TANDEM HYDROGENATION-ESTERIFICATION OF FURFURAL USING BIFUNCTIONAL METAL-SUPPORTED NANOPARTICLE CATALYSTS

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INSTITUTE FOR ADVANCED STUDIES UNIVERSITY OF MALAYA KUALA LUMPUR

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UNIVERSITY OF MALAYA ORIGINAL LITERARY WORK DECLARATION

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TANDEM HYDROGENATION-ESTERIFICATION OF FURFURAL USING BIFUNCTIONAL METAL-SUPPORTED NANOPARTICLE CATALYSTS ABSTRACT

The exploration of renewable resources such as rice husk for energy application is important against the fossil counterparts. Developing one-pot reaction methodologies is crucial for sustainable production of bio-derived fuels and chemicals, which typically requires a multifunctional catalyst system. This thesis reported on the one-pot process hydrogenation-esterification of furfural to furfuryl acetate using a bifunctional metalbased nanostructured catalyst, composed of rice husk (RH) derived SiO₂, Cu, Al, and Mg species (RHSiO₂-Cu-Al-Mg). Al and Mg metals were introduced to form RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg respectively to further improve the catalyst's reusability and performance. The catalyst's surface area was improved with the latter catalyst having a specific surface area of 150 m²/g. The catalytic efficiency of RHSiO₂-Cu and RHSiO₂-Cu-Al were also tested against RHSiO₂-Cu-Al-Mg as points of comparison. Various analytical techniques were used to elucidate the physicochemical, textural, and acid-redox properties of the catalysts. It was found that the RHSiO₂-Cu-Al-Mg catalyst contains an optimum amount of acid and redox sites, as demonstrated in the NH₃-TPD and H₂-TPR studies. Mg addition played a pivotal part in tuning the acidity of the RHSiO₂-Cu-Al catalyst to promote the in-situ esterification of furfuryl alcohol with acetic acid to yield furfuryl acetate. As a result, the RHSiO₂-Cu-Al-Mg catalyst exhibited the best performance in one-pot hydrogenation-esterification of furfural to furfuryl acetate (24.5% selectivity), outperforming various noble metal/silica-based catalysts. Following these results, single-atom catalysts (SACs) were developed from three metals; Pd, Ni, and Cu and their lattice strain influence on tandem hydrogenation-esterification of furfural were carefully monitored. It was observed that a low level of lattice strain in SACs tend to induce high and selective conversion of furfural to furfuryl acetate. SACs with high lattice

strains have low chemical transformation performance due to poor reorientation of the active site that minimized the H₂ coverage. These results validated that despite some SACs having > 95 % crystal structure perfection, small difference (< 0.1 %) in the lattice strain may induce SACs' relatively poor performance. Lastly this study focused on surface structures of nanoparticle catalysts which are mainly controlled by the hydrogen potential (pH) which are central to the promotion of selective catalysis for the production of fuels and chemicals-based substances that find domestic and industrial relevance. In this study, four different pH domains; 1, 3, 7 and 10 were employed to synthesis RHSiO₂-Cu-Al-Mg nanoparticle catalyst using the one-pot procedure. It was observed that the acidic domain (pH 1and 3) provided high lattice strain (0.425 % and 0.322 %) while the basic domain (10) provided low lattice strain (0.160 %). The lattice strain (0.127 %) at neutral pH (7) was less than that of the acidic but greater than basic domain. The activity of RHS iO₂-Cu-Al-Mg nanoparticle catalyst in terms pH of 1, 3, 7 and 10 are 95.8, 78.5, 95.1 and 94.3 selective to furfuryl alcohol respectively. Similarly at the same pH domain, the catalyst was 4.2, 21.5, 4.9 and 5.7 % selective to furfuryl acetate respectively during one step hydrogenation esterification reaction.

Keywords: Bio-oil upgrading; One-pot furfural conversion; Bifunctional catalyst; Rice husk silica.

PROSES HIDROGENASI-ESTERIFIKASI FURFURAL MENGGUNAKAN PEMANGKIN ZARAH NANO PELBAGAI FUNGSI BERASASKAN LOGAM YANG DISOKONG ABSTRAK

Penerokaan sumber-sumber boleh diperbaharui seperti sekam padi untuk aplikasi teknologi nano adalah penting sebagai pelengkap kepada bahan api berasaskan fosil. Teknologi tindak balas satu periuk merupakan proses penting dalam pengeluaran bahan api dan bahan kimia yang biasanya memerlukan sistem pemangkin yang memiliki lebih daripada satu fungsi. Tesis ini melaporkan proses penghidrogenan seiring dengan pengesteran secara "one-pot" atau satu periuk untuk menukarkan furfural kepada furfuryl asetat dengan menggunakan pemangkin berstruktur nano berasaskan logam dwifungsi, terdiri daripada sekam padi (RH) untuk menghasilkan SiO₂, Cu, Al, dan spesies Mg (RHSiO₂-Cu-Al-Mg). Untuk meningkatkan lagi kebolehgunaan dan prestasi pemangkin, logam Al dan Mg telah diperkenalkan untuk membentuk RHSiO₂-Cu-Al dan RHSiO₂-Cu-Al-Mg. Pemangkin menunjukkan pertambahan dari segi luas permukaannya dengan iaitu sehingga 150 m²/g. Perubahan ini berkait dengan sifat amorfus pemangkin baharu ini seperti yang diperhatikan dalam XRD. Kebolehan memangkin RHSiO₂-Cu, RHSiO₂-Cu-Al serta RHSiO₂-Cu-Al-Mg turut diuji. Pelbagai teknik analisis digunakan untuk menjelaskan sifat fizikokimia, tekstur, dan asid-redoks pemangkin. Didapati bahawa pemangkin RHSiO₂-Cu-Al-Mg mengandungi jumlah optimum tapak asid dan redoks, seperti yang digambarkan dalam kajian NH₃-TPD dan H₂-TPR. Penambahan Mg didapati memainkan peranan penting dalam mengawal tahap keasidan pemangkin RHSiO₂-Cu-Al untuk menggalakkan pengesteran secara *in-situ* furfuryl alkohol dengan asid asetik untuk menghasilkan furfuryl asetat. Hasilnya, pemangkin RHSiO₂-Cu-Al-Mg mempamerkan prestasi terbaik dalam proses penghidrogenan-pengesteran furfural kepada furfuryl asetat (dengan kadar 24.5% selektiviti), mengatasi pemangkin-pemangkin lain. Pada masa yang sama, pemangkin beratom tunggal (SAC) telah dibangunkan dengan tiga SAC berbeza daripada Pd, Ni, dan Cu dan pantauan secara teliti pengaruh ketegangan kekisi dalam struktur mereka terhadap penghidrogenan-pengesteran secara tandem terhadap furfural. Didapati bahawa SAC yang memiliki ketegangan kekisi rendah boleh mendorong perubahan furfural yang lebih tinggi dan seterusnya membentuk furfuryl asetat. Turut didapati bahawa SAC dengan ketegangan kekisi tinggi mempunyai prestasi transformasi kimia yang rendah disebabkan oleh orientasi semula tapak aktif yang meminimumkan liputan H₂. Hal ini mengesahkan bahawa walaupun SAC mungkin mempunyai > 95% kesempurnaan struktur kristal, perbezaan <0.1% dalam ketegangan kekisi mendorong kepada prestasi SAC yang lemah. Akhir sekali kajian ini memfokuskan kepada struktur permukaan pemangkin zarah nano yang dikawal terutamanya oleh potensi hidrogen (pH), merupakan teras kepada promosi pemangkinan terpilih untuk pengeluaran bahan api dan bahan berasaskan kimia yang mencari perkaitan domestik dan industri. Dalam kajian ini, empat domain pH berbeza; 1, 3, 7 dan 10 telah digunakan untuk mensintesis pemangkin nanozarah RHS-Cu-Al-Mg menggunakan prosedur satu periuk. Diperhatikan bahawa domain berasid (pH 1 dan 3) memberikan ketegangan kekisi tinggi (0.425 % dan 0.322 %) manakala domain asas (10) memberikan ketegangan kekisi rendah (0.160 %). Ketegangan kekisi (0.127 %) pada pH neutral (7) adalah kurang daripada domain berasid tetapi lebih besar daripada domain asas. Aktiviti mangkin nanozarah RHS-Cu-Al-Mg dari segi pH 1, 3, 7 dan 10 masing-masing ialah 95.8, 78.5, 95.1 dan 94.3 selektif kepada alkohol furfuryl. Begitu juga pada domain pH yang sama, pemangkin ialah 4.2, 21.5, 4.9 dan 5.7 % masing-masing selektif kepada furfuryl asetat semasa satu langkah tindak balas pengesteran penghidrogenan.

Kata kunci: Penambahbaikan minyak bio; penghidrogenan seiring dengan pengesteran secara satu periuk; pemangkin pelbagai fungsi; silika daripada sekam padi

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As the thesis was approaching its completion, I could not help but ponder who to thank in the acknowledgements and more importantly how will the order go? Alas, the pondering did not actually yield any true progress as I should have learned throughout this adventure called degree in Doctor of Philosophy. Let us now proceed in acknowledging the people whose mere presence enabled me to reach the end of the journey. It is only appropriate that we start with my mother and father. This journey would not have even started without them and I am not addressing their obvious contribution towards birthing me. It is more important that they raised me, supported me and were there for me, throughout literally everything. I do not presume that a mere mention in this thesis' would repay my debt nor do I presume such a debt could ever be repaid. I do believe that the completion of this thesis marks the beginning of my feeble attempt to repay that debt. I sure hope they do not charge any interest.

I've always said that if I did not gain anything else from my tenure here in University of Malaya, I have at least found my partner to accompany me for the remaining of my life. The realist in me does not ever truly believe in happily ever after but getting married to the one I think to be the love of my life is certainly making me believe that the glass may in fact be half full (despite basic science telling us that half full is half empty). Our meeting began with promises and compromises, it is high time I fulfill my part of the bargain we agreed upon January 12th 2014 (I certainly do hope I got the date right my well-being could very well depend on it). With that we've come to my dearly beloved daughter, who is at this very moment is crying because one of her toys ran out of battery.

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By the way, dear readers please continue reading this thesis. Much appreciated.

University

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LIST OF SYMBOLS AND ABBREVIATIONS

- HOMO : Highest Occupied Molecular Orbital
- LUMO : Lowest Unoccupied Molecular Orbital
- TPR : Temperature Programmed Reduction
- TPD : Temperature Programmed Desorption
- FESEM : Field Emission Scanning Electron Microscope
- HRTEM : High Resolution Transmission Electron Microscope
- XRD : X-Ray Diffraction
- OHE : One-Step Hydrogenation-Esterification
- SAC : Single Atom Catalyst
- HMF : Hydroxymethyl Fulfural
- THF : Tetrahydrofurfuryl Alcohol
- FAL : Furfural
- FCL : Furfuryl Alcohol

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CHAPTER 1: INTRODUCTION

1.1 General Overview

1.1.1 Utilization of Biomass and Reduction of Global Warming

The ever-increasing world's population created an ever-increasing energy demand to sustain the day-to-day functionality of its very own societies while allowing the push forward in the advancement of civilizations all over the world. Such demand comes from various necessities in human lives from providing heat and comfort to every household to industrial levels such as factory production or even transportation. In fact, with respect to industrial needs, transportation alone has been reported to account for 28% of the United States' overall energy consumption, which includes transportation of goods and even manpower to maintain the nation's economic propulsion. The number provided here does not even include the daily transportation of common people. Furthermore, we can expect the number to be even higher when it comes to a country with larger population such as China. It is of no wonder that the fuel industry remains to this day to be one of the most lucrative ones in any country around the world. As each nation strives to keep up with the dynamic global economy the fuel and energy industry can be akin to its very backbone. It is therefore paramount for us to not only maintain a relatively steady supply of fuel but also improve its viability in order to maintain economic stability all over the globe (Andrasko, 1990; Eseyin & Steele, 2015).

Fossil fuel, currently our main energy supply, can be generally divided into three main categories namely coal, oil and natural gas. A study done in Stanford in 2019 projected that should we continue the consumption of fuel at our current rate, our energy supply would actually run out in 53 years. This is barring any new discoveries of oil well which explains why such discoveries has always generated large interest all around the world. It should also be noted that fossil fuel comes with other set of problem when we look at it in terms of its effect on our environment. Currently, our global energy supply is a derivative of fossil driven substances such as petroleum and gasoline, substances which are of particular renown to be heavy contributor in the world's overall release of greenhouse gases (GHGs) into our environment (Andrasko, 1990). It is evident that greenhouse gases in particular CO_2 are agents of global warming and eventually climate change. The past century alone has shown that our planet's surface warmed up with the increment of 1.2-1.3 °C in the drylands while in the humid land the range lies between 0.8-1.0 °C (Huang et al., 2017). This is related to the high atmospheric CO_2 concentration, currently predicted to be ~475 ppm by 2099 according to NASA reports (Al-Ghussain, 2019). Concerning this, China alone produces more CO_2 than the whole western hemisphere combined due to its much larger population.

To further elucidate on the environmental issues with regards to the large consumption of fossil fuel, the emission of greenhouse gases also majorly contributes to the thinning of ozone layer. This is not to mention the direct effects of global warming such as rising of the sea level due to excessive melting in the South Pole and irregular weather patterns across the globe. Thus, factoring in fossil fuels' diminishing supply and negative impacts towards the environment, it can be said that the responsible thing for us to do as a society is to at least look into other energy sources, not to replace fossil fuel but to provide an alternative. The mechanism through which global warming takes place as a result of worldwide increase in greenhouse gases emission is highlighted in the following paragraph.

There are three wavelength ranges in the solar radiation spectrum. They are ultraviolet, visible and infrared. Each range contains a fraction of the sun's energy. Nearly half of the spectrum's solar energy is carried by infrared wavelengths. This is due to the high surface

temperature of the sun (5777 K) and the fact that most infrared wave lengths are very long. Minor amounts of the sun's radiation travel through the atmosphere and are absorbed by GHGs. They then reflect towards the space by clouds and aerosols. Methane and carbon dioxide absorb the wavelengths in the infrared area, while ozone absorbs them in the ultraviolet region. Water vapor absorbs waves at all wavelengths. The earth 's surface is where the majority of the solar radiation is concentrated, while the rest of it hits terrestrial objects, causing an increase in temperature. The earth 's surface gets warmer and the terrestrial objects get hotter, causing them to radiate short-wave ultraviolet radiation (due their low temperature (277 K compared with the sun) towards the atmosphere, which will then be absorbed into GHGs (Herzog et al., 2000).

In response towards the issue of global warming, nations around the world were inspired towards the adoption of Kyoto Protocol in 1997 and the 2015 Paris Climate Agreement by many countries. Briefly, the Kyoto Protocol binds industrial level countries and economic sectors to a certain limit of greenhouse gases emission while the Paris accord involved the establishment of a collective intent within the nations as well as an agreement to reduce the global surface warming to less than 2 °C with respect to preindustrial level (Höhne et al., 2017; Schleussner et al., 2016). In response to these agreement between various nations, there is an ongoing proliferation of research efforts to actualize the Paris Blueprint, among which is the valorization of biomass as an alternative energy supply on an industrial scale throughout the world. This was intended as a measure to motivate migration towards the use of renewable energy options with low carbon footprint. The valorization of biomass comes in different ways among which is the production of renewable fuels and chemicals from non-edible lignocellulosic biomass. This transition is a promising substitute for the conventional fuel, considering that it is a renewable and greener source of energy (L. Zhang et al., 2013a). As an added benefit, processing biomass in such a manner will help to overcome the waste issues of the agricultural industry while ensuring that this form energy has a relatively stable flow of supply. Hence, such usage of biomass provides an optional energy source for mankind and remediation to burning of biomass waste that could contribute to excessive CO₂ content in the atmosphere.

Before we proceed further, it is essential for us to highlight some of the characteristic of biomass specifically with regards to its potential as an alternative energy source to the population. The United States Energy Information Administration defined biomass as any renewable organic material that comes from plants and animals. It is a direct result of photosynthesis process in plants which converts the energy from the sun to chemical energy for storage and further usage. This form energy is a prevalent source of energy throughout the ecosystem, transferred from one life form to another through mostly our diets (Field et al., 2008). Biomass sources for energy include: (1) wood and its processing waste such as firewood, wood chips and sawdust; (2) agricultural crops and waste material such as soybean and corn; (3) bio-based materials in solid wastes such as paper and wool and (4) human sewage and manure.

To tap into its energy supply biomass can be converted via various processes, including direct combustion for heat production; thermochemical conversion to yield solid, liquid and gaseous fuels; chemical conversion and biological conversion to yield liquid form of fuels. Many processes have been used to convert biomass into fuels and chemical feedstock. Fischer-Tropsch (F-T), which is a gasification process, produces fuel-range hydrocarbons. F-T, however, is a capital and energy intensive process. Alternately, the pyrolysis process of biomass removes approximately 80 % oxygen to produce a liquid bio-oil that is acidic, unstable, thus requiring further processing in order to obtain fuels or chemicals.

One of the most promising ways to utilize biomass is solution-phase processing. Acid hydrolysis of cellulosic biomass yields a mixture of C_5 , C_6 sugars. These sugars can then be dehydrated to produce furanic and hydroxymethyl furfurals. The organic phase is where the furanic and furanic acids (HMF, FF) are extracted. Furanic aldehydes can easily be resinified under acidic conditions. Therefore, their yields are improved by extraction into the organic phase. The organic phase can also be easily isolated and subjected for additional reactions. Among these processes, direct combustion is the most direct and thus common method for the conversion of biomass to more useful form of energy. Direct combustion is often applied to generate heat sources for heating buildings, heating of water supplies, application in industrial processes and for steam turbines in electric generators (Cai et al., 2014).

Pyrolysis and gasification are the most common forms of thermochemical conversion of biomass. These are considered to be thermal decomposition processes in which the feedstock is heated in vessels known as gasifiers at elevated temperatures and pressure. This process is differentiated from direct combustion by differences in the temperatures and concentration of oxygen during the afore mentioned process. Pyrolysis is defined as the heating of the feedstock materials to 800–900 °F (400–500 °C) in the near or even complete absence of free oxygen. Pyrolysis of biomass yields fuels in the form of charcoal, bio-oil, renewable diesel, methane, and hydrogen. Bio-oil should be mentioned to be our main focus for this particular research. Hydrotreatment is commonly used to process the bio-oil obtained from the fast pyrolysis with hydrogen under process temperatures and pressures in the presence of a catalyst to produce renewable gasoline, diesel and jet fuel (Machado et al., 2016).

On the other side of the spectrum is gasification which involves the heating of organic matters to temperature range of 800–900 °C with injections of free oxygen and/or steam

in a controlled amount into the closed vessel in order to produce a mixture of carbon monoxide and hydrogen rich gas known as synthesis gas or syngas. Syngas is applied primarily for diesel engines, and for generating heat as well as electricity in gas turbines. The hydrogen can be separated from the gas via treatment and then be burned or used in fuel cells. The syngas can undergo further treatment to produce liquid fuels using the Fischer-Tropsch process similar in setup to the one mentioned earlier in this chapter. produced though a chemical process known as Conversely, biodiesel can be transesterification of vegetable oils, animal fats and greases into fatty acid methyl esters or FAME (Kabbour & Luque, 2020). Similarly, fermentation of these fatty acids tends to convert the biomass feedstock into ethanol while anaerobic digestion can also be applied to produce natural gas in a renewable form. Renewable natural gas also known as biogas or in some cases biomethane is a product of the anaerobic digesters commonly produced in various sewage treatment plants as well as in dairy and livestock operations. This product may also form in solid waste landfill. The possibilities in application of biomass as an alternative and renewable fuel have been the driving force behind many researchers' intent on working on ways to improve these methods and to develop other ways to convert and use more biomass for energy (Machado et al., 2016).

