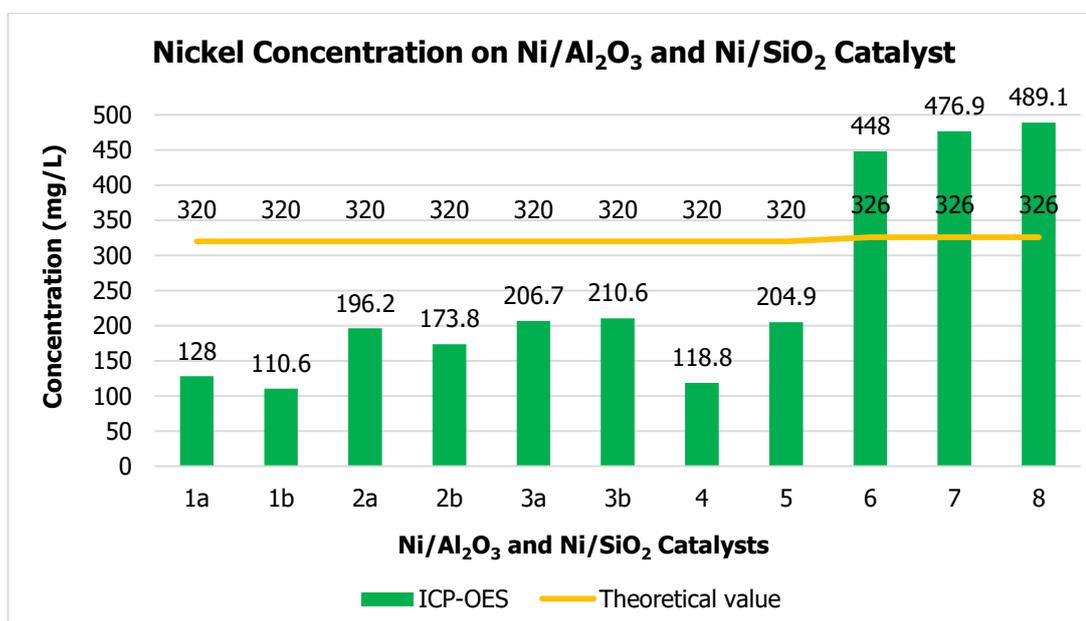
Figure 4.16: Comparison of results between ICP-OES and theoretical value on Ni concentration

Aluminium Concentration on Ni/Al$_2$O$_3$ and Ni/SiO$_2$ Catalyst
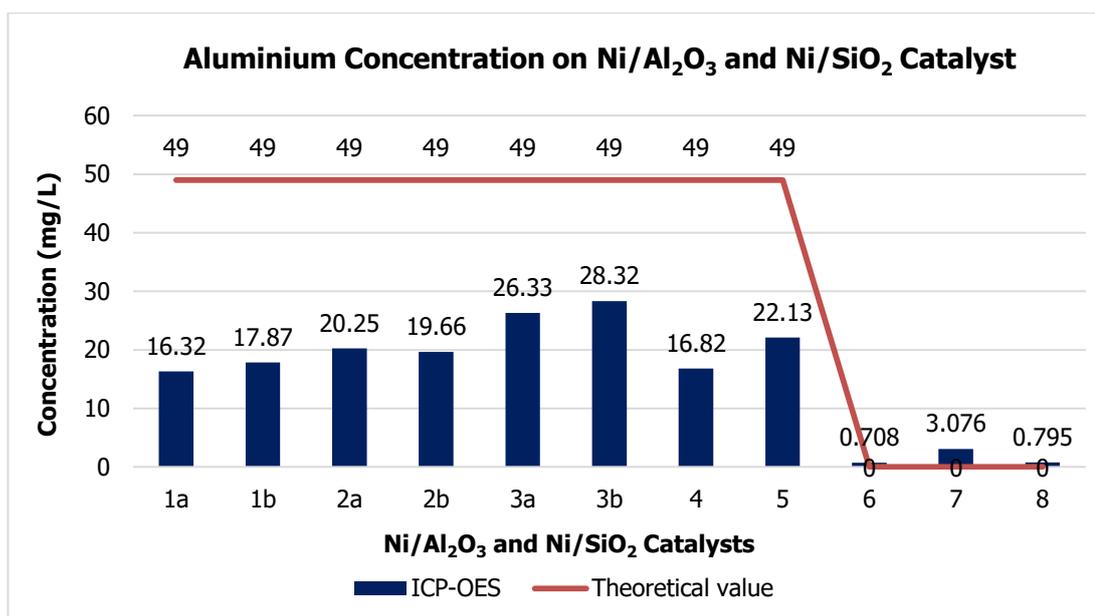
Figure 4.17: Comparison of results between ICP-OES and theoretical value on Al concentration