To put the above statement into perspective, in 2021 alone, biomass-based fuel provided up to approximately 4835 trillion British thermal units (TBtu), which is equivalent to 4.8 quadrillion Btu. This amount makes up to almost 5% of the overall total primary energy consumption of the United States. From this particular amount, it was estimated that around 2316 TBtu were obtained from biofuels, predominantly from ethanol, 2087 TBtu were sourced from wood-based form of biomass and finally, 431 TBtu were obtained from the biomass found in solid wastes, manure, and the byproducts of agricultural activities. This amounted to a total TBtu of total biomass energy used by sectors in 2021 as follows: industrial: 2313 TBtu (48%); transportation: 1477 TBtu

(31%); residential: 464 TBtu (10%); electric power: 435 TBtu (9%); commercial:147 TBtu (3%) (Field et al., 2008; Kabbour & Luque, 2020)

The above information highlighted the fact that the industrial and transportation sectors accounted for the largest percentage of biomass-based fuel, specifically in terms of energy content and largest percentage shares of total U.S. biomass consumption annually. Products from wood as well as paper industries utilizes biomass in a combination of heat and power plants to generate heat and electricity for the internal usage within each of their production line. Meanwhile, the liquid form of biofuels can be accounted for most of the consumption of biomass within the transportation sector while the residential and commercial sectors generally burn the firewood and wood pellets for heating. The electric power sector is even applying wood and biomass-derived wastes to generate electricity in order to provide for the needs within various sectors including their very own one. Lastly, the commercial sector also consumes renewable natural gas produced at municipal sewage facilities and at landfills. To further serve their needs, this particular sector is also involved in the trading of the renewable natural gas within the same sector or to other sectors (Luo et al., 2019).

On a molecular scale, biomass is defined to be a complex mixture of polymers that are further divided into smaller group of compounds (Nakagawa et al., 2013a; Zhang et al., 2007). Bio-refinery is essential in isolating useful components of the biomass otherwise known as platform chemicals. Some examples of biomass derived components that forms the building blocks chemical refinery include benzene, toluene, xylene ethylene and others. Pyrolysis tends to be the most commonly used method to directly tap into the energy potential of biomass, mainly due to the relatively fast process as well as nature of the product formed which is highly convenient for application in various sector. This said product as previously mentioned is known as bio-oil and is a mixture of various functional

groups rich in energy to be tapped into. These chemicals are the foundation in the formation of new families of molecules with many applications. To monetize these biomass derived components have to go through processes such as hydrogenation, hydrodeoxygenation, esterification, cracking and even tandem hydrogenationesterification (Xu et al., 2017). The main goal of utilizing these hydrotreating processes is to increase the energy value of bio-oil which contain most of the chemical component, and induce higher stability. Since bio-oil is a mixture of various chemical components, each requiring different treatments to suit their chemical make-up, it is mostly common for smaller scaled laboratory studies to focus on one or two targeted compounds, usually the ones that are particularly high in energy potential but also present significant detriment to bio-oil whether in terms of energy value, shelf life or chemical stability. Hence, significant effort has been directed towards the identification of all the possible components in bio-oil in order to allow planning for the relevant hydrotreatment of biooil depending on its chemical make-up. It should be clearly noted first and foremost that the feedstock introduced to the pyrolysis process will yield varying components of the bio-oil. For the sake of this particular research, a list of chemical components which are almost always present regardless of the feedstock have been compiled. The summary of the likely biomass derived components that are valuable in the hydrotreating processes is shown in Figure 1.1. The major groups of chemical compounds to be noted, particularly for the intent of understanding this thesis are aldehydes and organic acids. These two groups are of particular note in terms of energy potential especially in the case of the former but in the presence of the latter group, aldehyde becomes susceptible to chemical reactions detrimental to the shelf life of bio-oil rendering it unsuitable for long term application as a form of fuel.



Figure 1.1 : Chemical components of biomass derived bio-oil

1.2 Catalytic Conversion of Biomass Derived Furfural

As mentioned at the end of the previous section the components of bio-oil can be treated through various chemical processes. One of the categories of these processes that is of particular importance is hydrotreatment of the targeted platform chemicals within bio-oil. As the name implies, this form of chemical treatment involves the introduction of hydrogen gas at a steady rate in a closed vessel, most commonly at elevated temperature and/or pressure (these two parameters will determine the product formed at the end of the process). Hydrotreatment can be further divided into several categories depending on the reaction pathway the reactants follow and subsequently the product formation. Several of these processes include hydrogenation, hydrocracking and hydrodeoxygenation(Kabbour & Luque, 2020).

Many of the various platform chemicals found within bio-oil are highly oxygenated compounds, having at least one functional group that contain oxygen. Combined with the fact that most of these chemicals contain at least one double bond functionality, creates a severe susceptibility towards reaction between each individual component which impedes the overall stability of bio-oil. The stability of lignocellulose-based bio-oil, due to the presence of some oxygenates (e. g., furfural), is a major concern. However, these susceptibility within the structures of the chemical also enable relative ease of treatment particularly via hydrotreatment in a conducive set of parameters as discussed above. Hence, these chemicals are often targeted for further conversion into relatively more stable target molecules with better prospect for application, in this case as biofuel (Nakagawa et al., 2013a). This particular research thusly focused on furfural as the main model compound due to the nature of this particular platform chemical as discussed previously. From this point onwards, the discussion in this particular section will henceforth focus on furfural, focusing on its energy potential and relevant methods to fully harness said potential to the highest degree possible (Kabbour & Luque, 2020).

Furfural, C₃H₄O ₂ is a heterocyclic aldehyde containing a closed ring structure. It's also known as: 2-furancarboxaldehyde, furaldehyde, 2-furanaldehyde, 2-furfuraldehyde, fural and furfurol. It is a colorless, oily liquid that smells like almonds. When exposed to air, it quickly turns dark brown. Furfural, a heteroaromatic aldehyde with the molecular formula C₅H₄O₂ and a weight of 96.08, has an almond-like odor that is highly selective for removing aromatics from lubricating oils, diesel fuels and other substances. Its exceptional physical properties make it an effective extractant for these purposes. Furfural also forms cross-linked polymers in response to various stimuli. Furfural contains two highly reactive functional groups, the first of which is the aldehyde group which makes furfural a conjugated system, enhancing this compound's role as an essential starting point or a building block for various applications in chemical synthesis and reactions. This particular aldehyde functional group can further undergo many typical reactions that commonly takes place in various industries such as acylation, aldol and Knoevenagel condensations, acetalization, reduction to alcohols, reductive amination to amines,

decarbonylation, oxidation to carboxylic acids, and Grignard reactions (Luo et al., 2019). On the other hand, is the furan ring functionality also found in furfural. Contrary to the previous functional group the ring system is more susceptible to additional-based reactions such as hydrogenation, halogenation, oxidation, alkylation, ring opening and nitration reactions. The furan ring of furfural is much less accessible to the cleaving reaction of hydrolytic ring due to the withdrawal of electron and the subsequent spatial effect of the carbonyl group.

Furfural is used as a precursor to many downstream chemical industries. It can be converted into many solvents, fuels, and other intermediated chemicals. Furfural alcohol can be hydrogenated, and then used in the pharmaceutical industry as an intermediate chemical to produce ranitidine, an anti-ulcer drug. Furfuryl alcohol is formed by hydrogenating furfural alcohol. This solvent can be used to formulate herbicides in agricultural activities. The other important furfural derivatives are methyl tetrahydrofuran and furan due to their wide applications, for example as components in alternative fuels, lithium electrodes and heat-treated commercial foods. This demonstrates the importance of the upgrading process of furfural, a platform molecule, and why it is such a hot topic in biomass utilization research. Johann Wolfgang Dobereiner first isolated furfural in 1821 to make formic acid. In 1840, Dobereiner discovered that oily residues from plant matter could be obtained by reacting with sulfuric acids (Xu et al., 2020). Quaker Oats Company commercialized this process in 1922 to make more use of large amounts of biomass waste, specifically corn husks. It quickly became apparent that furfural can be used for many purposes, including as a process agent to generate lubricants. A wide variety of scents and flavors can be created by subtly changing the chemical structure. Furfural and its derivatives can be used as building blocks and starting materials to produce high-volume products, such as polyols. These are directly applicable as monomer precursors in the polyester industry. These can be used to make polyamides and

polyurethanes by oxidation or amination. Globally, large-scale furfural production is possible. Countries such as China and South Africa contribute to an annual production of more than 280,000 tons. In fact, furfural production worldwide amounted to more than 280,000 tons per year in 2001. China was the largest producer of furfural at a rate of 200,000 tons per annum (equivalent 71.42%). South Africa and Dominican Republic followed at 32,000 and 22,000 tons, respectively. Around 8,500 tons were produced annually in Thailand. Global market growth rates for furfural, and its derivatives are between 2.47-3.1% per annum. The main furfural market size is 370,000 tons annually and the price is 1,500 USD per ton. Furfural and furfural alcohol were the main consumers at 50,000 to 100,000 and 130,000 tons respectively. Japan, Europe, and the USA are the largest consumers of furfural derivatives and their derivatives at 48,000, 21,000 and 19,000 tons respectively. Pricing of furfural derivatives is highly dependent on the downstream market requirements. Furfural was priced at 900-1500 USD/ton, furfural alcohol at 1,400-1800 USD/ton, furfural resin at 1,000-2,000 USD/ton, and tetrahydrofuran at 5,600-6,800 USD/ton (Dashtban et al., 2012).

It should be addressed that furfural, due to its structure as shown in Figure 1.2 (labelled as FAL) does not contribute much to the hydrogen to carbon (H/C) ratio, in other words there is much untapped source of energy in this compound (Zhou, Zhu, et al., 2014). Furfural is also the main culprit in the short shelf life of bio-oil for the very reason that in the presence of acid the compound has very high tendency to polymerize. This is especially prominent in most bio-oils as they contain various organic acids such as acetic acid and formic acid as shown in Figure 1.1, (L. Zhang et al., 2013a). At higher concentration, furfural will even form a solid lump of its polymer which render the bio-oil shelf life to be obsolete hence limiting its application at an industrial scale. In this regard, furfural can be highlighted as one of the major components of bio-oil, that requires particular attention when considering the chemistry during bio-refinery process.

Conversion of furfural into more stable forms is necessary, not only for sustainable utilization of bio-oil, but also to enhance its profitability. This is in line with assurance of maximum energy value without too much waste while keeping to the concept of green energy consumption. Moreover, furfural's versatility in terms of its upgrade path requires careful consideration to ensure that its derivatives have significantly improved energy value and chemical stability.

Furfural have two main functional groups which can determine the product formed based on which of the group took place in the reaction (Zhou, Zeng, et al., 2014). One of the main factors in determining which reaction will take place during the refinery process is the type of metal used as a catalyst for the reaction (Kannapu et al., 2015). This is very much due to each metal's varying affinity towards the two functional groups available thus setting the precedence to which upgrade path furfural will be going through. This is another demonstration of the specificity and selectivity in a catalyst mentioned before when discussing enzymes as homogeneous catalyst (Sitthisa & Resasco, 2011a). The metal active components usually involve metals such as Au, Pt, Cu, Ni, Co, Fe, Pd and Cr (Lesiak et al., 2014b; Nakagawa et al., 2014; Nishimura et al., 2014; Srivastava et al., 2015; Vargas-Hernández et al., 2014; Villaverde et al., 2013a; Vorotnikov et al., 2012a; Wu et al., 2005b; Yang et al., 2014; W. Yu et al., 2011). There are many ways to introduce these metals to the SiO₂ such as impregnation (W. Yu et al., 2011), co-precipitation and post synthesis grafting. Introducing the metal active component in-situ during the gel formation stage will allow proper distribution of the metal throughout SiO₂ (Adam et al., 2010b; Adam et al., 2012a; Andas et al., 2013b).

In catalysis, the support material plays an important role in determining the efficiency of the catalyst by providing a platform for the active metals to be distributed thus increasing the probability for interaction with the reactant chemicals. The difference in

the support's morphological properties such as its surface area and pore diameter will affect not only the conversion but also the selectivity of the catalyst. The support also plays a role in determining the pathways for furfural's refinement. However, the supports' effects are more prominent in terms of the mechanism in which a specific reaction takes place. For example, in hydrogenation a chemically inert support such as silica, SiO₂ will tend to proceed the reaction via non spillover pathway of reaction (Halilu et al., 2016c). Recent developments point out that when the active metals are chemically bonded to the support, the interplay within the catalyst is also affected such as in terms of the lattice strain and overall crystallinity (Kasatkin et al., 2007; Strasser et al., 2010; Westsson et al., 2019). With the support seemingly to be customizable with simple adjustments to synthesis conditions such as pH and temperature, it created a platform for researches to tailor the catalysts in terms of their morphological and chemical traits to suit need of the reaction. This is even truer when considering reactions such as esterification of a furfural derivative, furfuryl alcohol, the support will not only be a dispersing medium for the active metals but can also act as a proton donor. This may require introduction of a dopant such as Al or sulphonic acid to be grafted on the surface and/or be chemically bonded within the structure of the support itself (Signoretto et al., 2013). Esterification via reductive route such as the one described here most often employ supports such as alumina or silica can be customized to have Brønsted acidity available throughout their structure. On the other hand, oxidative esterification of furfural can also take place with the utilization of supports such as zirconia, ZrO₂; ceria, CeO₂ and titania, TiO₂ (Menegazzo et al., 2014). This observed phenomenon provided more factors to be considered in synthesizing a catalyst for a specified reaction, not only in terms of the enhancement towards surface contact for the active metals but also the possibility of catalyzing a different reaction all together. These considerations not only affect the pathway of the reaction itself but also unlocks possibility for varying level of selectivity

depending on the support material chosen. These developments are the stepping stone in developing catalysts with the capability to catalyze multiple reactions in tandem to one another.

Many of the potential furfural derivatives are possible by further upgrading subsequent molecules. The parent material can easily be decarbonylated into furan. This is then hydrogenated to tetrahydrofuran (THF), which is a common laboratory solvent. THF can also be converted to Pt (111) to cause ring opening to butanol and then dehydration to propylene. The most popular furfural transformation currently is the selective hydrogenated. This is often done using non-environmentally-friendly methods. Furfuryl alcohol is a key intermediate in the production of lysine and ascorbic acid, and many lubricants (Fu et al., 2023).

Hydrogenolysis of furfuryl alcohol leads to 2-methylfuran. This molecule is in high demand in the energy sector and could be a future fuel, especially in the haulage industry. This molecule is obtained through the hydrodeoxygenation (HDO) reaction pathway of furfuryl alcohol. Many researchers have studied this pathway across multiple catalytic systems. It involves hydrogen being used as a dehydrator to the alcohol. In a single pot system, methyl furan is produced from furfuryl alcohol. This intermediate is then quickly consumed. The aromatic ring can be used to hydrogenate furfuryl alcohol to make tetrahydrofurfuryl alcohol, which is a precursor for 1,5 pentandiol. This valuable molecule is essential for the polymer industry (An & Li, 2022). One drawback to the HDO method is that furan rings are often hydrogenated before the HDO reactions can even take place. Tetrahydrofuran ring is formed by the competing hydrogenation reaction. This requires extreme conditions leading to the ring-opening and can cause fragmentation of carbon backbone. Hydrolytic ring-opening can be achieved under mild
conditions, followed by HDO. This allows for better preservation of carbon backbone. This method has been used recently to open aldol products. There are two main reasons why hydrolytic ring-opening furan fails to occur: 1) if exocyclic unsaturation is present and 2) if the 5-position furan ring does not contain a functional group. A one-pot method was developed by the same group to convert furfural's aldol products to alkanes. It involved Pd/C in glacial acetic acid with La(OTf). This procedure was recently described in a report with respect to formation of furoin substrates (Fu et al., 2023).



Figure 1.2 : Furfural hydro-processing pathway (Hoydonckx et al., 2000)

1.2.1 State of the Art Tandem Reactions of Furfural

Introducing a secondary active component to a supported metal catalyst will yield one such multifunctional catalyst that have been shown to be capable of carrying out reactions in tandem of one another (Wanjin Yu et al., 2011a). This type of reaction utilizes the product produced *in-situ* into a subsequent reaction using the said product as the reactant.

When properly carried out, these reactions provide not only intrigue from the scientific point of view but from economic point of view as well with the possibility of energy and time saving. As previously mentioned, doping a support such as silica may yield its material to be no longer inert but also capable of interacting with reaction product or the reactants themselves. Hence, if we take into consideration how the product of a certain reaction can react and form another product due to its interaction with the support, we can proactively provide the right reaction conditions or even introduce a secondary reactant to facilitate the formation of a secondary product. This processing flow is the backbone for most if not all tandem reactions studied in various researches (Xue et al., 2007).

Tandem reactions are highly efficient and selective by combining multiple reactions in one step (Yamada et al., 2011; Zhou, 2010). The tandem protocols are always focused on functional groups of their reacting moiety. For instance, tandem reaction involving stereo-selective synthesis of more than three-contiguous asymmetric centers have been realized by Suzuki and co-workers (Miyaura & Suzuki, 1995). The problem in efficiently executing this type of reaction is ensuring the supply line of the first product comes in steady supply for the second portion of chemical reactions (Lee et al., 2020). We can elaborate this problem into two categories: first of them is having to ensure a large concentration of the first product can be proliferated by the first active sites. The second being to ensure that the first batch of products reach the second active sites to complete the flow of tandem reactions (Zaccheria et al., 2012). In general, the remedy for both of these problem lies in the synergy of metal active sites and also the support, whether the latter acts solely as a dispersion medium or as secondary catalyst as well. If it is the case of the latter, the second issue raised here should not be as prominent owing to the fact that as long as the metal was efficiently distributed, the first and second active sites should be within close proximity of each other (Raza et al., 2021; Xue et al., 2007). Another important issue to be raised when acidity is part of the catalytic process, is the strength of the acidic sites. For one, in furfural's case it is as mentioned before highly susceptible to polymerization in the presence of acid. Thus, for this study a moderate acidity may in fact be the key in ensuring consistent production of furfuryl acetate (Wanjin Yu et al., 2011d).

With emphasis on tandem reaction of furfural (Nandiwale et al., 2020), the focus lies on the furan ring and/or the carbonyl group. Interaction with these two groups will be one of the major determining factors of the product formed through hydroprocessing of furfural. As for tandem reactions, the resulting product's functional group will also be paramount in determining the second portion of the reaction. For example, in this study, the focus lies on hydrogenation-esterification of furfural where the furfuryl alcohol produced will be subsequently esterified in the presence of acetic acid to furfuryl acetate. The other factor to look out for is regarding the overall synergy between the multiple active metals and the support (the metals may interact with each other or with the support and vice versa), resulting in effects observable when studying the final catalyst's physicochemical properties (Dasireddy et al., 2018; B. Nagaraja et al., 2003; B. Nagaraja et al., 2007).

Furfural which can thus be converted into furfuryl acetate, a compound with various applications as a biofuel additive, flavouring agent, and fragrance. It is of the essence and hence demands reiteration that the conversion of furfural to furfuryl acetate occurs over an efficient bifunctional catalytic system containing metal and acid sites or functionality (Hashim et al., 2020). In fact, it has been shown that the single-atom metal function is tuneable to have an outstanding catalytic activity that often promotes hydrogenation of furfural to in-situ furfuryl alcohol. The acid site facilitates the esterification of the in-situ furfuryl alcohol with acetic acid to produce furfuryl acetate. In typical bifunctional catalyst systems, metal active sites particularly at the atomic level do form metal-support synergistic interactions. The metal-support interactions (MSIs) are well-known to

strongly influence catalyst performance (Halilu et al., 2016c; O'Connor et al., 2018; Van Deelen et al., 2019). MSIs are especially important in supported single-atom by controlling the chemical activity of the catalysts (Lang et al., 2019). Supported single-atom metal catalysts and metal clusters have substantially different catalytic activity compared to their unsupported analogues due to quantum size effects (Li et al., 2003; Yang et al., 2013) and changes in the electronic structure (Lykhach et al., 2016). As a result, modifying supported metal catalysts to an atomic level has recently emerged as a revolutionary paradigm in single-atom catalysis, effectively bridging the gap between heterogeneous and homogeneous catalysis (Halilu et al., 2020; Kaiser et al., 2020; Mitchell & Pérez-Ramírez, 2020). Though MSI is effective, the promotion of furfuryl acetate production is unlikely using only single-atom metal active site without proper incorporation of Brønsted acid sites to form bifunctional attributes.

To form bifunctional single-atom catalysts, support materials such as SiO₂ or its derivatives such as mesoporous SBA-15 or MCM-41 prove viable for acid and singleatom sites functionalization. The acid-modified SiO₂, SBA-15, or MCM-41, are widely investigated as support materials for transition metal catalysts such as Cu, Ni, and Pd stabilized on their surface or bulk phase (Edelberg et al., 2020; J. Li et al., 2019). Evidently, the acid function from the modified support material supplies Brønsted acidity that facilitates esterification reactions (Jiang et al., 2016; Koekkoek et al., 2012; Kozlov et al., 2019; Pham et al., 2021; Xu et al., 2002). The non-reducibility of SiO₂ or its derivative at elevated temperatures prevents hydrogen spillover to the support and improves hydrogen coverage on the active metal function during hydrogenation (Halilu et al., 2011c). Combining the esterification and hydrogenation steps, SiO₂-supported bifunctional metal catalysts have been widely investigated to convert furfural through tandem hydrogenation-esterification reactions (Chen et al., 2017; Nandiwale et al., 2020;

Xu et al., 2015; Xu et al., 2016; Wanjin Yu et al., 2011a, 2011d). For instance, furfural, and acetic acid conversion were found to produce furfuryl acetate using Pd supported on acid-modified SBA-15 (Wanjin Yu et al., 2011a). The atomic structure of the active metal, in synergy with the Brønsted is significant in governing the catalytic activity during the tandem hydrogenation-esterification of furfural (Hashim et al., 2020; Wanjin Yu et al., 2011c). Distortion in the atomic structure of the active metal can limit the hydrogenation step that produce in-situ furfuryl alcohol substrate during tandem hydrogenation-esterification reaction (Chen et al., 2017; Chen et al., 2018; Halilu, Hussein Ali, et al., 2019c; Li et al., 2021; Nandiwale et al., 2020; Xu et al., 2015; Xu et al., 2016; Wanjin Yu et al., 2011a, 2011d; Zhang et al., 2018). Therefore, the role of structural distortion of metal-supported bifunctional catalysts on activity has not been reported for the tandem hydrogenation-esterification system. In essence, the metal support interaction properties such as charge transfer between the metal, particular in single-atom regime and the support, (Campbell, 2012; J. Li et al., 2019; Lykhach et al., 2016) interfacial reactions, (Halilu et al., 2016c) including lattice strain, are essential aspects of the underlying chemistry in tandem reactions.

To briefly summarize the important point to be taken note for observation of furfural's tandem reaction, the first step is the hydrogenation of furfural to furfuryl alcohol which requires the metal catalyst to be able to adsorb furfural at the carbonyl group rather than the furan ring while also having the ability to efficiently dissociate hydrogen, H₂ gas into their respective charged particle. These two requirements will determine how well a catalyst can perform in this particular set of tandem reaction. In terms of the esterification reaction efficient arrival of furfuryl alcohol to the acid site will ensure a good start to the second portion of the tandem reaction. Having the proper strength of acidic site will ensure formation of the targeted product.



Figure 1.3 : Visualization of tandem hydrogenation-esterification of furfural on a heterogenous catalyst.

1.3 Problem Statement and Significance of the Study

The main aim of this study was the efficient conversion of furfural to furfuryl alcohol and furfuryl acetate via tandem hydrogenation-esterification reaction in one pot. There were several studies previously carried out in order to convert furfural to furfuryl alcohol and furfuryl acetate in a one-pot reaction. As discussed previously, the yields of furfuryl acetate in particularly were very low suggesting there are much room for improvement in the process, which for this particular thesis would be focused on the catalysis, specifically, heterogeneous catalysis aspect of the reaction.

One of the most important aspects of ensuring efficient heterogeneous catalysis is ensuring availability of metal active sites to sufficiently come into contact with the targeted substrate, which can be quantified based on the ease of which the active metal is reduced from its ionic counterpart to its metal form, the form which allows efficient catalysis of hydrogenation process. In the case of tandem hydrogenation-esterification of furfural, the strength of the acidic sites also acts as major determining factor in the esterification reaction. These two factors can be regulated by the addition of Mg to metalAl-SiO₂ catalytic system to enhance ease of active metal reduction and regulating the strength of the acid sites. Furthermore, with the employment of sol-gel method, the pH during synthesis of the catalysts can be studied to further improve the ideal conditions for the synthesis of rice husk derived silica catalysts.

1.4 Research Philosophy and Scope

The main model compound for the study was selected to be furfural as it is one of the most prominent of the aldehyde group in biomass-based fuel and the main contributor for bio-oil's short shelf life. The targeted derivatives of furfural will be furfuryl alcohol and furfuryl acetate. The former is selected for being one of furfural's derivatives with the highest energy value. It should be stated that although methyl furan was found to have higher energy value, it leaves a significantly higher level of carbon footprint. To keep in line to the aim of producing an efficient and green fuel, furfuryl alcohol was selected. Furfuryl acetate was selected for its increased stability towards reaction especially polymerization under acidic conditions. This thesis will also focus on the developing of multifunctional catalyst by studying the effect of subsequent addition of each metallic species into the catalytic system. This will be studied in terms of each stage's morphological and chemical differences from one another. This will then be followed by studying the effect of three different active metals (Cu, Ni and Pd) which have been selected based on previous studies' assessment on each of their capabilities to catalyze the hydrogenation process, their ratio of efficacy to price and their overall interaction with other elements in the overall catalyst primarily the silica support. The next part proceeded into the study of pH variation during catalyst synthesis and its subsequent effect on the tandem reaction. Each of these studies will be accompanied by the respective analysis of the tandem hydrogenation-esterification reaction using methodology defined in the next chapters.

1.5 Research Objectives

This thesis proceeded to achieve its main aim via the following objectives:

- 1. To synthesize multifunctional metal catalyst supported on rice husk derived silica.
 - This objective was then further divided into three main area of studies: (a) gradual introduction of Al and Mg from the base silica supported catalyst;
 (b) multifunctional catalyst with different active metals (Cu, Ni and Pd) and
 (c) multifunctional catalyst synthesized at varying pH (pH 1, 3, 7 and 10).
- 2. To characterize the multifunctional metal catalyst supported on rice husk derived silica in terms of surface properties, reducibility, crystallinity and morphology.
 - The characterization of the three batches as stated above were carried out for each of the catalyst.
- To investigate the performance of the multifunctional metal catalyst supported on rice husk derived silica in hydrogenation esterification reaction using in-situ furfuryl alcohol and acetic acid.
 - Each of the catalyst performance was defined by furfural conversion and selectivity towards targeted products.
 - The catalysts were also subjected to varying reaction parameters and the effect of such variations towards the catalytic performance was defined using turnover frequency values.
 - In the case of catalyst batch with different metal SACs, the performances of the acidic active sites were defined in terms of the Goldschmidt constant.
 - The reusability of each catalyst was also studied in terms of furfural conversion percentage.
 - A reaction mechanism was then proposed based on the observations made during the various reactions.

1.6 Research Methodology

The research can be classified into three main phases: the catalyst synthesis phase, characterization and the catalytic testing phase. Each of these phases was carried out to completion for each of the catalyst batches stated previously in Section 1.5. Each of the catalyst batches was synthesized, characterized and tested as a catalyst for tandem hydrogenation-esterification of furfural and acetic acid. This was to ensure proper flow of data and selection of catalyst characteristics was achieved.

1.7 Thesis Outline

This thesis contains five chapters

- Chapter 1 Introduction: This chapter serves to deliver necessary information regarding the study reported in this thesis, problems that were tackled and the general philosophy in terms of solving said problems through utilization of the multifunctional heterogeneous catalyst. The information presented here is broad stroked in nature with the intent of introducing the readers to the main idea behind the study.
- Chapter 2 Literature Review: The second chapter provides the readers with the background concepts underlying the main themes addressed in this thesis, providing relevant information from previous studies carried out in the field of bio-fuel. This chapter attempts to deliver current state of the studies in bio-fuel with focus on the main model compound of the thesis, furfural and application of various catalysts in processes to upgrade it into more stable compounds.
- Chapter 3 Research Methodology: The chapter focuses on the detailed outlining of the synthesis, characterization and application of the multifunctional catalysts. It will also outline the flow of the research

conducted, providing details of the materials and instruments used to achieve the objectives of this study.

- Chapter 4 Results and Discussions: This chapter provides an extensive look into the results obtained from the characterizations and the catalytic testing of the multifunctional catalysts. The characterizations for each batch of catalyst as stated in Section 1.5 were divided into these categories; reducibility, acidity, chemical state of the active sites, crystallinity, morphological and surface characteristics. This allowed proper distinction of the different catalysts from one another and how they affect each catalysts' performance in the following subsection of this chapter.
- Chapter 5 Conclusions and Recommendations: Here the main takes conceived from the analysis done is detailed with respect to the objectives of the study. The recommendations provided here were provided with the intent of providing a good starting point for researches conducted in this particular field of catalysis.

CHAPTER 2: LITERATURE REVIEW

2.1 Catalysis Overview

Catalysis can be defined as a process in which the rate and/or the outcome of the reaction is influenced by the presence of a substance (the catalyst). Further, the catalyst should not be consumed during the course of the chemical reaction and that it can be subsequently removed so that it will not be constituted as an impurity in the final yield. Catalysis has been called one of the most significant technologies in the world. It is widely used in industry for production as well as in waste treatment to remove contaminants. Catalysis is used in biological processes by our bodies (Roduner, 2014). All living matter needs enzyme catalysis, as can be exemplified in photosynthesis which is by far the most essential catalytic process. This is what is seen in most of our earliest and most evolved forms of life. Catalysis is therefore generally defined as the action in which a catalyst of promotes a set of chemical reactions. This substance acts to accelerate the rate of the reaction while retaining its original properties. The term catalysis can also be defined as increasing the rate of reaction of a chemical process in the presence of a catalyst (Schlögl, 2015).

Hence, a catalyst can be defined as any material which accelerates a chemical process while not being consumed during the said process. This is achieved via the catalyst providing an alternate reaction pathway through the formation a different transitional state which requires a lower activation energy, E_a compared to non-catalyzed route. To put it simply, activation energy is the amount of energy required to initiate a reaction between several elements or even compounds, which are often identified as substrates of the respective reaction. With regards to a reaction with a significantly high activation energy, the initiation of the reaction may proceed rather slowly, or in some cases not at all. In order to speed up the initiation of the said reaction, the necessary activation energy can be introduced into the reaction system. However, for the sake of efficiency a catalyst which lowers the energy requirement will be employed to effectively speed up the reaction. Activation energy units are defined in terms of energy units and some of the most commonly used units used are kJ/mol or J/mol (Singh & Tandon, 2014).

The catalyst lowers the activation energy by forming bonds with the reacting molecules which will form the products and subsequently detach from the catalyst (Chorkendorff & Niemantsverdriet, 2003). From this understanding, Ostwald (1895) further proposed a definition of the catalyst to be material which accelerates a chemical reaction without affecting the position of the equilibrium and thermodynamics of the reaction (Kakaei et al., 2019). This alternate pathway allows for more molecules to overcome the energy activation barrier thus transforming into the product. It can be said that a catalyst lowers the activation energy of a reaction between substrate by allowing the substrate to form a different transitional structure that requires a much lower activation energy compared to the usual transitional structure. The mechanism through which an alternative transitional structure is formed will be discussed further below.

The Arrhenius equation (Equation (2.1)) further provided an insight into the mechanism of catalysis. The kinetic rate constant is inversely proportionate to the activation energy, E_a . Thus, a lower activation energy will result in a higher rate constant and therefore a much faster reaction (Singh & Tandon, 2014).

$$k \equiv Ae^{\left(\frac{-E_a}{RT}\right)}$$
 Equation (2.1)

- k = rate constant
- A = pre-exponential factor
- $E_a = activation energy$
- R = molar gas constant
- T = absolute temperature



Figure 2.1 : Energy diagram of a catalytic process. Image adapted from (Chorkendorff & Niemantsverdriet, 2003)

Without the presence of a catalyst, the reaction proceeds via the standard visualization of the Arrhenius equation, in other words if A and B collides to produce sufficient energy to overcome the activation energy barrier, a product will be formed with the difference in energy between the product and the reactants defined as change in free Gibbs energy more commonly noted as ΔG . In the presence of a catalyst, the catalyst spontaneously binds the two reactants thus making the complex formation to be exothermic in nature. This lowers the activation energy barrier thus, results in a much higher rate constant, as shown before in the Equation (2.1) (Lynggaard et al., 2004).

Generally, a catalyst may fall under two main categories; homogeneous catalyst and heterogeneous catalyst. The former is a catalyst which functions by having its molecules dispersed in the same phase as the molecules of the reactants involved while the latter functions by existing within a separate phase from the reactants. Catalyst plays various role be it in natural processes or industrial processes. Take enzymes as an example of homogenous catalyst in chemical processes that take place in our daily lives. These proteins are highly selective in forming bonds to specific reactants with shapes complementary to the active sites available on the enzyme. This phenomenon hereby exhibits the importance of catalyst selectivity which must be recreated in man-made catalyst processes. This work however focuses on heterogenous catalysis which also finds application in various processes in our daily lives. Take as an example the conversion of carbon monoxide, CO in our vehicles at the surface of noble metals in the exhausts. Briefly, this process involves adsorption of CO and oxygen gas, O₂ on the metal's active sites. Both of the compounds will be dissociated which will be followed by one of the oxygen compounds forming bond with CO compound to eventually form CO₂ which is a naturally found gas in our atmosphere. This process once again clues us into the importance of a catalyst active sites in providing selectivity towards the targeted product formation (Roduner, 2014; Schlögl, 2015).

A heterogeneous catalyst speeds up a reaction with fluid phase products and reactants, while allowing the reaction to continue as normal. It does this by stabilizing reactive intermediaries that would not form in the fluid phase. A catalytic reaction occurs in porous catalyst particles by transporting reactants from the bulk to the catalyst's exterior (external Mass Transfer Resistance), transport of reactants through pores to the interior of catalyst (internal Mass Transfer Resistance), reaction of adsorbed reactants, formation of adsorbed products, desorption, transport of products to the surface of catalyst and return of products to the main body (Klaewkla et al., 2011).

Heterogeneous catalysis is also known as surface catalysis because it occurs between a solid and a gas. This process has three main stages: (1) adsorption (physisorption, chemisorption) of reactants onto the catalyst surface, (2) chemical reaction at the surface and (3) desorption of products from catalyst surface. These are some of the most important points to remember about catalysts' actions. In theory, catalysts will never alter the thermodynamics or the reactions. A catalyst does not favor a thermodynamically impossible reaction. The reaction would continue even without the catalyst. However, it might not be possible to observe or use the catalyst in certain contexts. The catalyst increases both the rates of forward and reverse reactions, but does not alter the equilibrium composition. The question is: Since a catalyst can't change the equilibrium composition, why do we say that the catalyst's selectivity is the most important property? Keep in mind that a catalyst can affect different reactions to alter the reaction selectivity. At 150-300 °C as well as under atmospheric pressure, the reaction between the gaseous alcohol and nitrogen is more than an oxidation reaction (Naik & Doraiswamy, 1998; Shi et al., 2022).

The current trend in catalysis is such that catalysis often takes place over nanosized materials. The remarkable advances in catalysis science that have been made in the past few decades can be directly linked to the advancements in nanotechnology. The arsenal of engineers and chemists alike is expanding the scope of catalysis science. This is due to the development of new strategies and techniques for producing functionally advanced and complex catalysts. The most important task of catalysis science is to design and manufacture active and selective catalysts. This can be done using both wet chemistry and synthetic tools. Complexity is one reason nature took millions of years to develop its enzymatic catalytic systems. Living cells can achieve unprecedented catalytic selectivity by implementing complexity in the structure and chemistry of enzymes. This is the model that catalysis science should follow and can be achieved using strategies and techniques from the toolbox for nanotechnology. The ultimate goal of the nanotechnology toolbox is to achieve the desired chemicals with the highest selectivity and catalytic efficiency. This goal can be achieved through chemical and structural complexity (Shi et al., 2022).

In more recent years, the trend in the field of catalysis has shifted to the application of single-atom catalysis. It has been shown to be an effective technique with great performance, cost efficient as well as improvement in terms of catalytic activity and selectivity. Within single-atom catalysts, isolated individual atoms are dispersed on, or is

some cases coordinated with, surface atoms of the supporting material. This led to the maximized atomic efficiency of the active metals, while also providing an alternative with regards to tuning the activity and selectivity of catalytic reactions (Cheng et al., 2019a).

The common sense says that coordination and crystallographic termination should determine the catalytic action. This is often assumed in heterogeneous catalysis. These molecular factors are compared to microscopic counterparts, and the main question is how these can be used to enhance catalytic properties. In the microscopic world, these factors are size, composition, architecture, and morphology. The correlation between particle size and morphology is strong. Crystallographic termination and coordination are also strongly associated. Composition and architecture are manifestations of surface ensemble. The nanoparticle's size, composition, and structure can be controlled so that catalytic properties of catalysts made from such nanoparticles are unique. Many cases of improved catalytic properties, and even trends in catalytic behavior were reported over the years after the advent of nanotechnology. However, wet chemistry has many limitations. It does not have a viable solution for the production of small particles. These are not yet integrated into the unified picture that includes colloid, surface and interface chemistry. The generic synthetic routes for the preparation of monometallic and multicomponent nanoparticles oxyphilic elements are another area where colloidal chemistry fails. These particles usually belong to the first- or early-group of transition metals. The roles of surface-capping agents and surface-directing agents is not clear. It is possible that ligands could be used to benefit homogeneous catalysis, but this has yet to be proven and placed in a generic context. This is similar to single-site organometallic catalytic catalysts (Linek & Vacek, 1981).

In-situ characterization is key to understanding the dynamic world catalysis. This is particularly important for colloidal chemical synthesizers, as colloidally produced nanoparticles are often kinetically trapped within their as-synthesized form and are thus metastable under the conditions of catalytic reaction pressure, temperature and time. High-surface-area metal oxides are often used as supports and cocatalysts in colloidal chemical synthesis . They can also undergo crystallographic or morphological transformations when exposed to reactive and thermal gases. Catalysis is a dynamic process that can alter the bulk and surface properties of nano-sized catalysts. These tools and techniques are used to identify and understand molecular factors that regulate catalytic processes. An ideal probe in situ should have high spatial and temporal resolutions, surface sensitivity, chemical and elemental speciation, as well as high spatial and time resolutions. There isn't a single technique that can meet all of these requirements simultaneously. Scientists in this field face a daunting task: developing techniques that allow for the probing of individual catalytic site(s), measurement of single reaction events, and turnovers is a major challenge. Combinatorial strategies are crucial for the evaluation of an innumerable pool of nano catalysts that, thanks to colloidal chemistry are made available for catalysis. No combinational method has been developed for colloidal chemistry and no protocols have been created to produce nano catalysts. The computationally guided colloidal synthesizing of nanoparticles by colloidal guidance is an area that is rapidly growing and has the potential to be a major force in both colloidal and catalysis (Klaewkla et al., 2011; Linek & Vacek, 1981).



Figure 2.2 : Illustration outlining heterogeneous catalysis of CO to form CO₂. Image adapted from (Chorkendorff & Niemantsverdriet, 2003)

The role of catalyst is one that is versatile and applicable in almost all of the modernday conundrums that we face today. Most of these require efficient use of resources and energy to be thoroughly adhering to the need of the population while maintaining a good economical flow of work. These days application of catalyst is almost inseparable from various industries and this work will be focused on its application in fuel production industry, in particular alternative form of fuel which can complement fossil fuels' shortcomings.