Sodium Concentration on Ni/Al$_2$O$_3$ and Ni/SiO$_2$ Catalyst
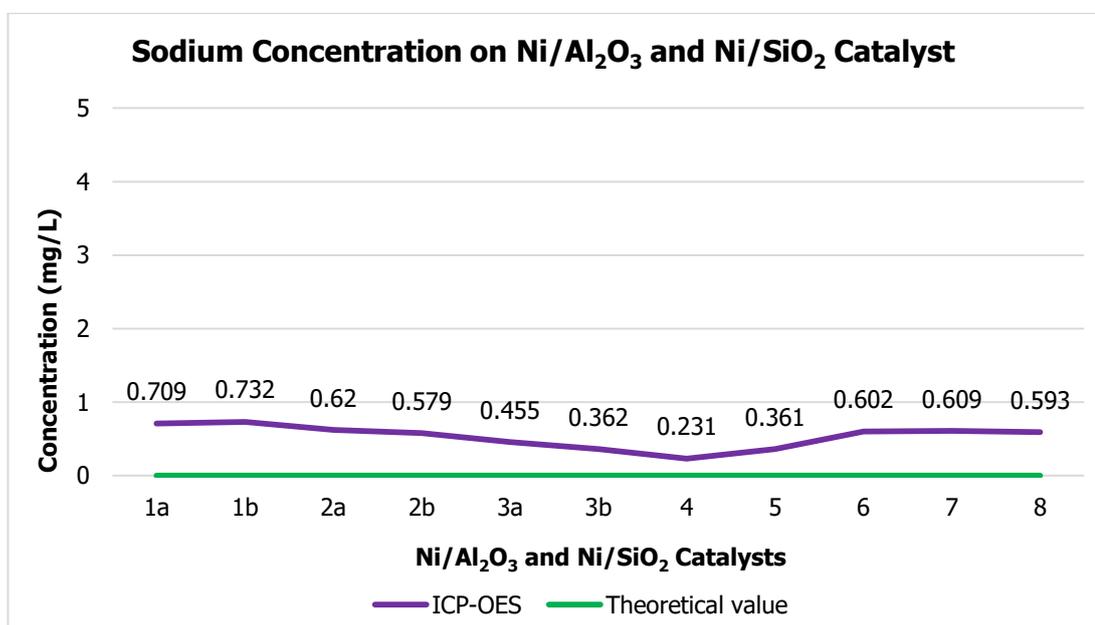
Figure 4.18: Comparison of results between ICP-OES and theoretical value on Na concentration

4.5 VIS Spectrophotometry

VIS spectrophotometer was employed to determine the concentration of residual ions such as nitrates, chlorides and sulfates upon the washing of calcined samples. The results obtained are depicted in Table 4.3 below. Based on the data attained from the visible spectrophotometry analysis, it can be seen that some of the samples showed

negative readings on the ions concentration. This is probably due to too little amount of nitrates, chlorides and sulfates ions present in the sample solutions for detection. As VIS spectrophotometer is only able to detect concentration within ppm level. Thus, it is suggested to employ another characterization technique which is capable of detecting ion concentration up to ppb level.

On top of that, it is expected that the samples washed with acetone (highlighted in green) exhibit lower ions concentration as compared to those samples washed with deionized water. The outcomes of this analysis has proven the fact that there are smaller concentration of nitrate and sulphate ions present in the sample solutions. However, the results do not make sense when it comes to chloride concentration, which is similar to the case of EDX analysis that indicates higher chlorine content on the surface of the samples. This might be because the acetone is ineffective in removing the chloride ions.