2.2 Bio-Oil Refinery using Furfural as Model Compound

To address the climate change and energy security concerns arising from the lack of renewable fossil fuels, sustainable low-carbon biofuels from lignocellulosic biomass or oleochemical sources are urgently needed. A short history into the biorefinery concept can tell us that such processes were applied to create the biofine process in 1990. This process converts biomass to furfural or levulinic acids. Two reactors are part of the biofine process. One is a downstream pre-mixer for steam hydrolysis and one is a wellmixed unit for levulinic acids production. The process could yield a theoretical yield of approximately 70% from C_5 sugars. This is of roughly 50% conversion of the biomass. This co-production model allowed the use of the paper mill sludge as feed for biofine at 3,000 tons per year for the Caserta commercial plant. This process produced furfural as well as levulinic acids by stripping or distilling, which required large amounts boiling water and high levels of energy (L. Zhang et al., 2013a).

Due the majority of carbon feedstocks used today are derived from petroleum and natural gas, the search for sustainable biofuels has a significant impact on the wider chemicals industry. The development of the biorefinery concept to co-produce sustainable fuels and chemicals can transform the global energy and material markets. This requires the development of catalytic methods capable of selectively transforming oxygenated biomass into alternative chemical intermediates or fuels. Lignocellulose is a coveted biomass energy source mainly due three factors; (1) abundance; (2) low cost and (3) sustainability. These three main factors are linked to the fact that lignocellulosic biomass is naturally produced in most agricultural activity.(Lange et al., 2012) This form of biomass is not without its own demerit, mainly due to its recalcitrant nature due to its complex composition (Herrera et al., 2020; Moravvej et al., 2021). Such composition reduces the rate of efficiency from which energy can be extracted from lignocellulose original form. There are mainly two ways by which the maximum energy potential of lignocellulosic biomass could be utilized; the first method being direct extraction from the biomass itself which requires processes such as pyrolysis and gasification in order to derive a less complex form of energy source. In particular one such product of fast pyrolysis of lignocellulosic biomass is bio-oil, a complex mixture of the lignocellulose derived model compounds ranging from organic acids (example: acetic acid), aldehydes (example: furfural), phenolics (example:guiacol), esters (example: n-propyl-formate), carbohydrates (example: levoglucosan) and water, H₂O (Ding et al., 2021; Hu &

Gholizadeh, 2020; Kabir & Hameed, 2017; Kumar et al., 2020). The content of bio-oil may vary based on the type of biomass used, primarily the wood used. Depending on the source a mixture of pyrolytic product (bio-oil, bio-char and pyrolytic gases) can be yielded with varying ratio. Most commonly, when pyrolyzed at the range of 500 to 550 °C, 60-80% of bio-oil yield can be easily achieved, making it the main product of pyrolysis of lignocellulose based biomass (Kumar et al., 2020). In terms of research, one major drawback in studying bio-oil as a whole is the complexity of it which hinders its swift upgrading to be production ready as a form of fuel. However, it is much easier to identify some of the major problem hindering bio-oil to be used as a fuel despite already undergoing upgrade process. Some of the major problems include the low energy density of most of bio-oil's component, the chemically unstable components contribute in decreasing the oil's shelf life depreciating its economic value and the low miscibility of its sugar derived component even in the hydrocarbon-based oil (Chen et al., 2019; Mutsengerere et al., 2019). These problems, as the previous statement implied are rooted in the individual component of bio-oils, as such looking into the following alternative method in energy extraction from lignocellulose will provide some valuable understanding.

The alternative involves the process of unlocking usually via extraction of specific sugar-based compounds from lignocellulose. The sugars will usually be upgraded to a more energy efficient form which mainly used to be ethanol (Lange et al., 2012). Recent developments have prompted the research community to seek other form of upgraded compound which include glucose derived hydroxymethylfurfural (HMF) which will then be converted to dimethylfuran (DMF) or even hydrocarbons within diesel-range (Román-Leshkov et al., 2007; Sınağ et al., 2003). Other examples include conversion of cellulosic glucose to levulinic acid (LA) to be further converted into methyl tetrahydrofuran (MTHF) and ethyl levulinate (EL) (Chang et al., 2019; Kruse et al., 2003).

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Furan-based chemicals are one of the main derivatives of biomass feedstocks making it a viable representation of the overall molecule class distribution present in biomassbased liquid fuels such as bio-oil. Thus, it is definitely worth focusing our effort in upgrading furanic derivatives present in bio-oil, in order to add value to the oil in terms of becoming a valuable liquid fuel. As of recently, many researches have been focused on the derivatives of bio-furan, which includes 5-hydroxymethylfurfural (HMF) and furfural which represent the cellulose and hemicellulose-based furan groups, respectively. This is mostly due to the them sharing a core structure which facilitates upgrading and therein application in various fields such as green fuel technology, as we have previously discussed. As such, these chemicals more commonly than not exhibit chemical properties which render them particularly susceptible to reactions such as hydrogenation, oxidation and condensation. Such properties not only allow ease in application of furan-based compounds not only as part of the green energy system but also in other fields such as the synthesis of rubbers, chemicals and pesticides among many commonly known examples. Out of these compounds furfural provides a unique platform for upgrading to be a significant platform chemical in biofuel production (Yan et al., 2014).

A brief look into furfural's formation from lignocellulosic biomass reveals that it is a derivative from xylan, a component of the afore mentioned biomass (Li et al., 2016). Furfural is made from agricultural biomass that has been enriched with pentosan, a polypentose. Quaker Oats have also noted to use oat hulls for its main raw material, for furfural production in 1921. The production technology was not improved due to low demand until 1980. However, due to environmental concerns stemming from these old production methods, the production of value-added chemicals and fuels from lignocellulosic biorefinery concepts has gained greater attention worldwide. The utilization of feedstocks and the improvement of economics are now centred on integrated strategies that include co-production with other high-value products, such as furfural

(Gómez Millán & Sixta, 2020). The improved production concept makes it possible to produce furfural on an industrial scale.

To go into further detail, the production process is usually initiated by first breaking down the pentosans into monomeric pentoses through hydrolysis process. The pentoses can then be dehydrated through an acid-catalyzed dehydration process to form our targeted product, furfural. This particular dehydration process can be deemed slightly ambiguous due to contradicting theories presented in different literatures to explain its underlying mechanism. This may be due to these particular literatures simply discussing the mechanism of furfural formation from xylose under different catalytic systems, thus rendering all of the proposed mechanism to be true with respect to their different catalyst materials. Despite, this ambiguity, most of the studies commonly pointed out that furfural can be produced through the dehydration of five-carbon sugars such as xylose and arabinose, commonly found to be a derivative of the hemicellulose portion of lignocellulosic biomass. This particular point of the mechanism hinges on the role pf the 1,2-enediol intermediate present when the reaction is carried in an acidic medium (Shivhare et al., 2021).

On the other hand, a mechanism was also proposed which is centered around the concept of acyclic dehydration of xylose to furfural rather than through the formation of 1,2-enediol intermediate as discussed above. The mechanism postulated that the dehydration is first initiated by the protonation of the hydroxyl group bound to the carbon atom in the presence of hydrogen ions. This will yield a compound to act as the transition state, such that it has a trivalent, positively charged oxygen atom. This electronegative oxygen atom will initiate the formation of a more positively charged carbon atom through the release of one water molecule (Machado et al., 2016). Consequently, the neighboring C-O bond will fission and cause the migration of a hydrogen atom within the molecule,

thus leading to the protonation of hydroxyl oxygen to trigger the loss of another water molecule. The carbon atom, now in a trivalent state can now combine and form a more stable ring structure compared to the previously found double bond in the precursor. This mechanism will form furfural at the end via the 1,4-elimination of hydrogen ions (Luo et al., 2019).

This particular scheme has drawn significant inquiries when compared to the first dehydration mechanism, while also coming under question when a variation of this mechanism was also proposed. The variation requires the direct rearrangement of the pyranose structure, an added step after protonation and dehydration have taken place. In order for this particular mechanism to take place, the protonation has to take place at the oxygen atom, whether at C1 or C2 position. The quantum mechanical modeling on these three proposed mechanisms provided an in-depth look into the energy barriers of the transition states involved in the processes. It further revealed that the energy calculations favored intramolecular rearrangement route rather than the ring-opening of pyran at lowest energy barriers. Furthermore, the study of xylan-derived polysaccharides through thermally cleaving the glycosidic group proved that xylan can be hydrolyzed and then dehydrated to finally yield the said product (Khemthong et al., 2021). This study compliments the findings from another study focusing on the open-chain hypothesis and the two-pyranose rearrangement mechanism as discussed above. It can be drawn from their findings that the cyclic dehydration mechanism's kinetic model matched the observations and experimental values thus lending credence to this particular hypothesis. Despite all of these findings, the mechanism of furfural still requires further study and experiments in order to thoroughly understand the underlying mechanism. As analytical methods such as Nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FT-IR), and Isotope technologies advances, their application can no doubt greatly benefit the elucidation of this particular process (Xu et al., 2020).

It is also worth discussing briefly the Vedernikov's method and its similarity to the previously proposed mechanisms. The Vedernikovs' method was created in 2001 by Latvia's State Institute of Wood Chemistry to increase furfural yields and reduce cellulose loss. This process only required a small amount of concentrated acid or salts for hydrolysis and dehydration reactions. This process has two advantages: the furfural production yield is increased from 55% to 75%, based on the theoretical value, and the 5fold decrease in cellulose degradation. In 2006, Iran's first commercial plant was constructed using Vedernikovs' technology (Cai et al., 2014). This technology has been shown to increase the theoretical yield by up to 90% if ethanol is made from residual cellulose. C₅, C₆ sugars from lignocellulosic biomass are hydrolysed with mineral acid. They then dehydrate to furanic aldehydes such as furfural, 5-methylfurfural, and hydroxymethyl furfural. Furfural derivatives can be hydrogenated to hydroxymethyl furfural to produce similar boiling points and octane values to ethanol. These are suitable for use as an additive in alternative fuels. However, because of its short carbon chain, however, it cannot be used as a drop-in fuel. Therefore, a C-C reforming reaction is required. Furfural can be used to synthesize longer-chain hydrocarbons by using aldol condensation, dimerization reactions and hydrodeoxygenation. These reactions can result in C_8 up to C_{13} + alkanes (Dashtban et al., 2012).

Furfural's versatility in terms of the functional groups present in its overall structure is a clear indicator for its potential for application in fuel technology. To elaborate further with regards to the of this thesis, furfural contains unsaturated C=O and C=C bonds which are both particularly susceptible to addition of hydrogen atoms which will tentatively lead to hydrogenation reaction. However, due to there being multiple functionalities being available for the hydrogenation reaction take place at, the catalytic pathways and consequently each of their varying products are complex. This is not inclusive of the consideration that comes from the stability of the product depending on the reaction condition and the surrounding medium which could further complicate matters (Xu et al., 2020). Alas, it is good for us to identify some of the more common products from hydrogenation of furfural which are furfuryl alcohol, 2-methylfuran, tetrahydrofurfuryl alcohol, tetrahydro furfural, 2-methyltetrahydrofuran. Owing to the varying possibilities of product that come from this single reaction, most studies have concluded that control of catalyst parameters such as but not limited to particle size play a much larger role here when compared to hydrogenation of other biomass-based platform chemicals such as levulinic acid, a common derivative from the cellulose-based feedstocks. With regards to the latter, previous research pointed out that the metal particle size merely affected the overall reaction as a common manifestation at the surface of the catalytic reactivity. In contrast to that, when furfural undergoes hydrogenation, studies have suggested that catalyst particle size exert far more weight in the overall performance and outcome of the reaction. Other than performing regular catalytic functions such as reducing activation energy the catalyst plays a vital role in regulating the selectivity of the product formed through regulation of the particle sizes (Gupta et al., 2018). This is highly impactful such that all of these studies suggested that a well-defined strategy in promoting catalyst within a particular range of particle sizes will almost definitely allow a more definite control of the catalytic selectivity via the alteration of the adsorption configuration of the reactant onto the catalyst surface.

In tandem to the advancement in understanding the role of catalyst particle size, large variety of metal catalysts comprising of transition metals such as Ru, Pd, Pt, Ni, Cu and Co were investigated. These metals were most commonly studied in the form of either monometallic and bimetallic catalysts. To further compliment the progress made such as stated in the previous paragraphs, the catalysts were under particular scrutiny in terms of their individual ability to control the selectivity of the product formed. Despite the leaps made in progress, a full control of the selectivity was deemed far too much of a technical

difficulty once again due to the large variety of products that can be formed. Hence, it was determined that the control of catalyst chemical, morphological and surface properties is the most efficient way to exert some degree of control in the product formation as previously exhibited through the importance of particle sizes of the catalyst. This approach of customizing the catalyst, tailored to suit the need of a particular reaction, in this case hydrogenation of furfural is the foundation of not only this particular thesis but also other researches, in the past or future which will undoubtedly create platform for the overall improvement in the performance of this particular reaction, especially if we are considering mass production (An & Li, 2022; Fu et al., 2023).

Furfural as we now have established is very much a versatile and facile compound when it comes to undergoing upgrading processes to form energy-rich and stable compounds for fuel productions. As mentioned previously, this is mainly due to its multifunctionality of furan ring and carbonyl carbon, which ease the interaction of this platform chemical whether to the catalyst or to other reactants. This property of furfural allows the formation of a wide range of derivatives depending on the upgrading route that was taken. Some of the notable once include furfuryl alcohol (FAL), furfuryl acetate (FAc), furan, methylfuran, the previously mentioned HMF and DMF(Hanly & Henson, 2014; Herrera et al., 2020; Lange et al., 2012). When it comes to selecting the upgrade path of furfural, the choice of furfural derivative to be formed will be the determining factor. Such a weighty decision involves specific criteria which in this case include increase in energy density and increase in miscibility in hydrocarbon-based fuels which in this case is the bio-oil. Furthermore, if we briefly go back into the discussion regarding bio-oil's drawback as an alternative fuel, most of the problems stated previously can be very much improved when upgrading of furfural is taken into consideration. This is due to the fact that furfural alone makes up of almost 4% of bio-oil's chemical makeup, a large number considering that aldehyde cumulatively make up almost 15% of the oil's overall component (Xiong et al., 2020). The tackling of furfural will provide several options to future researches with regards to processing platform chemicals. Considering the information presented, a deeper look into the various upgrading pathways of furfural seems to be in order as it not only is a main component in bio-oil but also an untapped source of energy on its own merit.

Ershov et al. even reported that all furfural derivatives contain a variety of oxygenated compounds, which are suitable for use as fuel components. They are less oxygen-rich than the octane boosts (ethanol, N-methylaniline, and methyl tertiary ether) and produce high volumetric heat of burning (25.2 to 30.7MJ/L). Furfural derivatives have low heat of combustion, low boiling points (ranges between 31.1 °C and 189.0 °C), and low crystallization times (below 50 °C), making them suitable for use as antiknock additives and octane boosts. The engine test revealed that 2-methylfurane and furfuryl amine had promising functional and physicochemical properties as octane boosters (Ershov et al., 2017).

To be very specific to this study, focus will lie on the formation of furfuryl alcohol, FOL and furfuryl acetate, FAc which are the products formed via hydrogenation and esterification, respectively. The selection is based on the merit of both furfuryl alcohol and furfuryl acetate having a good H/C ratio, thus good energy values making it highly suitable for application as fuel (Hoydonckx et al., 2000). Granted, with such goal in mind dimethylfuran provide the highest value, however this particular compound has been found not as environmentally friendly as the other two owing to the fact that its CO₂ footprint is the highest among furfural derivatives (Lange et al., 2012). Briefly, furfuryl alcohol is an important monomer in the synthesis furan resins. They are used widely in thermoset polymer matrix composites and cements as well as adhesives, coatings, coatings and casting/foundry. This molecule can also be used as an epoxy resin diluent, a modifier of phenolic or urea resins and an oil well. It is also a carbon binder. The salt of FA can also be used in the synthesis lysine and vitamin C as well as lubricants and plasticizers. It is important to note that furfuryl alcohol can also be used as an intermediate in the production of additional hydrogenation products, such furfuryl acetate, which could be a fuel alternative with better combustion performance and a higher Research Octane number (RON = 103) that gasoline (RON = 96.6).

Since the inception of this study focuses on green catalysis, the product aimed for biofuel production should adhere to the same values. Since furfuryl acetate is in fact a derivative of furfuryl alcohol, this situation provided a platform for this study to narrow down into tandem reaction with the *in-situ* furfuryl alcohol becoming the reactant for the subsequent esterification reaction. This can be achieved in the presence of acetic acid, an organic acid making up around 1 to 2 % of the bio-oil component, thus creating a window of opportunity to address the corrosivity of bio-oil due to its acidic components (Nogueira et al., 2014).

2.3 Methods of Converting Furfural to Stable Fuel Molecules

With the increasing prominence of the need to convert the bio-oil components or more specifically furfural into energy rich substances, many methods have been developed to arise to the need and tackle the issue head on. Before we look into the methods relevant to this specific study, it is in line with good flow of theoretical work to look into other methods involved in lignocellulose-based bio-oil and furfural upgrading. This is to allow us to understand the different advantages and drawback of each method. Furthermore, at the end of the day the core concept of furfural upgrading is the same in which the functional groups available will be undergoing transformation depending on the different catalyst involved and the subjected reaction conditions (Dutta et al., 2012).

2.3.1 Steam reforming

One such method is the steam reforming method which involves the use of either fluidized or fixed bed reactor at high temperature with introduction of suitable catalyst (Sayas & Chica, 2014; Shi et al., 2014). To provide a brief description of the method, furfural in steam form is passed by a bed of catalyst most commonly supported by commercially available supports such as silica, SiO2 and alumina, Al2O3. Often employed as the active metal in this process is nickel, Ni. The derivative of furfural formed at the end of the reaction will be collected. This process can be categorized as gas-phase reaction in which furfural is dispersed in steam with the presence of hydrogen, H. What determines the efficiency of the catalyst is the level of dispersion of the metal active components within the structure of the support, the higher the dispersion, defined as amount of metal in a unit area, the more efficient the catalytic process. One major advantage of this process is the medium in which the reaction takes place, gas-phase which will ensure good conversion of furfural to the desired product as the reactant molecules will have more energy to collide onto the active sites for conversion. The downside of using this method is the high rate of coke formation beginning at temperature 575 °C and the severe drop of catalytic activity of the catalyst after single usage. This problem will directly impede the application of this catalyst at industrial scale. Although the removal of coke from the catalyst is a relatively simple process, in this case utilization of high heat at 400 °C to burn of the deposited coke, it is still far less economical especially considering that it was reported that coke formation is very prominent after only a single use of the catalyst (Sayas & Chica, 2014).

2.3.2 Molecular distillation

Another method is the molecular distillation of bio-oil itself which refines the oil by separating it into different fractions based on the differing components boiling point or other chemical properties such as viscosity or density (Elkasabi et al., 2014; Guo et al.,

2010). This process allows for elimination of detrimental components of bio-oil from the hydrocarbon medium allowing for almost immediate use as fuel without further upgrading. The advantage of distilling bio-oil is that the process treats the substances very gently thus avoiding degenerative processes such as polymerization, decomposition and oxygenation. This is especially useful in the process of highly polymerizable compounds such as the aldehyde group in bio-oil. The method is also versatile in nature in the sense the separation can be done via various specification mostly involving the boiling point of each substance, while others may choose to separate based on the density of the components. Ultimately, the customizable distiller involved in this process provide precision and control over the final production of bio-oil obtained. However, the method is only applicable to heat sensitive substances and require a large amount of energy to effectively separate the components of bio-oil. Furthermore, this method focuses on the upgrading of bio-oil via removing some of the less stable substances, which could be considered a waste, in the sense that these substances including furfural have untapped energy waiting to be converted (Elkasabi et al., 2014; Pinheiro Pires et al., 2019).