Table 4.3: Results from HACH Spectrophotometer

Samples	Anions Concentration (mg/L)		
	NO_3^-	Cl^-	SO_4
1a	0.0	0.5	-1.0
2a	0.1	1.4	0.0
3a	0.3	0.9	0.0
1b	-2.6	1.7	-3.0
2b	-0.9	0.9	0.0
3b	-0.7	1.8	-1.0
4	0.2	0.8	-1.0
5	-1.3	1.1	-1.0
6	0.3	0.7	-1.0
7	0.2	1.2	0.0
8	0.7	0.3	0.0

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1   Conclusion

In this project, Ni/Al_2O_3 and Ni/SiO_2 catalysts have been synthesized through coprecipitation method using different combination of support precursors and selective washing, followed by several characterization techniques such as SEM-EDX, ICP-OES and VIS spectrophotometry to provide both physical and chemical information of the catalyst samples. The following project objectives have been achieved where:

a) The effect of change of support precursor has been studied. The results obtained from both EDX and ICP-OES analysis have shown significantly high nickel concentration on Ni/SiO_2 samples compared to the Ni/Al_2O_3 catalysts, which could be due to different level of supersaturation achieved during the coprecipitation process. For alumina-based catalysts, it is thought that nickel and aluminium were not fully precipitated during the coprecipitation process.

b) The effect of change of anion salts has been studied. From the EDX result, the sulfur and chlorine content on the catalyst samples can be seen to be significant for catalyst synthesized from sulfate and chloride salt respectively.

c) There is trivial amount of sodium impurities found in both Ni/Al_2O_3 and Ni/SiO_2 catalyst samples where both show around the same level of sodium. The aluminium content is found notably in Ni/Al_2O_3 samples while minor amount is present in Ni/SiO_2 samples, which meet the expectation.

d) The effect of washing condition on the residual ions has been studied. Acetone and hot deionized water were used as solvent for particular samples to see their effects in removing the anions. The results from EDX and VIS spectrophotometry have depicted relatively low sulphur and nitrate ion on acetone-washed samples, but not for chloride ion which reflect otherwise. It is believed that acetone is not a good washing solvent in eliminating chloride ions.

5.2   Recommendations for Future Work

This project has covered several important grounds that started from synthesizing of nickel supported catalysts, to the characterization of catalysts to determine the presence of residual ion that acts as the catalyst poison. Several recommendations for future work include:

a) Employing ion chromatography (IC) for better analysis in identifying the concentration of anions or cations present in the samples which can go down to ppb levels.

b) Other characterization techniques such as Transmission Electron Microscope (TEM) and Brunauer-Emmett-Teller (BET) can be employed to study the nickel catalysts in greater extent. TEM can be used to determine the particle size of nickel metal while BET can provide information on specific surface area, pore size and porosity of the catalysts.

c) Employing acetone as the main washing solvent to remove impurities or residual ions on the surface of the catalysts as it can effectively reduce the degree of poisoning that can lead to catalyst deactivation.

d) Ensure that full supersaturation is achieved during the coprecipitation process, and thus a closer study of coprecipitation condition is required.

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APPENDICES

APPENDIX A: Calculation for Preparation of Catalysts by Coprecipitation Method

Ni/Al₂O₃

Coprecipitation reaction equation:

$$6Ni(NO_3)_2 \cdot 6H_2O + 2Al(NO_3)_3 \cdot 9H_2O + 9Na_2CO_3$$
$$\rightarrow Ni_6Al_2(OH)_{16}CO_3 \cdot 4H_2O + 18NaNO_3 + 8CO_2 + 42H_2O \qquad \text{(Eq. 3)}$$

Calcination reaction equation:

$$Ni_6Al_2(OH)_{16}CO_3 \cdot 4H_2O \rightarrow 6NiO + Al_2O_3 + 12H_2O + CO_2 \qquad \text{(Eq. 4)}$$
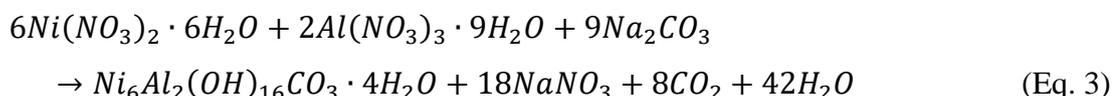
During the synthesizing process of nickel-alumina (Ni/Al₂O₃) catalysts, the requirements tabulated in Table A.1 below must be fulfilled.