2.3.3 Supercritical fluids (SCFs) and emulsification

SCFs may also be applied in converting model compounds such as furfural. This method usually involves the use of autoclave reactors with batches in 100-150 mL of samples using organic samples such as ethanol, methanol, water and CO₂ (Duan & Savage, 2011; Li et al., 2011; Z. Tang et al., 2010; Zhang et al., 2012). Using SCFs is a green method which requires low temperature. The process usually involves the extraction of useful components of lignocellulose such as the sugar group which can then be further upgraded to harness their energy more readily. This method is considered efficient in terms of its extractive capability. Regardless, this process still does not render fuel-based compounds and is more of an additional step to capture certain lignocellulose-based compounds with energy providing potential. Thus, economically, an alternative

method should be considered. Furthermore, the usage of the organic solvents is not economically feasible due to them being very expensive. Despite being a facile and efficient method, employment of SFCs in extraction of energy rich lignocellulosic products suffers at the industrial level mainly due to the expenses involving the materials used.

On the other hand, emulsification is a relatively cheaper method in converting bio-oil model compounds to fuel efficient compounds. This method often employs the use of surfactants and/or ultrasound waves to improve bio-oils' properties such as friction, anti-wear and behavior at extreme pressure. The surfactant breaks down the oil component in the medium to reduce the overall negative traits of the bio-oil. The improvements of these properties often result in subsequent improvement in the oil's lubricity and lengthens its aging time (Ikura et al., 2003; Leng et al., 2018). It should be of note that despite these improvements several key issue in bio-oil could not be resolved such as the acidity remaining in the medium, thus its corrosive nature remains. Furthermore, the chemically unstable components of the mixture remains and the issue stemming from them stays unchecked.

2.3.4 Hydro-processing methods of converting furfural

We now come to hydro-processing methods such as hydrogenation, catalytic cracking and dehydroxygenation strictly involves introduction of hydrogen gas into the fray along with application of suitable temperature and catalysts. As this process specifically hydrogenation is heavily involved in this study, the background provided here will be with reference to furfural as model compound, representative of the bio-oil components. These processes are chemical in nature and highly suitable in tackling the conversion of highly unsaturated compounds such as furfural and vanillin (Rao et al., 1999). The underlying chemistry of such processes can be retraced to start as an addition reaction,

specifically H atom is added to either the carbonyl carbon or the alkene groups in the furan ring (Taylor et al., 2016). Depending on the reaction conditions set for the reaction to take place at, the transition state of furfural may revert to a stable via electron sharing within the currently available atoms or may result in direct loss of a part of the original compound, which usually will be the carbonyl portion of the compound, with the help of solvent present. An example of the latter pathway is cracking process, which takes place at high pressure and temperature, in the case of furfural a temperature exceeding 300 °C and pressure beyond 40 bar are almost always a prerequisite for the reaction to take place (Sitthisa & Resasco, 2011a). On the opposite end of the hydro-processing spectrum lies hydrogenation process. As furfural is highly unsaturated, hydrogenation in particular is the simplest pathway to achieve conversion to relatively favorable compounds, as it requires relatively lower temperature and pressure. Most studies attribute such reaction conditions to be approximately 100-150 °C and 10-20 bar (Sitthisa et al., 2011; Wang et al., 2019). Major products of eliminative processes such as hydrodeoxygenation and cracking include furan and its derivatives, depending on degree of cracking in certain cases. On the other hand, major products of hydrogenation include furfuryl alcohol, dimethyl furan and hydroxymethyl furfural. Once again this will depend on the degree of the reaction taking place, in this case hydrogenation. It should be noted that the nature and properties of the catalyst used will play a direct role in determining the reaction pathway of furfural processing. Some factors include the active metal used, the surface area and crystallinity of the overall catalyst. The strength of the active metal involved will also proceed the reaction to a varying degree producing different products (Lee et al., 2014). For example, Ni and Pd can both catalyze hydrodeoxygenation reaction. However, Pd in the right conditions will outperform Ni, due to its superior catalytic properties, with respect to the previously mentioned reaction (Wegenhart et al., 2014). In the case of compounds with multi-functional groups, it is absolutely vital to ensure high degree of capability in terms of targeting a certain transformation at a particular functional group, in order to produce useful products.

2.4 Hydrogenation of Furfural

Industrial hydrogenation involves high temperatures and pressures, as well as a wellknown catalyst like copper chromite. This is extremely harmful on both the ecological and economic scales. This catalyst can operate at high pressures (up to 30 bar) as well as high temperatures (around 200 ^oC). This catalyst has acceptable selectivity for furfuryl alcohol, and moderate activity. However, it must be replaced due the rapid deactivation of toxic chromium compounds and their rapid evolution. It is extremely undesirable to use toxic Cr₂O₃. This material cannot be disposed of in landfills. Therefore, it is important to find energy-efficient alternative catalytic packages that can operate at lower temperatures and pressures and contain fewer toxic components. There are many alternative metals that can be used to heterogeneously catalyze the hydrogenation of furfural and furfuryl alcohol. There are both monometallic and multi-metallic nanoparticle systems that can be used for liquid phase or vapor phase hydrogenation. Pd, Pt, Co, Ni, Pt, Co, Cu, Ru, Ir, and Rh are some examples of metals that can be used (Gupta et al., 2018). A variety of bimetallic catalytic catalysts have been investigated to optimize systems for a specific product or reduce precious metal costs. Non-noble metal catalysts have been gaining much attention over the last few years due to their similar properties to noble metal catalysts in heterogeneous and homogeneous catalysis. Furfural hydrogenation, which is a process that produces furfural, has been extensively tested using a variety of non-noble metallic catalysts such as Cu, Co and Ni. Cu-based catalysts are well-known for their low cost, accessibility, and satisfactory hydrogenation selectivity. The scientific community is now moving towards using this metal in catalytic hydrogenation processes. Below are a few examples to give an overview. For instance, Sun et al. have studied the morphological effects of copper nanocrystals that are not

supported on furfural hydrogenation. The TOF of Cu nanowires was three times greater than that of Cu nano-disks. This suggests that there is a significant morphology-dependent effect. Despite this, Cu nanowires were unable to convert furfural at 200*C (38%) even when they were exposed to 30 bars of H ₂ pressure (Xu et al., 2020).

Furthermore, Wang et al. Wang et al. also studied the effects of the basic and acid features of the support on Cu-based catalysts performance using five different supports: ZMS-5 (Al₂O₃), SiO, ZnO and MgO. The total acidity of copper modified supports was found to be: Cu/ZSM-5 (687.4 μ mol/g), > Cu/Al2O3 (268.9 4 μ mol/g), > Cu/SiO2 (210.6 4 µmol /g),> Cu/MgO (12.2 4 µmol /g), > Cu/ZnO (17.2 4 µmol /g), > Cu/SiO2 (9.44 μ mol/g), > Cu/ZSM-5 (0.4 μ mol/g). Cu/ZSM an acid-supported catalyst, caused a poor mass balance, which led to the creation of oligomers (Zhao et al., 2021). Basic support such as Cu/MgO gave rise to furfuryl alcohol and a better mass balance. Moreover, Hu et al. Hu et al. With Cu/CaAlO, 96% furfuryl alcohol was achieved and 100% gammabutyrolactone yield (GBL) was observed. Furfural hydrogenation was shown to accelerate 1,4-butanediol dehydrogenation to GBL. Furfuryl alcohol selectivity was also greatly reduced by the formation of methylfuran in H₂ conditions. It is possible to attribute the impressive catalytic performance the catalyst to the presence of Cu nanoparticles that are defective, strong Lewis bases sites and Cu⁺ species at the catalyst surface. The superior transfer hydrogenation performance of Cu/AC catalyst was also associated with the uniformly sized and well distributed Cu nanoparticles on activated carbon of high surface area with the appropriate proportion of Cu^{2+} and Cu^{0-} . This catalyst offered 92% methylfuran yield. Last but not least, Zhang et al. also proved that Cu⁺/Cu⁰ are both necessary as the active species for the furfural reduction reaction, and that the deposition of thin Al₂O₃ layer on CuCr₂O₄*CuO overall resulted in the increase in catalyst activity while simultaneously decreasing the activation energy of furfural hydrogenation (Zhao et al., 2021).

There are vast differences between the classic liquid phase reaction and the vapor phase. The liquid phase can contain a mixture of the substrate and a ground catalyst. A source of hydrogen can also be bubbled, kept in a static or pressurized state. You can remove aliquots periodically and analyze them off-line. Vapor phase reactions, on the other hand, are self-contained systems. A catalyst is placed inside a quartz tube, and positioned in the middle of a furnace. The substrate is heated to boiling point, where vapor is formed. This is followed by a hydrogen stream of approximately 1 bar. Due to the high temperature, which can be very destructive, and high levels of coke caused by thermal decomposition pathways, the continuous flow system produces many products. Usually, molecules can be detected online using an instrument.

2.4.1 Catalyst support system

A support system provides a medium for dispersing the active metals in order to create a form of control within the catalyst system via tuning of parameters during synthesis. Supports for solid catalysts are essential as they help increase the efficiency of supported metals and metal oxides. They also act as a catalyst active center. Chemically inert, or it can interact with the active catalyst (actual catalyst), the support can be chemically inert. The interactions between the reactants and the support material in liquid, solid, or gaseous form must not be destructive. The catalyst activity and selectivity are affected by the interactions between the support material and the active catalyst. Although the support material does not directly contribute to catalytic reactions, it may indirectly contribute by adsorbing reactants close to embedded catalysts. Materials used as catalyst support materials must have high chemical stability, high surface areas, and the ability to disperse metal or metal oxide particles well over their surfaces. This is especially important for expensive metals such as gold, silver and platinum. To obtain a catalyst with a high surface area, nanoparticles made from noble metals must be exposed to the support sides. This will allow the chemical reaction to take place (Yan et al., 2014). The catalyst's physical form, texture and mechanical resistance give it its activity, especially for bifunctional catalysts. The performance of supported metals is affected by the surface chemical (functional group) and physical properties. These requirements are considered when using various carbon compounds and oxides as catalyst support materials.

There are many commercially available catalyst support materials including silica, alumina, zinc oxide, magnesium oxide and even graphene. In heterogeneous catalysis, the zeolites and mesoporous aluminosilicates have been extensively used as catalysts and supports. Because of their large surface area and high pore volume, mesoporous material is one of the most promising catalysts. They also have the potential to be modified and controlled for pore distribution. Because of the proper diffusion of molecules through catalyst pores, the surface acidic sites can interact with them directly, which promotes conversions. Because of its larger pore sizes (2-100nm), mesoporous catalysts offer a new option in comparison to zeolites. This allows for a greater number of molecules to be transformed into the catalyst (Yan et al., 2014). The formation of porosity on two or three different length scales with interconnectivity between pores and a hierarchical structure would make it more useful for many applications. This is because reactant molecules must be able to easily access the pores. A commercial support pellet is usually made by compressing fine mesoporous or micro-porous particles. Between the agglomerated particles, macropores are formed. These macropores enable fast mass transfer to primary particles. The primary particles are where the active sites of a supported catalyst are located. Bimodal silica gels were recently used as catalyst supports. This is the macropore structure that forms during the synthesis. Consideration of each support system's physicochemical properties such as surface area, pore diameter and pore volume all of which can be determined using BET analysis will provide a clear vision on the catalytic properties that can be selected to suit the need of individual reactions. However, this
section will focus on silica or silicon dioxide due to its properties which shall be further discussed below.

Silicon dioxide, SiO₂ has been investigated for application in various fields due to the material's versatility, low production cost and chemically stable nature (Halilu et al., 2016a; Sitthisa & Resasco, 2011a; Sitthisa et al., 2011; Vargas-Hernández et al., 2014; Villaverde et al., 2013a; W. Yu et al., 2011). There are various ways to synthesize silica nanomaterial including flame spray pyrolysis, sol-gel process and micro-emulsion technique (Zulfiqar et al., 2015). Sol-gel process in particular presents advantages such as ease in control of the particle size and shape. These characteristics are highly sought after in the field of catalysis as they can determine the rate of catalytic activity. Combining those characteristics with the inherent chemical inertness of SiO₂, brings about a material with high capability to act not only as a support to the active metal components but also enabling direct control of the direction in which the reaction takes place. Silica (SiO₂) is considered to be one of if not the best catalyst support material because of its exceptional chemical and physical properties.

Porosity is an important factor in increasing the effectiveness of the catalysts. The stability and activity of embedded catalysts is affected by the shape and size of the pores. Porous silica-based support supports with metal nanoparticles exhibit greater catalytic activity due to the easier access to the active sites (Yan et al., 2014). There are many types of porous silica particle that can be used as catalyst supports. These materials are ideal catalyst supports due to their high chemical stability and inertness. It is easy to see the different arrangements of the catalyst embedded within porous silica. Porous silicas are chemically and thermically stable materials that have uniform pore size and distribution, high surface area and high adsorption capacities. You can adjust the temperature, reaction time, silicates/silica sources, surfactant concentration, calcination

conditions, etc. to control the size and shape of porous silica particles and their structure. Porous silica materials are strong because of their pore size and uniformity. There are many reports in the literature about silica and porous silicon materials and their uses. Their versatility and their use in various industrial or technological applications is evident. Mesoporous silica particles are particularly useful in many fields, including energy, environmental, biomedical and support. They can also be used for drug delivery, vaccine development and biomass conversion. They are highly effective nano adsorbents that can be used to remove various toxic pollutants due to their unique porosity and order. Because of the ease with which they can functionalize both the external and internal surfaces of their pores, porous silica particles have been used for extended periods of time. Porous silica particles are also useful as strong support matrix for catalytic applications.

In early 1990, the first report on the synthesis ordered mesoporous silicon material was published. There are many new and improved synthetic methods for the synthesis porous silica particles. These new techniques offer some advantages over older methods. These techniques allow for control over the synthesis conditions and growth process. It is possible to make silica nanoparticles that have pore sizes ranging from mesoporous (below 50 nm), microporous (1 to 2 nm), to macroporous (5 to 50 nm). Mobil Crystalline Materials-41 and Santa Bar-bara Amorphous (SBA-15), which have hexagonal pores, are the most popular silica materials. Other types include Hiroshima Mesoporous Materials (HMM-33), Technical Delft University, (TUD-1), and folded sheets mesoporous material (FSM-16), MCM-48. Porous silica materials are becoming more popular as catalyst supports due to their excellent chemical stability and ability to incorporate various nanomaterials (catalysts). MCM-50, SBA-11 and SBA-12 have been reported to be excellent adsorbents and catalytic support.

These materials can be used to support metallic clusters through impregnation, reduction, or direct incorporation of metal precursors into the silica structure via sol-gel process. Both single silanol and geminal silanol group can be used as weak Bronsted acidic site. It is possible to increase Bronsted acidic activity by incorporating a trivalent metal such as aluminium directly into the lattice or post-synthesis grafting. Strong Bronsted acid sites can be generated by the tetrahedral replacement of aluminium in the mesoporous structures. However, weak Lewis acid sites can be created by the presence tri-coordinated aluminium species within the framework. Strong Lewis acid sites can also be present if aluminium is not included in the framework. TPD of probe molecules such as pyridine, ammonia, and FTIR is used to characterize the strength of acidic sites. Different activation and desorption energies can be distinguished between acid sites. It has been extensively studied how Al and transition metal elements are incorporated within the frameworks of MCM-48 and MCM-41 mesoporous silica (Jin et al., 2019). It is well-known that silica structural regularity decreases with increasing levels of aluminum in the framework. However, there is an increase of pore wall thickness which provides better stability for catalytic processes. On a side note, another previous work included aluminium in mesoporous MCM-41 silica with different Si/Al rates and without octahedral coordinated aluminium. The aluminosilicate samples that had Si/Al ratios between 41 to 112 showed a tendency to have a decreasing trend in d spacing values. This indicates that the MCM-41 mesoporous hexagonal structure is still intact. The material's poor porous organization was indicated by the smaller and less intense peak for the sample with Si/Al ratio 1/4 10.

It is possible to use mesoporous silicon in basic catalysis. However, most applications in literature involve acidic catalysts. This is done by incorporating moderate or strong acidic sites into the silica framework. Many reactions have used mesoporous catalysts, including conversion of phenol and generation of p-cymene. The use of mesoporous

silicon as a template or catalytic support for the synthesis carbon nanotubes has been a significant application in the past ten years. The mesoporous silicon ensures adequate dispersion of catalytical metal due to its large surface area. This generates small-sized metallic clusters that produce carbon nanotubes with smaller dimensions, homogenous distribution, and good structural regularity. The pores in mesoporous silica act as a template for carbon nanotubes. They are removed by acidic treatment to remove the mold (Shinde et al., 2021).

There are important things to remember both when the catalyst particles are being loaded onto the porous silica supports and during post-synthesis loading. In-situ synthesis can result in the catalyst particles being embedded within the porous supports. This may increase the mechanical stability of the porous support. However, the post-synthesis loading the catalyst particles into the porous supports can cause pore blocking. Postsynthesis immobilization of catalyst particles must not be larger than the pore size. Blocking pores will stop reactants in different states from entering the pores, and thus the overall conversion rate will be very low. It is important to covalently immobilize catalyst particles after synthesis. Strong bonds can hold the catalyst particles together with the support and the catalyst's surface. The catalyst's surface can be damaged for surface modification or subsequent covalent immobilization reactions. This will reduce its efficiency. The stability and catalytic efficiency of the support matrix can be greatly affected by the percentage of the catalyst being loaded relative to its weight. For the catalyst to perform efficiently in the reaction being catalyzed, it is important that the catalyst is loaded at the right level. The efficiency of the material is also affected by the shape of the pores created or existing on the porous matrix/particles. The shape of the pores and the catalyst particles should be identical to ensure that the particles can fill the pores. High stability is guaranteed by the covalent immobilization of catalysts after synthesis, in situ synthesis, and deposition of catalyst particles on porous silica-based support.

Some issue can also be brought up when SiO₂ more often than not comes from the non-green precursors such as tetraethyl orthosilicate (TEOS). Hence, studies involving green silica precursors such as rice husk have been actively carried out (Adam et al., 2010b; Adam et al., 2012a; Ahmed & Adam, 2007; Andas, Adam, & Rahman, 2014; Bhagiyalakshmi et al., 2010). Using rice husk derived silica is a greener approach in comparison to commercially available precursors, with the same properties and the added benefit of vast resource (S. Chandrasekhar, 2003). The rice husk requires minimal preparation, which includes washing with water and controlled burning (Adam et al., 2012a).

Sol-gel method is often employed in the synthesis of SiO₂ as it allows tuning of its morphological properties such as particle size and shape (Zulfiqar et al., 2015). According to Chandrasekhar et al. (2003) SiO₂ phase formed during this stage tends to be amorphous which renders it potent for catalyzing chemical reactions such as hydrogenation(S. Chandrasekhar, 2003). The types of silica precursors include tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS) and sodium silicate solution (SSS). Rice husk (RH) is a green source of silica with more than 90% of its ash containing silica. Chandrasekhar et al. (2003) further pointed out that with controlled burning conditions the silica in the resulting ash form will have higher tendency to be in amorphous form, which due to its ultra-fine size and high surface area which are both highly sought after properties for a catalyst (S. Chandrasekhar, 2003). Sidheswaran and Bhat (1996) further provided details for treatment using HNO₃ prior to RH being burnt and concluded that the process yielded a more pure silica (Sidheswaran & Bhat, 1996).

In principle, tri-valent siliconium coordinated [Si(OEt)₃]⁺ intermediates is incapable of initiating condensation even at neutral environment due to absence of protonating agent for Si(OEt)₄ against the potent penta-valent coordinated [(OEt)₄SiOH]⁺ irrespective of environment (Coltrain & Kelts, 1994). These intermediates determine the integrity of silica particles and its derivatives during gel formation for clustering as well as functionalization. This interplay creates a platform for producing mix or hybrid phase in many functionalized materials into quantum dots and ordinary nanoparticle. In order to understand the phenomena clearly, attempts have been made using B3LYP/6-31G level of theory to indicate the transition states of the pentavalent siliconium intermediates and was suggested to follow single step of SN₂-type mechanism (Schaffer & Thomson, 2008). This therefore controls the onset of silica functionalization or condensation into useful material for handy applications. However, the presence of hybrid structures of quantum dots and ordinary nanoparticle, potent material hydro-processing applications. A number of studies revealed isolated phases of modified silica or silica as quantum dots (Darbandi et al., 2005; Nann & Mulvaney, 2004) or nanoparticles (Halilu et al., 2016c; Hashmi & Hutchings, 2006; Strelow et al., 2016) based on non-renewable source.

Introducing metals into the SiO₂ phase can be done via few different methods such as co-precipitation, impregnation and solid-solid wetting (B. M. Nagaraja et al., 2003). Reverse microemulsion, flame synthesis, and the widely used sol-gel are some of the methods that can be used to create silica nanoparticles. The surfactants molecules are dissolved in organic solvents to form spherical microcells in reverse microemulsion. The polar head group of surfactants reacts with water to form microcavities that contain water. This is sometimes called reverse micelles. The microcavities can be used to synthesize silica nanoparticles. This is done by carefully controlling the additions of silicon alkoxides or catalysts into the medium containing the reverse micelles. Reverse microemulsion has two major disadvantages. It is expensive and it can be difficult to

remove surfactants from the final products. The method worked well for coating nanoparticles with different functional group for various applications. High temperature flame decomposition can also produce silica nanoparticles. Chemical vapor condensation (CVC) is another name for this process. CVC is a process that produces silica nanoparticles by reacting silicon trichloride, SiCl₄ with oxygen and hydrogen. The main drawback of flame synthesis is its difficulty in controlling particle size, morphology and phase composition. This is still the most popular method to commercially produce silica powders.

As an example, Cu will be used for further demonstration of the process that took place. Given the nature of amorphous SiO₂, it is advantageous to introduce the metal insitu during synthesis of SiO₂ to properly distribute Cu throughout the support (Adam et al., 2010b; Adam et al., 2012a; Ahmed & Adam, 2007; Andas et al., 2013b; Andas, Adam, & Rahman, 2014; S. Chandrasekhar, 2003). This process yields a singular copper silicate phase, which is a rigid crystalline structure (Sheng & Zeng, 2015). This process also saves much time rather than to synthesize the SiO₂ and then to introduce the metal postsynthesis. The following mechanism has been proposed by Sheng et al. (2015) in which the precursor will be attacked via OH⁻ to release silicate ions which will then form copper silicate after reacting with Cu²⁺ (Sheng & Zeng, 2015). These statements are better visualized in Equation (2.2).

The sol-gel method is the most widely used synthesis technique for porous supports because of its simplicity and effectiveness in producing monodispersed porous silicon particles. In situ synthesis is becoming more popular as well as loading the catalysts under the same conditions. It is most often reported that the soft (easily biodegradable) template approach is preferred to generate porosity. A variety of catalysts such as bimetallic and noble metal nanoparticles or composite nanoparticles are embedded in porous silicabased supports. The sizes of the various catalysts embedded within the materials were used to adjust the pore sizes. The previously mentioned reactions have been supplemented with a variety of new reactions. The latest research also covers the study of the recyclability and stability of catalysts immobilized onto silica-based catalyst support. This proves that the silica network is both hydrothermal and solvothermal stable (considering that various solvents can be used in the different reactions). This is both a technological and economic point of view. All reports indicated that the immobilization of catalysts on porous silica-based catalyst support supports leads to improved catalytic performance in various chemical reactions. Some of the most interesting reports report chemical reactions that are catalyzed using porous silica nanoparticles or organic functional group bearing porous silicas.

$$SiO_{2} + 4OH^{-} \longrightarrow SiO_{4}^{4+} + 2H_{2}O$$

$$2SiO_{4}^{4-} + (2-x)Cu^{2+} + (5+2x)H_{2}O$$

$$\longrightarrow Cu_{2-x}H_{2+2x}Si_{2}O_{5}(OH)_{4} + (4+2x)OH^{-}$$

5

Equation (2.2)

Sol-gel is widely used to make silica, glass and ceramic materials. It can be made pure and homogenous under mild conditions. The process involves hydrolysis and condensation of metal alkoxides (Si(OR)₄) such as tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$) or inorganic salts such as sodium silicate (Na₂SiO₃) in the presence of mineral acid (e.g., HCl) or base (e.g., NH₃) as catalyst. Hydrolysis of TEOS molecules creates silanol group. The condensation/polymerization between the silanol groups or between silanol groups and ethoxy groups creates siloxane bridges (Si-O-Si) that form entire silica structure. There are two main stages to the formation of silica particles: growth and nucleation. To describe silica's growth mechanism, two models have been suggested: monomer addition and controlled aggregate. Monomer addition models describe that particle growth happens after an initial burst in nucleation. This is done by

adding hydrolyzed monomers to the primary particle surface. The aggregation model, on the other hand, explains that nucleation takes place continuously throughout the reaction. The resulting nuclei (primary particle) will then aggregate to form smaller, trimmer and larger particles (secondary particle). Based on the reaction conditions, both models can lead to either a spherical network or a gel network. Many researchers attempted to determine the size and composition of primary particles using a variety of techniques. Green et al. The primary particles were measured at 10.3 nm in methanol and 20.7 nm in ethanol, respectively. Later, Rahman et al. produced silica nanoparticles that were homogeneous, stable and with a mean particle size of 7 $.1 \pm 1.9$ (in ethanol). Stöber et. al. reported a pioneering work in the synthesis silica particles that was spherical or monodispersed. They produced silica particles with sizes ranging from 5 to 2000 nm using aqueous alcohol solutions with silica alkoxides and ammonia (basic condition). Many contemporary research papers describing the formation of nano-sized silica particles have been derived from the Stöber method. Stöber method has the advantage of forming monodispersed spherical silicon particles, as opposed to acidcatalyzed systems that usually result in gel structures.

The optimal synthesis condition refers to a combination or combinations of optimal reactions parameters of the sol-gel method. This allows for the production of silica nanoparticles that are small, homogenous and monodispersed. By manipulating reaction parameters, you can control the rate of polycondensation reactions to produce smaller nanoparticles. The majority of studies agreed that increasing ammonia concentrations led to a larger particle size. Small amounts of anion electrolyte additions (ammonium salts of Br, I and Cl) resulted in monodispersed silica particles that ranged from 20 nm up to 34nm, depending on the used anions. Conductivity profiles were used as an alternative to zeta potential. All anions could reduce particles size by 73-78%. Br and I⁻ had the greatest effect, while Cl⁻ had the lowest. The silica powder synthesized was free of cation

impurities. Mixing modes were crucial in determining particle size and distribution of silica nanoparticles. Mode-A produced monodispersed powder of an average particle size of 10nm. Powder quality has been further improved by using a freeze dryer. Rahman et. al. reported a stable, homogeneous and highly dispersed silica nanoparticle that was 7.1 nm in primary size range. Rahman et al. also reported that the optimal conditions for solgel processing were achieved under low frequency ultrasound. This optimized technique is easy to use and repeatable, and yields a high yield of approximately 75% nanometer silica within a primary size range.

With decreasing particle sizes, the amount of atoms on the surface is greater. Silica nanoparticles less than 5 nm have more Si atoms than the surface. The surface should contain one or more silanol group (SiOH). The silanol group concentration per gram of silica will determine how chemically modified silica is. This includes grafting organofunctional groups or incorporation of metal ions. Information about the silanol group distribution on silica surfaces can be found in the number of silanol units per area. The specific surface area is interrelated with silanol group concentration (Ekeoma et al., 2022). As the particle size decreases, the silanol number increases. The silanol number of these nanoparticles decreases with decreasing particle size, suggesting that they could be chemically reactive and therefore suitable for catalytic applications. One of the most remarkable characteristics of ceramic nanoparticles is their unusual adsorption capabilities. The nanoparticles have a higher ability to chemically adsorb, and even dissociate, a wide range of dangerous organic molecules than their commercial counterparts. The unique adsorption property at nanoscale is directly linked to the increased surface area(Yu et al., 2020).

In fact, regulation of metal-support interaction has been shown to be a favorable method in controlling the metal particle sizes and its dispersion within the support system matrix. A combination of supporting silica,SiO₂ and a small amount of titania, TiO₂ was shown to be able to improve upon Cu dispersions by a significant amount. The presence of TiO₂ within the structure of silica improves upon silica's characteristic abundance in terms irregular grains and micropores. TiO₂ allowed for finer distribution of the grains at the cost of decreasing the specific surface area, which increased as the amount of TiO₂ introduced was increased. Furthermore, it was also found that introducing TiO₂ helped in promoting the presence of Cu particles at smaller size which consequently improves the dispersion of the active metal. This has been attributed to formation of Ti-O-Si structure that helps in enforcing smaller particle size. It was also known that in a system comprised of just Cu and silica, CuO and the hydroxy group of silicon oxide provided at the catalyst surface to form Si-O-Cu structures, which are known to have stronger interaction thus making the precursor reduction to be relatively more difficult. Thus, the presence of TiO₂ promoted formation of highly dispersed, small CuO particles, which assists in easing of the reduction process of the precursor (Natsir & Shimazu, 2020).

There are further experimental proofs that demonstrate the interaction of particle size of active metals and their supports affecting the efficiency of hydrogenation of furfural. Cu/ZnO, $(Cu_{x_3}Zn_1-x)_5(CO_3)_2(OH)_6$) is an aurichalcite has been shown to promote hydrogenation of furfural at a significant level. This was induced by the cumulative effect of Cu particle sizes as well as its interaction with the support. These were achieved through the adjustment of Cu/Zn ratio during synthesis, in other words the specific dispersion mode of copper and zinc species during coprecipitation to form the final form of the catalyst system (Gupta et al., 2018). It was shown that when the ratio was increased from 0.4 to 1.1, the Cu particle increased along with it, from 6.7 nm to 13,1 nm. This led to an added effect in terms of decreased Cu particle dispersions (14.9% to 7.6%) and Cu surface area (23.4 m^{2g}g cat⁻¹ to 21.3 m^{2g}g cat⁻¹).

In another aspect, synthesis of silica with regards to application within the field of green catalysis, can also be looked in terms of the silica precursor. With respect to that, it would not only be poetic, but also cost efficient to obtain such precursor from a green, alternative source as opposed to the commercially available ones. With such aim in mind, several researches have utilized the application of rice husk ash which contain silica as a precursor for the synthesis of silica (Adam et al., 2012a). Adam et al., successfully achieved the extraction from rice husk ash and the subsequent synthesis of silica support with commendable catalytic performance. Many other contemporary studies have applied this green precursor in order to establish a somewhat cyclical green catalysis process, from the synthesis of a green catalyst to production of green product, alternative to commercially available ones. The process of extracting silica as rice husk can be simply described in two main tasks. First of those is the washing of the rice husk, using low concentration of nitric acid, while the second being the burning of the husks until its ash is formed. Silica can then be readily accepted using basic solution, most commonly sodium hydroxide, which extracts the silica in its salt formed with the hydroxide. The extracted silica can then follow any of the synthesis route discussed previously (Adam et al., 2010b; Andas et al., 2013b; Andas, Adam, & Rahman, 2014; Andas, Adam, Rahman, et al., 2014).

2.4.2 Metal function and reaction selectivity

Certain metals are capable of dissociating hydrogen. This is when the H-H bond is separated without activation. The bond is then subjected to enough energy to overcome its energy potential. Pt, Pd and Ni metals have the ability to dissolve molecular hydrogen, without activating the covalent bonds. It has been extensively shown that the Pd(100), facet is much more active than the Pd (111) facet. Furthermore, due to non-activating channels for adsorption, hydrogen can spontaneously dissociate at the (100). Norskov and colleagues have also reached the same conclusion. When calculating Cu(100) surface's

reactivity compared to Cu(111), The dissociation energy barriers between Cu(100) and Cu(111) surfaces are approximately 0.1 eV different, they were found to be about the same. Cu, Ag, and Au are unable to achieve this result because they cannot dissociate the bond with no additional support. This could be done by high temperatures, bond activation, or by supplying hydrogen at sufficient pressure to force hydrogen onto the metal's surface. Thus, it must be stressed that one of the most important abilities that a catalyst for hydrogenation reaction should possess is high capability in dissociating hydrogen gas into individual atoms which can then be free to interact with the adsorbed reactant which in this case is furfural. Different metals have varying degree of capabilities in dissociating the H-H bond. Pt and Pd are some of the most sought after metals in this application due to their capabilities to dissociate molecular hydrogen H without ever breaking the covalent bond. This provides the very much needed lower level of activation energy which increase the efficiency of the overall process. A study had previously demonstrated that Pd at its facet of (100) dissociate hydrogen more readily than Pt (111). Furthermore, considering that the surface is of non-activating channel, hydrogen will instantaneously dissociate at the surface level. Metals such as Cu and Au however are incapable of achieving similar feat (Taylor et al., 2016). They require elevated temperature and increased pressure introduced via a constant stream of external hydrogen gas in order to dissociate hydrogen, in other words an external energy needs to be supplied for these metals to achieve hydrogen dissociation at molecular level. It should be noted that these observations were taken without taking into consideration the interplay between the metal active phase and the support material.

Thus, the very reason noble metals are often used for hydrogenation reactions is because of hydrogen activation. Each element has its own electronic and chemical characteristics that can have an impact on the reaction. This is why precious metals are so expensive and scarce. Research into cheaper alternatives is underway to find more affordable options. This is why nano-alloys containing small amounts of precious metals are so popular. The materials frontier has been surpassed and isolated atomic entities have been shown to be highly valuable for hydrogen dissociation on inert material such as Cu or Ag. Pt and Pd atoms can quickly dissociate molecular hydrogen, causing a spillover effect on the host material. This phenomenon has been extensively studied on single crystals in ultra-high vacuum, and more recently on physical catalysts to create continuous flow reactors. Cu has been found to be unique in the selectivity it shows towards the hydrogenation of the carbonyl group of furfurals due to Cu having the tendency to repulse the furan ring of furfural and favoring the interaction with the carbonyl group. Sitthisa et al. proposed that the strong repulsion is mainly due to the overlap of the 3d band of surface Cu atoms & anti-bonding orbital of the ring based on their spin-polarized DFT calculations (Sitthisa & Resasco, 2011a; Sitthisa et al., 2011). These studies further showed that the catalysts were deactivated via leaching or through severe carbon deposition (coking) (Andas, Adam, Rahman, et al., 2014; Yan et al., 2014) which limits the number of usages for a batch of catalyst, creating a detrimental effect in their application in field. This effect is very prominent when using Pd and Ni in tandem in a bimetallic system (Yan et al., 2014).

The ultimate goal of catalyst research is to create customizable materials. One of the main objectives of this thesis is to synthesize selective hydrogenation catalysts. Hydrogenation refers to the reaction of a bond with molecular hydrogen. This is done to reduce or otherwise saturate it. This reaction is generally performed with Pt, Pd and Cu metallic species. Because many systems contain more than one point for unsaturation, the term "selective" is used. This is well illustrated by the hydrogenation from ethene-to-ethane. The molecule has a single C=C bonds. A heterogeneous catalyst is used to make margarines. This process was extensively used in the past with nickel, which is a cheap and abundant metal that can easily dissociate hydrogen. It has also been extensively used

in other areas of chemistry. Supported nickel on a silica-based support called kieselguhr allows the reaction to occur at 150 $^{\text{O}}$ C. It is still widely used today, even though it was developed and tested over 60 years ago. Other hydrogenation catalysts, such as those made from palladium, have been developed to ensure high purity. Recent reports have shown that nickel-based materials can have toxic properties, which has encouraged the creation of cleaner hydrogenation catalysts. Carbonyls, and partial hydrogenation alkynes are two other hydrogenated functional groups. The C=O (carbonyl) is often regarded as an easy bond to hydrogenate. It can be found in many positions, generating aldehydes and carboxylic acids. Conversely, competitive hydrogenation will often take place when it is combined with another unsaturated system. The reaction will result in one or both functional groups being saturated. This is not always a good option. Catalytic systems have been created to avoid hydrogenation of specific groups. Conjugation in a system or unsaturated bond in general can alter the chemical properties of molecules.

In hydrogenation process, the formation of product relies on the capability of the catalyst to adsorb both H atoms and the reactant species on its surface (Halilu et al., 2016a), along with the orientation in which the reactant is adsorbed on the surface (Sitthisa & Resasco, 2011a; Sitthisa et al., 2011). Therefore, sufficient amount of metal active components must be dispersed throughout the support in order to allow proper distribution of reactants, which then facilitates the hydrogenation reaction (Vargas-Hernández et al., 2014). The main issue here is the ease of interaction between the reactant species and H atom, which in general is the hydrogenation reaction. Hence, it is absolutely vital for the catalyst in hydrogenation process to have good distribution in the supporting material while having tunable morphological properties to facilitate the size of the reactant, while also reducing the detrimental effect of deactivation by coking.

Hydrogenation has the ultimate goal of improving stability and fuel quality. It reduces the content of organic acids, aldehydes, and other reactive compounds. These chemicals not only cause high corrosiveness, acidity, and can also pose many barriers to applications. Many Chinese researchers have made significant progress in upgrading pyrolysis-based bio-oils with hydrogenation technology. Bio-oil was traditionally upgraded using single hydrogenation technology. Traditional hydrogenation refers to the treatment of pyrolysis oil under certain conditions such as high pressure (10-20MPa), specific temperature, hydrogen flow rate and a proper catalyst. You can obtain bio-oil by pyrolysis with many catalysts such as Al₂O ₃- based catalysts and Ru/SBA-15 catalysts. The following results were generally observed in the upgrading experiments: the pH value, water content, and H element content all increased in different degrees, while dynamic viscosity decreased to a certain extent. The experiments showed that the properties and stability of the pyrolysis bio-oil were enhanced by hydrotreating these catalysts with esterifying carboxyl groups. The largest scale hydrogenation reactor in China is currently a cylindrical reactor measuring 120 mm in depth and 32 mm inside.

This is also a good time to once again look into the effects of morphological and structural properties of the catalyst system on the hydrogenation reaction. Mainly, variation in particle sizes would be a major contributor to changes in catalytic activity during a reaction. The role of particle size effects as previously discussed is very prominent especially when it comes to hydrogenation of furfural which may yield several different products depending on the selectivity of the catalyst. For example, when Ru supported in silica, with particle sizes in the range of 2 to 25 nm were applied to hydrogenation of furfural, the conversion was very much proportional to the change in particle sizes. This was observed when calculation for the turnover frequencies for the pathways of converting furfural to furfuryl alcohol (hydrogenation) and to furan (decarbonylation). More precisely, when Ru sizes were increased at the same pressure,

the turnover frequencies for hydrogenation process increased from 237 to 307 h⁻¹, while the decarbonylation turnover frequencies decrease from 98 to 1 h⁻¹. The similar trend was also consistent even when the pressure was increased from 10 bar H₂ to 25 bar H₂. This signifies that furfural hydrogenation is the dominant pathway while decarbonylation can be considered to be a side reaction, therefore the tendency observed was strengthened with increment in particle sizes in the range stated above. It should be of note that when the Ru particle size was over 17 nm the tendency is favorable for C=O hydrogenation into furfuryl alcohol, while decarbonylation is favored at particle size below 17 nm (Yu et al., 2020).

This particular discrepancy provided the platform to further probe into the kinetics specific to the governance of furfural hydrogenation using Ru. This led to the observed increment in terms of activation energies when particle size of the catalysts was increased. The energy for furfuryl alcohol formation was observed to decrease from 29 kJ mol⁻¹ to 14 kJ mol⁻¹. In contrast the energy for furan formation was shown to increase from 30 kJ mol⁻¹ to 46 kJ mol⁻¹. These observations imply that change in particle size triggered a compensational reaction due to the opposing structure sensitivities of these two different reactions. Such trends were also observed when studying the particle size effects on the kinetics of furfural transformation of Pt catalysts capped using PVP, done at vapor phase. The latter experiment was done within the size range of 1.5 to 7.1 nm prepared via alcohol reduction method. Once again, it was reported that activation energy is highly dependent on the particle sizes. Specifically, at similar reaction conditions of 473 K and 93 kPa H₂ the Pt particles below 2 nm tend to form furan via decarbonylation pathway, while Pt particles larger than 3 nm show tendencies to form furfuryl alcohol via hydrogenation at the carbonyl group of furfurals. The smallest Pt particles, at 1.5 nm can result in activation energy as high as 107 kJ mol⁻¹, in contrast to the 62 kJ mol⁻¹ found for furan formation to take place. A sharp drop in activation energy to a value of 32 kJ mol⁻¹ was observed when the particle size increased to 1.9 nm thus yielding an activation energy threshold lower than that of the furan formation at 59 kJ mol⁻¹.