Table A.1: Synthesizing Requirements

Catalyst	Aspects	Conditions
Ni/Al₂O₃	Molarity of $Ni(NO_3)_2 \cdot 6H_2O$ (M)	0.3
	Molarity of $Al(NO_3)_3 \cdot 9H_2O$ (M)	1.0
	Molarity of Na_2CO_3 (M)	4.5

a) Preparation of 0.3 M of $Ni(NO_3)_2 \cdot 6H_2O$:

$$Molecular\ Weight\ of\ Ni(NO_3)_2 \cdot 6H_2O = 290.7\ g/mol$$

$$Concentration\ of\ Ni(NO_3)_2 \cdot 6H_2O = 0.3\frac{mol}{L} \times 290.7\frac{g}{mol}$$

$$= 87.21\frac{g}{L}$$

$$= \frac{17.442\ g}{0.2\ L}\ (0.06\ mol)$$

b) Preparation of 1 M of $Al(NO_3)_3 \cdot 9H_2O$:

$$Molecular\ Weight\ of\ Al(NO_3)_3 \cdot 9H_2O = 375\ g/mol$$

$$\text{Concentration of } Ni(NO_3)_2 \cdot 6H_2O = 1\frac{mol}{L} \times 375\frac{g}{mol}$$

$$= 375\frac{g}{L}$$

$\text{Since the molar ratio of } Ni: Al = 3:1,$

$Ni: Al = 0.06\ mol : 0.02\ mol$

$$1M = \frac{0.02\ mol\ of\ Al}{x\ L\ of\ deionized\ water}$$

$x = 0.02\ L$

$$\text{Mass of } Al(NO_3)_3 \cdot 9H_2O = 0.02\ mol \times 375\frac{g}{mol}$$

$$= 7.5\ g$$

$$\text{Concentration of } Ni(NO_3)_2 \cdot 6H_2O = \frac{7.5g}{0.02\ L}$$

c) Preparation of 4.5 M of Na_2CO_3 :

$$\text{Molecular Weight of } Na_2CO_3 = 106\ g/mol$$

$$\text{Concentration of } Na_2CO_3 = 4.5\frac{mol}{L} \times 106\frac{g}{mol}$$

$$= 477\frac{g}{L}$$

$$= \frac{47.7g}{0.1\ L}$$

Table A.2 summarised the amount of deionized water and chemicals needed to prepare the solutions for synthesis of catalyst.

Table A.2: Summary of Calculations for Solutions Preparation

Substances	Mass (g)	Volume of Deionized Water (mL)
$Ni(NO_3)_2 \cdot 6H_2O$	17.442	200
$Al(NO_3)_3 \cdot 9H_2O$	7.5	20
Na_2CO_3	47.7	100

Ni/SiO₂

Coprecipitation reaction equation:

$$3Ni(NO_3)_2 \cdot 6H_2O + 2Na_2SiO_3 \cdot 5H_2O + Na_2CO_3$$
$$\rightarrow Ni_3Si_2O_5(OH)_4 + 6NaNO_3 + CO_2 + 26H_2O \qquad \text{(Eq. 5)}$$

Calcination reaction equation:

$$Ni_3Si_2O_5(OH)_4 \rightarrow 3NiO + 2SiO_2 + 2H_2O + CO_2 \qquad \text{(Eq. 6)}$$
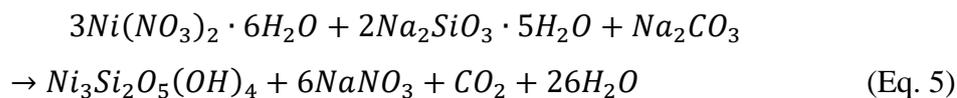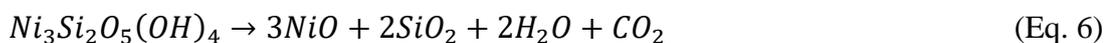
During the synthesizing process of nickel-silica (Ni/SiO₂) catalysts, the requirements tabulated in Table A.3 below must be fulfilled.

Table A.3: Synthesizing Requirements

Catalyst	Aspects	Conditions
Ni/SiO₂	Molarity of $Ni(NO_3)_2 \cdot 6H_2O$ (M)	0.6
	Concentration of $Na_2SiO_3 \cdot 5H_2O$ (wt%)	2.0
	Concentration of Na_2CO_3 (wt%)	10.0
	Molar ratio of $Ni:Si$	1 : 0.21

a) Preparation of 0.6 M of $Ni(NO_3)_2 \cdot 6H_2O$:

$$Molecular\ Weight\ of\ Ni(NO_3)_2 \cdot 6H_2O = 290.7\ g/mol$$

$$Concentration\ of\ Ni(NO_3)_2 \cdot 6H_2O = 0.6\frac{mol}{L} \times 290.7\frac{g}{mol}$$

$$= 174.42\frac{g}{L}$$

$$= \frac{17.44\ g}{0.1\ L}\ (0.06\ mol)$$

b) Preparation of 2 wt% of $Na_2SiO_3 \cdot 5H_2O$:

$$Molecular\ Weight\ of\ Na_2SiO_3 \cdot 5H_2O = 212.1\ g/mol$$

$$2\ wt\ \% = 2g\ in\ 100\ mL$$
$$= 0.00943\ mol\ in\ 100\ mL$$

Since the molar ratio of $Ni: Si = 1: 0.21,$

$Ni: Al = 0.06 \, mol : 0.0126 \, mol$

$$Volume \ of \ deionized \ water \ required = \frac{0.0126 \, mol \ of \ Si}{0.00943 \, mol \ per \ 100 \, mL}$$

$$= 134 \, mL$$

Thus, $Na_2SiO_3 \cdot 5H_2O$ solution was made in excess by dissolving 3g of $Na_2SiO_3 \cdot 5H_2O$ in 150 mL of deionised water to produced 2 wt% of Si solution. Since only 134 mL is required for the reaction, 16 mL of Si solution was then pipetted out.

c) Preparation of 10 wt% of Na_2CO_3 :

$10 \, wt \, \% = 10g \ in \ 100 \, mL$

Table A.4 summarised the amount of deionized water and chemicals needed to prepare the solutions for synthesis of catalyst.

Table A.4: Summary of Calculations for Solutions Preparation

Substances	Mass (g)	Volume of Deionized Water (mL)
$Ni(NO_3)_2 \cdot 6H_2O$	17.44	100
$Na_2SiO_3 \cdot 5H_2O$	3	150
Na_2CO_3	10	100

APPENDIX B: Preparation of Solutions Used in ICP-OES

1. **Preparation of 1M HNO₃**

$$1M \; HNO_3 = \frac{1 \; mol \; HNO_3}{1 \; L \; of \; Deionized \; Water}$$

$$Molecular \; Weight \; (MW) \; of \; HNO_3 = 63.01 \frac{g}{mol}$$

$$Mass \; of \; HNO_3 = Number \; of \; Moles \; \times MW$$

$$= 1 \; mol \; \times \; 63.01 \frac{g}{mol}$$

$$= 63.01 \; g \; of \; HNO_3$$

2. **Preparation of Sample Solution for Ni/Al₂O₃ catalysts**

$$Percentage \; of \; Ni \; in \; Ni/Al_2O_3 = \frac{MW \; of \; 6Ni}{MW \; of \; [6NiO + Al_2O_3]}$$

$$= \frac{352.2 \; g/mol}{550.2 \; g/mol}$$

$$= 0.64$$

Assume 0.5 g of Ni/Al_2O_3 is taken for sample solution preparation,

$$0.64 = \frac{x \; of \; Ni}{0.5 \; g}$$

$$x = 0.32 \; g$$

To prepare 320 ppm of sample solution,

$$\frac{0.32g \; of \; Ni}{1 \; L \; of \; 1M \; HNO_3} = \frac{0.0128g \; of \; Ni}{0.04 \; L \; of \; 1M \; HNO_3}$$

$$0.64 = \frac{0.0128 \; g \; of \; Ni}{x \; of \; [Ni/Al_2O_3]}$$

$$x = 0.02g \; of \; Ni/Al_2O_3$$

Therefore, 0.02g of Ni/Al_2O_3 sample was added to 40 mL of 1M HNO₃ to produce 320 ppm of Ni sample solution.

3. **Preparation of Sample Solution for Ni/SiO₂ catalysts**

$$Percentage\ of\ Ni\ in\ Ni/Al_2O_3 = \frac{MW\ of\ Ni}{MW\ of\ [NiO + SiO_2]}$$

$$= \frac{58.7\ g/mol}{134.8\ g/mol}$$

$$= 0.435$$

Assume 0.5 g of Ni/SiO_2 is taken for sample solution preparation,

$$0.435 = \frac{x\ of\ Ni}{0.5\ g}$$

$$x = 0.22\ g$$

To prepare 320 ppm of sample solution,

$$\frac{0.22g\ of\ Ni}{1\ L\ of\ 1M\ HNO_3} = \frac{0.0087g\ of\ Ni}{0.04\ L\ of\ 1M\ HNO_3}$$

$$0.435 = \frac{0.0087\ g\ of\ Ni}{x\ of\ [Ni/SiO_2]}$$

$$x = 0.02g\ of\ Ni/SiO_2$$

Therefore, 0.02g of Ni/SiO_2 sample was added to 40 mL of 1M HNO₃ to produce 320 ppm of Ni sample solution.