On a broader note, particle size has also been shown to be of significant influence in determining the selectivity of hydrogenation of furfural. This phenomenon is directly related to the degree of exposure of metal active sites for interaction with the reactants, which in this case is furfural. This is further related to factors such as adsorption modes of reactants and the proceeding reaction pathways. This is very much viable in theory, however, for practical purposes in the laboratory customizing catalyst properties to suit the need of a particular reaction may prove to difficult in the grand scheme of the study to be conducted. Hence, some researchers found a work around from actually controlling the characteristics of a synthesized catalyst to control selectivity of the process. One such method is the specific blocking of certain active sites to suit a particular reaction. This involved application of thiolate self-assembled monolayers (SAMs) polymers including 1-octadecanethiol (C18) and benzene-1,2- dithiol (BDT) as blocking agents. They were then used to coat Pd/Al₂O₃ used for furfural conversion. This method was found to work for furfural related reactions involving four upgrading processes, (1) furfural decarbonylation into furan, (2) furfural hydrogenation into furfuryl alcohol, (3) furfuryl alcohol dehydrogenation into furfural and (4) furfural hydrodeoxygenation into 2methylfuran (Liu et al., 2022). When compared to one another, it was found the reaction pathways are highly affected by the blocking agents used. For example, C18 is effective in restricting terrace site availability of Pd, while BDT can carry out the same restriction order while also inhibiting the adsorption of reactants over the edges of the active sites. Coating the catalyst with Pd was found to moderately improve upon the selectivity enhancement of the targeted product, which in this cited study were furfuryl alcohol and 2-methyl furan (total of 34% selectivity), which is a direct result of furfural decarbonylation process to be inhibited by the blocking agents (Wang et al., 2018). The application of blocking agents as of now can be considered to be a satisfactory compromise to the direct influence of controlled catalyst synthesis should the catalyst system under study proved to be too difficult to tune in terms of vital characteristics such as particle size (Alijani et al., 2019; Rogers et al., 2017).

All in all, controlled synthesis of catalyst procedure is the ideal method in obtaining metal catalysts with fine-tuned characteristics with high catalytic performance. Hence, various synthesis methods including wet impregnation, co-precipitation, deposition precipitation and sol-gel have been developed and tested at different synthesis parameters for the very purpose of fine-tuning metal supported catalysts for various practical applications. The difficulty in optimizing each of these procedures lie in establishing a working protocol that covers selection of raw materials and suitable processing flow, that consistently produce catalyst of desired properties at the end of production line. This is not to mention effect of conditional factors such as synthesis temperature and time on the properties of the catalysts.

Take for example the selection of metal salts as precursors for the metal active sites. The salts require further treatments through calcination and reduction to produce functional active sites. Factoring the metal salts is not a matter to be neglected as different metal salts have been shown to result in varying morphological properties. Nakagawa et al.,[49] used different salts, namely, PdCl₂ and Pd(NH₃)₄(NO₃)₂ to produce Pd/SiO2 catalysts to be applied in the hydrogenation of furfural. These catalysts were referred to as Pd/SiO₂-Cl and Pd/SiO₂-N, respectively (Nakagawa et al., 2012). The two catalysts were prepared by the same impregnation procedure, calcined at the same temperature (773 K) and reduced at the same temperature as well (373 K). Yet, they resulted in distinct particle sizes Pd/SiO₂-Cl (7 nm) producing larger particles than Pd/SiO₂-N (4.1 nm). This difference resulted in different activity rate for each of their respective hydrogenation

reaction. Pd/SiO₂-Cl with larger sizes led to a higher furfuryl alcohol selectivity of 69%, while Pd/SiO₂-N was found to favor the promotion of furfural conversion with a more mixed product distribution, in other words, lower selectivity. This was attributed to a stronger adsorption of furfural over the much larger Pd/SiO₂-Cl. This stronger bond between the reactant and active sites blocked other incoming reactants from being adsorbed onto the catalyst surfaces resulting in lower conversion compared Pd/SiO₂-N. The smaller sized Pd/SiO₂-N instead favored hydrogenation on the furan ring (C=C). The larger Pd particles provided stronger bond to the reactants while a smaller particle can exert a much weaker bond which favored furan ring hydrogenation (Yu et al., 2020).

Other than selection of metal salts as precursors, selection of synthesis temperature can also influence the characteristics of the end product. In fact, effect of temperature in regulating particle sizes of the catalyst has been extensively reported over the course of the years. Take the preparation of Ni/SiO₂ using Ni(NO₃)₂ as the precursor at different temperatures of 673 K, 773 K and 873 K. These were prepared using incipient wetness method. The increment in temperature corresponded to the increment in particle sizes from 2.6 to 4.0 nm. The subsequent hydrogenation process was carried out as follows, firstly is the hydrogenation of furfural into furfuryl alcohol, followed by further hydrogenating the alcohol into tetrahydrofurfuryl alcohol. The initial turnover frequencies over the metal particle surface were calculated and revealed that the value for furfural hydrogenation were more or less constant despite the different size of Ni particles. However, conversion of furfuryl alcohol into tetrahydrofurfuryl alcohol was shown to be a derivative of the particle size. Ni/SiO₂-773, having the median particle size of 3.2 nm among the tested catalysts performed the best in terms of the catalytic activities with the turnover frequency value of 1.3×102 h⁻¹ and 3.4×102 h-1 for the both steps of the hydrogenation reaction, respectively (Nakagawa et al., 2012).

Similar effect of temperature conditions on the resulting catalyst was reported in studies involving bimetallic catalysts involving Cu and Ni alloy supported on MgAlO (Cu-Ni/MgAlO) (Stepanova et al., 2021). These catalysts were fabricated with double layered hydroxides precursors for the hydrogenation of furfural into tetrahydrofurfuryl alcohol in which both the C=O and C=C functionalities were targeted for hydrogenation, similar to the study mentioned in previous paragraph. By varying the reduction temperatures in the range of 673 to 923 K, the bimetallic alloys synthesized via modified co-precipitation method was shown to gradually agglomerate at an increasing rate. The difference in agglomeration rates resulted in different turnover frequency values, which were calculated over the total amount of Cu and Ni. In this study, TOFC=C values were much lower than TOFC=O values in all variants studied which is indicative of the furfuryl alcohol hydrogenation to tetrahydrofurfuryl alcohol being the rate-determining step in the overall process. This represented the close relationship between the bimetallic particle size and turnover frequency, represented by the volcano-shaped variation, where at 5.2 nm the alloy exhibited highest turnover frequency value of 34.45 h⁻¹ making it to be the optimized catalyst to be applied for reusability test where no sintering phenomenon was observed when compared to the fresh batch of catalysts.

As far as practicality goes, doping hetero metal species to form an alloy or bimetallic catalysts is one of the best methods to introduce multiple active elements into the catalyst while achieving good particle size regulation and reactivity towards furfural conversion. Nakagawa et al. even reported such benefits in their investigation on Pd-Ir bimetallic system which not only improved the reaction rates but also the turnover frequencies based on the total amount of Pd and Ir particles. These values were defined as the respective metals' initial rates in the conversion of furfural to tetrahydrofurfuryl alcohol. In this study Pd/SiO₂, and Pd-Ir/SiO₂ were derived from the active metals' respective chloride precursors. Interestingly, the bimetallic catalyst yielded smaller particle size of

approximately 3.5 nm, almost 50% smaller than the particle size of the monometallic catalyst at 7.0 nm. The study further reported the reaction rates of furfural and furfuryl alcohol (named k_1 and k_2 , respectively) to be 0.7 mmol gcat⁻¹min⁻¹ and 0.18 mmol gcat⁻¹min⁻¹ for each of the reaction elements, respectively. The values of turnover frequencies were also consistent with the reaction rates suggesting that the catalyst with smaller particle sizes, Pd-Ir/SiO₂ (k_1 = 11 mmol gcat⁻¹min⁻¹) and k_2 =3.9 mmol gcat⁻¹min⁻¹) show an overall better performance in catalyzing the hydrogenation reaction. The values of turnover frequencies for Pd-Ir/SiO₂ were found to be TOFC=O (1.1×104 h⁻¹) and TOFC=C(0.4×104 h⁻¹). Such variation in the activity were attributed to the changes in the overall adsorption structure and strength of furfural and the intermediate furfuryl alcohol at the catalytic active sites. The strong adsorption that took place at the active sites were correlated to the addition of Ir which also significantly affected the regulation on particle sizes within the overall catalyst structure (Liu et al., 2014; Nakagawa et al., 2014).

One of the major determinants in the change in product selectivity is the changes within the structure of the catalysts as demonstrated in the bimetallic system previously stated. A study involving a catalyst system of Cu-Ni/γ-Al₂O₃ demonstrated that increasing the Ni portion in the Cu to Ni ratio from 4 to 1 clearly affected the hydrogenation of furfural in terms of the overall selectivity. With increment in the amount of Ni added, it was observed that the selectivity deviates towards deeper product of furfural hydrogenation, such as 2-methylfuran. To be more precise, at temperature of around 403 K, furfural conversion to furfuryl alcohol is much more favored , especially when compared to monometallic systems such as Cu/SiO₂. These deviations were observed to be more prominent as more Ni was introduced into the catalyst system. Similar trends were observed at the higher temperature of 473 K, with the difference mainly being the selectivity shifted towards formation of deeper hydrogenation product, mainly 2-

nmethylfuran. It should be noted that the report mentioned sintering of the metal particles at this particular temperature under the pressure setting of 4 MPa of H_2 . The effect of particle dispersion which we found to be complimentary to these afore mentioned studies were reported by Xiao et al., in which Cu-Co/C catalysts were pyrolyzed from Co-doped Cu-BTC metal framework precursor to yield a highly dispersed active metal within the structure. It was found that pyrolyzation of the catalysts done at 873 K produced a smaller range of particle sizes for the individual metals in a bimetallic catalyst, compared to monometallic Cu. At the optimum Co to Cu ratio of 0.4, furfural was selective towards furfuryl alcohol formation at 97.7% with 98.7% furfural conversion achieved. The benchmark Cu monometallic catalyst gave 46.6% conversion with 81.3% selectivity towards the targeted product. The authors attributed such improvement in the bimetallic system to the smaller particle sizes and better dispersion of the metal active sites which promotes activation of C=O bond. Consequently, the dispersion effect in the bimetallic system could very well be the main contributor to the inhibition of sintering during recycling processes as reported. The slight decrease in both values of conversion and selectivity occurred began to be prominent during the fourth cycle test of the selected catalyst Cu-Co/C-873 at 413 K, which was attributed to the coke deposition instead of the suspected agglomeration of the catalysts (Luśnia, 2018; Yu et al., 2020).

Addition of non-metallic heteroatom have also been attributed to the improvement of various catalysts' particle sizes and particle dispersion. Melamine was applied as a source of nitrogen to replicate N-doping of the catalyst system comprised of Ni supported on activated carbon (Ni/N-AC) (Baithy & Shee, 2020). This particular catalyst was then applied to furfural hydrogenation to a considerable degree of success. Along the way, it was reported that two factors majorly contributed to the Ni particle size and dispersion which are pyrolysis temperatures during N-dropping and melamine amount introduced into the system. The catalyst named Ni/N-AC-1-1073 signifying 1 g of melamine added

and calcined at 1073 K in N₂ has an overall improved particle size and dispersion as well as better performance in term of tetrahydrofurfuryl alcohol yield. The largely uniform dispersion of N and Nu heteroatom in the support, as confirmed by elemental mapping produced strong bond between Ni particles and the pyridinic-N species. This phenomenon inadvertently led to enhanced electron density surrounding the Ni particles, ameliorating the bond between active sites and the reactants. Moreover, the loss in Ni dispersion observed only led to negligible decrease in selectivity during the recyclability tests after five cycles, further lending credence to this particular doping method (Stepanova et al., 2021).

Recently a novel upgrading method named one-step hydrogenation-esterification (OHE) was established to convert acids and aldehydes to stable and combustible components. Bifunctional catalysts were used for OHE reaction, including Al-SBA-15-15 supported palladium bifunctional and bifunctional Pd catalysts. This means that they had properties of esterification and hydrogenation. This is a major advantage over traditional hydrogenation for OHE. Yu et al. screened out 5% of Pd/Al (SiO)₃ and found that this OHE reaction is simple and efficient. Tang et. al. also tested the OHE reaction. demonstrated the effectiveness of the bifunctional catalyst system for combined hydrogenation/esterification and a synergistic effect between metal sites and acid sites over respective catalysts. The bifunctional catalyst was also improved by taking certain measures to increase its catalytic efficiency. The use of bifunctional catalysts makes the new hydrogenation process much more efficient than the old method (Wanjin Yu et al., 2011a).

To obtain high-quality fuel, it is important to upgrade bio-oil before its practical use, particularly with regards to individual components that are reactive, such as furfural as we have discussed extensively. It is of particular note that the quality of bio-oils is greatly improved by converting organic acids into their equivalent esters through catalytic esterification. Catalytic esterification is a method of enhancing the quality of bio-oils. It has been widely used in China. The etherification process was usually carried out in either a 250 ml and 300 ml autoclave. The catalysts used were ion exchange resins and MoNi/Al₂O₃, respectively. The upgraded bio-oil had lower acid numbers, higher water content, and better viscosities. The stability and corrosion resistance of bio-oil was also promoted. Junming et. al. reported their observations on ozone oxidation in bio-oil and the production of improved bio-oil through subsequent esterification (Mariscal et al., 2016).

Yao et al. and. Zhou et al. both managed to analyse the component in esterified biooil by using gas chromatography/mass spectroscopy and Fourier transform IR spectroscopy. The former detected that 1,1-dimethoxypropan-2-one was the most abundant species in the fraction of 60-80 °C. The most abundant species in the residue were phenols, followed by ketones and hydrocarbons. They described that upgrading significantly increased the dispersity and removal of organic droplets from the bio-oil. The main components of the upgraded bio-oil are still particularly heavy species. Many studies have been conducted in recent years to upgrade bio-oil using catalytic esterification reactions with solid acid catalysts from China. It was found that solid acid catalysts had high catalytic activities to efficiently convert organic acids such as propionic acid, acetic acid and formic acid into esters. However, bio-oil's stability and fluidity could be further improved (Mariscal et al., 2016).

With this comprehensive discussion on hydrogenation and esterification as individual routes selected to upgrade different components of bio-oil, we can now proceed to discuss into multifunctional catalyst systems such as the ones applied for OHE process previously mentioned in this section. This catalyst system is the main foundation for this particular thesis allowing hydrogenation and esterification of furfural to be carried out in tandem to one another, within the same reaction vessel.

2.5 Multifunctional Catalysts in Hydrogenation-Esterification of Furfural

Bio-oils contain a variety of oxygenated compounds. It is difficult to understand the reactions and correlation between catalyst structures and catalytic performance. To deal with this complexity, we can use reactions of model compounds. This have been show to help in designing better OHE catalysts. The OHE reaction between acetaldehyde and butyraldehyde, as well as acetic acid, is possible over a bifunctional catalyst such as 5%Pt/A12 (SiO3)3, 5%Pt/HZSM-5, or Pt/SBA15/PrSO3H (Tang, 2008, 2010). The crude bio-oil as we know full well by now contains large amount furfural, which is more than acetaldehyde and butyraldehyde. Furfural and other furan derivatives can be very difficult to work with and can deactivate catalysts in significant amounts (Deng and Yang, 2009; Yang and al. 2010, respectively). For bio-oil upgrade, converting furfural is an important aspect. In the past several decades, extensive research has been done on single hydrogenation of furfural into furfuryl alcohol. However, furfuryl alcohol can polymerize in the presence of acidic compounds (Choura and al. 1996; Kijen'ski et. al. 2002). It is therefore still very difficult to convert active furfural from crude bio-oil into a stable compound. Hence, researches have been carried out to further convert furfuryl alcohol into furfuryl acetate. More interestingly, in an effort to reduce the production cost and reaction time, many researches have been carried out to carrying out both hydrogenation and esterification in a one pot reaction, with the reactions taking place in tandem of one another, preceded by hydrogenation of furfural to furfuryl alcohol and followed by esterification of furfuryl alcohol to furfuryl acetate, in the presence of an acid component, most commonly ethanoic acid.

To go back to the fundamentals of this particular tandem reaction, a different second component may very well result in a different selectivity (Lesiak et al., 2014b). For example, when doped with the basic K atom, the selectivity shifted towards formation of decarbonylation products such as furan. This is largely due to the interaction between K and the active metal, which due to the former's basic nature, results in in electron transfer to Pd. This phenomenon lead to an increase in Pd's electron density and this condition favors the decarbonylation of FAL.(Zhang et al., 2011) The second component may also be a metal oxide. (Jiménez-Gómez et al., 2016) In this case, the amphoteric ZnO was added with varying ratio to Cu metal to modify the electron density. Here ZnO even assumes the role of the support which is to improve the dispersion of the active component. Nagaraja et al. (2007) even pointed out that the interaction between Cu and oxygen vacancies provided by MgO managed to increase the overall surface area of the catalyst which led to increase in conversion (B. M. Nagaraja et al., 2007). Cu/ MgO catalysts used in this investigation have demonstrated high selectivity towards furfuryl alcohol, despite the fact that a wide range of products, including furan and tetrahydrofuran as well as methyl furans, are possible in the hydrogenation of furfural. The primary determinants of the selectivity towards furfuryl alcohol are the defective sites at the Cu and MgO interfacial regions and the appropriate Cu particle size. Due to the coprecipitation method's higher concentration of Cu species at the surface, Cu/ MgO catalyst produced a significant amount of furfural conversion without sacrificing its preference for furfuryl alcohol. Therefore, designing a commercially viable nonchromium catalyst for the vapor phase hydrogenation of furfural, specifically to synthesize furfuryl alcohol at atmospheric pressure, is greatly aided by the advantage of the coprecipitation method in yielding more Cu metal species that are in interaction with MgO through the oxygen vacancies of MgO. This study also highlighted that The Cu-MgO coprecipitated catalyst exhibited high activity and selectivity towards furfuryl

alcohol over other products. This was evident from the XPS analysis, which showed a higher Cu/Mg atomic ratio and lower Cus/Cup ratio with CM4 (16 wt.%Cu) than with any of the other catalysts tested at 453 K.

We will find that adding acidic element into the fray will also provide interesting results. Mainly when introducing acidic element Al is often chosen for the simple method of introduction, usually in-situ during sol-gel synthesis (Gilkey et al., 2015; Hensen et al., 2012). The presence of Al brings about the rise in number of Lewis and Brønsted acid sites (Gilkey et al., 2015; W. Yu et al., 2011). These acid sites are of moderate strength and are very useful in heterogeneous catalysis of furfural in that it provides an alternate path for hydrogenation through Meerwein-Ponndorf-Verley (MPV) mechanism. In heterogeneous catalysis this mechanism proceeds at the electron deficient Lewis acid sites, where metal hydrides are formed. An added benefit of adding these second metal components is the enhanced surface defect in the structure of the catalyst. Halilu et al. (2016) pointed out that the increased surface defect provided more contact between the reactant and the active surface which therefore results in higher conversion of the desired product (Halilu et al., 2016a).

Another interesting progress in heterogenous catalysis is the study of single atom catalysts in an effort to increase selectivity therefore efficiency of the catalyst during chemical processes. There have long been catalysts based on single atoms in various forms. In retrospect, the ability to visualize Single Atom Catalysts (SACs) presence in previously unfamiliar catalytic systems has sparked tremendous new interest. The researcher's efforts in atomic design of host materials and the exploration of nuclearity trends is unlimited. In terms of SAC synthesis, areas of focus encompass improving strategy to attain ultra-high anchoring and precisely control the speciation and nuclearity of atomically-dispersed catalytic metal species.