4. **Preparation of Stock Solution of Nickel, Ni**

$$Molecular\ Weight\ of\ Ni(NO_3)_2 \cdot 6H_2O = 290.79 \frac{g}{mol}$$

$$2000\ ppm\ of\ stock\ solution\ for\ Ni = 2000 \frac{mg}{L} = 2\ g/L$$

$$\frac{MW\ of\ Ni}{MW\ of\ Ni(NO_3)_2 \cdot 6H_2O} = \frac{2\ g/L}{x}$$

$$\frac{58.7\ g/mol}{290.79\ g/mol} = \frac{2\ g/L}{x}$$

$$x = 9.9\ g/L$$

Thus, 9.9 g of $Ni(NO_3)_2 \cdot 6H_2O$ was added to 1 L of 1 M HNO₃ to produce 2000 ppm of Ni stock solution.

5. **Preparation of Standard Solution of Nickel, Ni**

$$M_1V_1 = M_2V_2$$

$where$

$M_1 = Concentration\ of\ stock\ solution\ (2000\ ppm)$

$V_1 = Volume\ of\ stock\ solution$

$M_2 = Concentration\ of\ standard\ solution\ (10, 50, 100, 500\ ppm)$

$V_2 = Volume\ of\ standard\ solution\ (30\ mL)$

$(2000\ ppm)V_1 = (500\ ppm)(30\ mL)$

$V_1 = 7.5\ mL\ of\ stock\ solution$

Hence, 7.5 mL of Ni stock solution was then diluted with 22.5 mL of 1M HNO₃ to produce 30 mL of 500 ppm standard solution.

6. **Preparation of Stock Solution of Sodium, Na**

$$Molecular\ Weight\ of\ Na_2CO_3 = 106\frac{g}{mol}$$

$$2000\ ppm\ of\ stock\ solution\ for\ Na = 2000\frac{mg}{L} = 2\ g/L$$

$$\frac{MW\ of\ Na}{MW\ of\ Na_2CO_3} = \frac{2\ g/L}{x}$$

$$\frac{23 \; g/mol}{106 \; g/mol} = \frac{2 \; g/L}{x}$$

$$x = 9.217 \; g/L$$

Thus, 9.217 g of Na_2CO_3 was added to 1 L of 1M HNO$_3$ to produce 2000 ppm of Na stock solution.

7. **Preparation of Standard Solution of Sodium, Na**

$$M_1V_1 = M_2V_2$$
$$(2000 \; ppm)V_1 = (500 \; ppm)(30 \; mL)$$
$$V_1 = 7.5 \; mL \; of \; stock \; solution$$

Hence, 7.5 mL of Na stock solution was then diluted with 22.5 mL of 1M HNO$_3$ to produce 30 mL of 500 ppm standard solution.

8. **Preparation of 50 ppm Potassium, K**

$$50 \; ppm = \frac{50 \; mg \; of \; KCl_2}{1 \; L \; of \; Deionized \; Water}$$

Thus, 5 mL of 50 ppm KCl_2 was added to both the Na standard solution and also the sample solutions to prevent ionisation interference.

9. **Preparation of Stock Solution of Aluminium, Al**

$$Molecular \; Weight \; of \; Al(NO_3)_3 \cdot 9H_2O = 375 \frac{g}{mol}$$

$$2000 \; ppm \; of \; stock \; solution \; for \; Al = 2000 \frac{mg}{L} = 2 \; g/L$$

$$\frac{MW \; of \; Al}{MW \; of \; Al(NO_3)_3 \cdot 9H_2O} = \frac{2 \; g/L}{x}$$

$$\frac{27 \ g/mol}{375 \ g/mol} = \frac{2 \ g/L}{x}$$

$$x = 27.778 \ g/L$$

Thus, 27.778 g of $Al(NO_3)_3 \cdot 9H_2O$ was added to 1 L of 1M HNO_3 to produce 2000 ppm of Al stock solution.

10. Preparation of Standard Solution of Aluminium, Al

$M_1V_1 = M_2V_2$

$(2000 \ ppm)V_1 = (500 \ ppm)(30 \ mL)$

$V_1 = 7.5 \ mL \ of \ stock \ solution$

Hence, 7.5 mL of Al stock solution was then diluted with 22.5 mL of 1M HNO_3 to produce 30 mL of 500 ppm standard solution.

APPENDIX C: Raw Data of EDX

APPENDIX D: Raw Data of ICP-OES