Figure 2.3 : Representation of lattice strain effect on hydrogenationesterification of furfural

Particularly for Tandem hydrogenation-esterification of furfural using SAC, there are still several challenges in ensuring a low-coordinated metal atom speciation to induce metal function activities per metal atom. Tandem reactions which combine multiple chemical changes in one step, have the proprieties of using any heterogeneous catalyst that depends on the functional groups of reacting moieties. The significance of functional groups of reacting moieties have been demonstrated by Suzuki et al (1998) during their demonstration of the tandem reaction involving stereo-selective synthesis of many contiguous asymmetric centers. Furthermore, in keeping up with the tandem reaction, there is need to optimize the size of the single metal particles and their uniform coordination with an appropriate support material Conventional metal-based catalysts are not uniform in dimensions, which decreases their metal-atomic efficiency and often leads to unwanted side reactions.

Tandem reaction have been applied to furfural substrate to selectively produce ester over Pd/Al₂(SiO₃)₃ or Pd/C+Al₂(SiO₃)₃ (Wanjin Yu et al., 2011d), while in another (Wanjin Yu et al., 2011a), Raney Ni (RN) or Mo, Sn, Fe and Cu were also applied to similar reactions (Xu et al., 2016). Cu/SBA-15(Xu et al., 2015) (Chen et al., 2017) was also applied for similar production. However, the amount of targeted ester, in this case furfuryl acetate are too low to be of any significant impact. This is very much due to one of the major drawbacks with tandem hydrogenation-esterification of biomass derived furfural is the acidity of the catalyst support material.

The tandem reaction using hetropolyscid containing single atom tungsten (W) supported on SiO2 (H₃PW₁₂O₄₀/SiO₂) transformed furfural to Levulinic. The Lewis acid sites imparted by active W-metal sites adsorb hydrogen proton for catalytic transfer hydrogenation of FUR to FAL, while the predominant Brønsted acid sites catalyze the hydrolysis of FAL to LA focusing on functional groups are the furan ring and/or the carbonyl group. The Tandem reaction have been applied to furfural substrate at moderate reaction condition to selectively produce ester with lower by-products yields over Pd/Al₂(SiO₃)₃ or Pd/C+Al₂(SiO₃)₃. Apart from using hybrid of carbonaceous and aluminous material as support that is less suitable, mesoporous silica such as SBA-15 was used to produce Pd/SBA-15 catalyst which was active to convert furfural and acetic acid to furfuryl acetate. OHE might be one of efficient methods to up the light fraction of raw bio-oil. Moreover Cu/SBA-15 was used to promote almost complete conversion of furfural, hydroxy acetone, and guaiacol and AcOH into ethanol and esters, with the fraction of acid compounds drastically declining from 25.0 wt % to 0.4 wt%. The portfolio of reports on hydrogenation-esterification using various heterogeneous catalyst have pointed out the necessity to solve the common issue of high process condition, tendency of active catalyst leaching out and consequently impeding the first hydrogenation step. In the second esterification stage, most of the reported catalyst have been attempting to modulate the Brønsted acidity.

It is useful for the readers at this point that we should give a brief recap and outlook of the current catalysts available for the process of hydrogenation-esterification process, especially in terms of their limitations and how to improve on such factors. Supported nanocatalysts in almost any chemical reactions is almost always heavily influenced by the size of metal particles, dictating catalytic performance (Lang et al., 2020). The general consensus across the various studies have bee that in order to achieve high specific activity, at commercially acceptable cost, reducing the size of the active metal particles are almost compulsory. This is especially true in the case of noble and transition metal catalysts. Noble metals such as Pt, Pd, Ru, Rh and Ir are dependable active metals in various fields such as the petrochemical industry, medicine production, environmental protection and new energy applications. However, they come at very high costs due to their relatively lower natural abundances. Considering this noble metal catalysts cannot be described as sustainable especially with the ever-increasing demands. Hence, it is paramount that we minimize of the application of such expensive catalysts without compromising in the simultaneous retention in catalytic activity levels (Cheng et al., 2019a; Lang et al., 2020). Thus, many studies have now gone back to tailoring transition metal-based catalysts to operate at sufficient levels in terms of conversion and selectivity. This comes with challenges in ensuring the active metals are at sufficiently small increase metal-reactant interactions while also ensuring the targeted products are formed. Such challenges are significantly amplified when dealing with multifunctional catalysts such as in the case for hydrogenation-esterification reaction. Not to mention the additional factors such as the need to maintain certain level of acidity within the overall catalytic system which is the case for this particular tandem reaction, as established in the first chapter of this thesis.

2.6 Single Atom Catalysts

Even when metal clusters are used, there may still be some wasted atoms or potential reaction sites. Clusters can be reduced to create single-site materials, called Single Atom Catalysts. This improves the material's atom efficiency. Because they possess isolated metal atomic sites, this class of metal-supported catalysts is called "single site catalysts". The chemical nature of the so-called isolated atom site is disputed. It often

depends on positional effects like its proximity to other metal atoms or its interaction with the support (charge transfer), similar to SMSIs. The name would suggest that the material has 100% metal dispersion, an oxide support and random isolated atomic species. This is often noble metal. Single Atom Catalyst can refer to many materials. This is because the single reaction site could be on dimers, trimers, or small aggregates atoms to form small clusters (either 2D or 3D depending on the nature of the individual atom or the size of the molecule) (Cheng et al., 2019b).

The nomenclature of a material will vary depending on how it is organized. The true SAC is the only place where there is no atomic structure. This is strictly where isolated species are found with no order amongst them. These catalysts have been used in a variety of applications, including the hydrogenation and reduction of nitroarenes, selective hydrogenation, hydrogen peroxide production, and the water gas shift reaction for metal clusters. The atomic species used in the above applications were Pt, Ir, and Au.

The 'Single Site Heterogeneous catalyst' (SSHC) is the next type of single atom-based catalyst. This classification of materials uses 'single site' atoms that are spatially separated. Thomas et. al. discussed this distinction. Because they are partially isolated, each spatially separated atom of the SSHC has the same characteristics as other atoms. A combination of the true SAC with the SSHC is another type of SAC. In this case, although atomic entities may be evenly distributed across the support, they are not completely isolated. This is the "Atomically Dispersed Supported Metal Catalyst" (ADSMC). Surface structures like dimers, trimers, and 2-dimensional clusters are formed by the atoms. This branch of Single Atom Catalysts is often very active but it's difficult to identify and determine the actual active site (Lang et al., 2020).

A wide range of synthetic methods exist to create SAC materials. Some of these are new to the field, like a laser ablation method where the laser beam is directed at a rotating

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disc of the desired metal. After heating the surface, a vapor/carrier gas of the metal/molecular is produced. This is then deposited onto the oxide support. This method is also known as the "Mass selected soft landing" because of the low kinetic energy (1 eV), at which atoms come into contact with the support. Another has been expertly carried out by the Flytzani-Stephanpoulos group where Au atoms are leeched from a larger Au based material by using high-pH conditions in the presence of sodium cyanide. These sophisticated techniques have been successful in the past but it was discovered that nanoparticle synthesized methods can still be used to create atomic species. Wetness impregnation, which uses very low metal concentrations, can lead to variations in atomic morphologies. This is similar to the creation of nanoparticles. The sizes can vary greatly and atoms can aggregate to form different arrays. A metal precursor reacting with a base can also be used to create a metal complex. This is called deposition precipitation. If the metal concentration is too high, it can lead to cluster formation. Co-precipitation is another interesting way to create SACs. This is when the support material is reduced in situ and the intended atomic components are added. This method is generally used when FeOx is being used as the support. During the reduction process, defects and vacancies in the iron oxide structure are created which serve as anchors for the atomic species (Ding et al., 2019).

Although the atoms can be synthesized, there are a variety of characterization techniques that can be used to determine the structural properties of single atomic entities and their presence. In some cases, however, these techniques can prove destructive in order to image or detect single atoms/clusters.

CHAPTER 3: RESEARCH METHODOLOGY

3.1 Chemicals

Table 3.1 shows the chemicals used throughout this study.

Chemical	Purity (%)	Company/Source		
Rice husk	100	Penang, Malaysia		
Sodium hydroxide, NaOH	≥97	Merck Millipore		
Nitric acid, HNO ₃	65 w/w	Riendemann Schmidt Chemical		
Copper (II) nitrate Penta hemihydrate, Cu (NO ₃) ₂ .5H ₂ O	≥99	Riedel-de Haën		
Nickel (II) nitrate hexahydrate, Ni (NO ₃) ₂ .6H ₂ O	≥99	Sigma Aldrich		
Palladium (II) nitrate dehydrate, Pd (NO ₃) ₂ .2H ₂ O	≥99	Sigma Aldrich		
Aluminium Isopropoxide, AIP	≥98	Sigma Aldrich		
Magnesium nitrate, Mg (NO ₃) ₂	≥99	Merck Millipore		
Furfural	≥99	Sigma Aldrich		
Acetic acid, glacial	≥99	Sigma Aldrich		
Ethanol	≥99.8	Sigma Aldrich		
Pyridine, anhydrous	≥99.8	Sigma Aldrich		

Tab	le 3.1	1:	Chemical	s used i	in the	study	of	multifun	ctional	cataly	st
						•				•	

3.2 Catalyst Synthesis

3.2.1 Preparation of Rice Husks (RH) as a Silica Source

Firstly, the RHSiO₂ were washed with distilled water and left to dry at room temperature for 24 hours. The dried RH was stirred in 1M HNO₃ for 24 hours at ambient condition and then washed to reach pH \sim 7, followed by oven drying at 100 °C for another 24 hours. The acid leached RH was thereafter treated in a furnace at 600 °C for 6 hours to achieve complete combustion to RH ash (RHA); a potent silica source.

3.2.2 Preparation of RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg (Batch 1)

The development of catalyst was carried out by gradual addition of metal components into the base catalyst, labelled RHSiO₂-Cu. This was achieved through the sol-gel method with the three metals acting as a dopant, introduced simultaneously in order to achieve chemisorption within the supporting silica. To begin, 600g of the RHA was mixed with 250 mL of 1 M NaOH and then stirred for 24 hours to extract the silica. Drop-wise addition of aqueous Cu (NO₃)₂.2.5H₂O to the silica to an adjusted pH 3 using 3 M HNO₃ was carried out until gel starts to form. The formed gel was aged in-situ for 48 hours, followed by centrifugation at 4000 rpm for 10 minutes. The as-prepared RHSiO₂-Cu was thoroughly washed with deionized water and then oven dried for 18 hours at 80 $^{\circ}$ C prior to calcination at 600 $^{\circ}$ C, with the ramping of 1 $^{\circ}$ C/min for 6 hours.

For the synthesis of RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg catalysts, the steps were repeated as above, but prior to the addition of copper precursor, the Al and Mg precursors were dissolved in 25 mL of HCl and then added drop-wise. The dissolved metal solution was added to the mixture of aqueous Cu (NO₃)₂.2.5H₂O and silica before the pH was once again adjusted to pH 3. The amount of metal precursors added were such that all metals were as follow: Cu: 10% (w/w); Al: 5% (w/w) and Mg: 5% (w/w)

3.2.3 Synthesis of RHSiO₂-M-Al-Mg (where M= Cu, Ni and Pd) (Batch 2)

Similar to the previous method, 600g of the RHA was mixed and then stirred with 250mL of 1M NaOH for 24 hours to extract the silica. AIP and Mg (NO₃)₂ dissolved in 25mL of HCl and then added drop-wise. The amount added were such that both metals will make up 5% each of the overall catalyst weight. Drop wise addition of aqueous Cu (NO₃)₂. 5H₂O over an adjusted pH using 3M HNO₃ was done to the silica until the desired pH of 3 was reached for each batch of catalyst. The formed gel was aged in-situ for 48 hours, and was followed by centrifugation at 4000 rpm for 10 minutes. The catalysts were thoroughly washed with deionized water and then oven dried for 18 hours at 80°C prior to calcination at 600 ^oC, at 1°C/min, for 6 hours. This sample was then labelled RHSiO₂-Cu-Al-Mg. The process was then repeated with, Cu (NO₃)₂.5H₂O being replaced with Ni (NO₃)₂.6H₂O and Pd (NO₃)₂.2H₂O for production of RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg, respectively.

3.2.4 Synthesis of RHSiO₂-Cu-Al-Mg at Varying pH (Batch 3)

Similarly, 600g of the RHA was mixed and then stirred with 250mL of 1M NaOH for 24 hours to extract the silica. AIP and Mg (NO₃)₂ dissolved in 25mL of HCl and then added drop-wise. The amount added were such that both metals will make up 5% each of the overall catalyst weight. Drop wise addition of aqueous Cu (NO₃)₂. 5H₂O over an adjusted pH using 3M HNO₃ was done to the silica until the desired pH of 3 was reached for each batch of catalyst. The formed gel was aged in-situ for 48 hours, and was followed by centrifugation at 4000 rpm for 10 minutes. The catalysts were thoroughly washed with deionized water and then oven dried for 18 hours at 80 °C prior to calcination at 600 °C, at 1°C/min, for 6 hours. This sample was then labelled RHSiO₂-Cu-Al-Mg 3. These steps were repeated with the pH adjusted to pH 1, 7 and 10 prior to aging process to yield samples named RHSiO₂-Cu-Al-Mg 1, RHSiO₂-Cu-Al-Mg 7 and RHSiO₂-Cu-Al-Mg 10, respectively.

3.3 Catalyst Characterizations

3.3.1 X-ray Photoelectron Spectroscopy (XPS) Analysis

X-ray Photoelectron Spectroscopy (XPS) is an analysis technique sensitive towards surface characterization that provides valuable information about surface composition, oxidation state and elemental content in materials. XPS instruments are most commonly equipped with two anodes Mg and Al to release monochromatic radiation that can be used to irradiate sample under study. The technique is of low energy requirements thus is classified as 'soft x-rays'. Being a surface sensitive technique; the small distance from which electrons can escape (approximately 1-3 nm) allows for swift analysis. The irradiated material can then undergo ejection of an electron from its core when supplied with appropriate amount of energy. The core hole will be in excited state making the material's overall electronic configuration will be unstable. This will result in demotion
of any outer electrons in order to fill the hole to eventually return the atom into a stable state.

The specific kinetic energy profile of the photoemission is intrinsic to a specific element and its chemical nature such as its oxidation state. The binding energy can now be defined as the amount of energy which needed to be supplied to promote an electron to its subsequent Fermi level (excited state). This energy also provided a unique identification to the element under analysis. The resultant energy and its photoelectron's position can be plotted into a graph to generate the XPS spectrum. The electron's binding energy is calculated by subtracting the sum of element's kinetic energy and work function of the spectrometer (depending on the instrument used) from the incident photon energy.

3.3.2 Temperature Programmed Reduction (TPR) Analysis

The next two characterization processes employed the use of the Thermo Finnigan, TPDRO instrument which simplifies the process of determining desorption-based analysis such as reducibility of a particular catalyst. This instrument capable of conducting sample pre-treatment in tandem to analysis allows for the desired time saving. Specifically for this study, the temperature-programmed reduction (TPR) analysis was carried out using the TPDRO 1100 series, which is equipped with a thermal conductivity detector (TCD). The catalysts were pre-treated by heating each of them in a cell at 120 $^{\circ}$ C for 1 h within a continuous flow of Helium, He gas. After that, a mixture of gas composed of 10 % of H₂ in He was introduced to the samples in their respective analysis to reduce the active metal species present in the catalysts up to 250 $^{\circ}$ C in the span of 1 h. Along with the data of thermal reducibility of each catalyst, the amount of H₂ gas adsorbed were also calculated. The data from TPDRO also revealed three different sets of metal dispersion, which are indicative of active metals (Cu, Ni or Pd), Al and Mg.

Thus, these dispersion values were used to represent the overall metal dispersion for each components of the multifunctional catalyst.



Figure 3.1 : Temperature-Programmed Desorption, Reduction, Oxidation (TPDRO); Thermo Finnigan (TPDRO 1100)

3.3.3 Ammonia, NH3-Temperature Programmed Desorption (TPD) Analysis

The same instrument as in the TPR analysis was utilized in the temperatureprogrammed desorption (TPD) of ammonia analysis. This analysis was carried out using the TPDRO 1100 series equipped with a TCD detector. The catalysts were pre-treated by heating each of them in a sample cell at 120 $^{\circ}$ C for 1 h in the presence of He. After that, 10 % of NH₃ in He was used in their respective analysis to allow NH₃ adsorption onto the respective active metal species in the catalysts at 250 $^{\circ}$ C for 1 h. Along with the data of thermal desorption of NH₃ gas for each catalyst, the amount of NH₃ gas adsorbed were also calculated.

3.3.4 Pyridine-Fourier Transformation Infrared (FTIR) Analysis

Fourier Transform spectroscopy employs the infrared, IR region of the electromagnetic spectrum to determine the mode of bonding in a surface species of a sample. This can be achieved by the irradiation of the sample under study, dispersed in potassium bromide, KBr powder or liquid solvents. This process will allow absorption of the IR wave by the sample to allow excitation of the vibrational modes within the

functional groups of the sample. This excitation process generates dipole moment which has unique wavenumber depending on the bond present. Hooke's law elegantly visualizes the relationship between the frequency (\vec{v}) of the vibration with the force constant (k) and the reduced mass of the system (μ) as shown in the equation below.

$$\overline{\upsilon} = \frac{1}{2\pi} \sqrt{\frac{\kappa}{\mu}}$$
Equation (3.1)

Pyridine FTIR analysis is simply FTIR analysis conducted with the samples exposed to pyridine under vacuum condition to allow its adsorption onto the acidic sites of the catalyst. Employing the concept of base FTIR analysis allow us to identify the type of acidic bonds present in the catalyst, specifically either Lewis or Brønsted acid, the latter of which is vital for esterification of furfuryl alcohol and acetic acid. The Pyridine infrared analysis was done for all catalysts by using Perkin Elmer, model FTIR-Spectrum 400. Before this, the catalysts were exposed to pyridine under vacuum conditions to allow adsorption on their surfaces.

Alongside the experimental data, a set of simulation was conducted for multifunctional catalyst of different active metal. This is because different active metals will form bonds with the silica support differently from one another. The geometry of the Al-O(H)-S-pyridine cutout plane was built using the Gauss view environment in Gaussian 09 software.²² The Al-O(H)-S-pyridine was optimized using the Hartree-Fock theory at the ground state, with singlet default spin mode and 3-21G basis set. Afterward, the frequency analysis of the optimized Al-O(H)-S-pyridine geometry was determined at the same level of theory to extract different harmonics of the pyridine adsorption on the Brønsted acid sites.



Figure 3.2 : Fourier Transformation Infrared (FTIR); IFS66v/S

3.3.5 Brunauer-Emmet-Teller (BET) Analysis

BET analysis employs the physisorption process of most commonly nitrogen gas which occurs at the temperature of 77.5 K or -195.65 °C. External pressure was also introduced on the surface area of the material to be measured ,thus allowing the physical adsorption the nitrogen gas onto the material's surface. The surface area bounded to nitrogen gas, N₂ can be calculated through the determination of the resulting monolayer coverage. This interaction is centered around the interplay of van der Waals forces between the material and the gas. Pressure is gradually increased throughout the length of the analysis until an equilibrium between adsorption and desorption can be presumed to have been achieved. The specific surface area is calculated from the linear region of a plot obtained similar to Langmuir theory, which will be used to indicate formation monolayer coverage. This will proceed with the assumption that the packing between nitrogen molecules is within 0.162 nm². This study utilizes the desorption data obtained the BET surface area and the pore volume using the Micromeritics Tristar II 3020.



Figure 3.3 : Brunauer–Emmett–Teller (BET); Micromeritics Tristar II 3020 3.3.6 X-ray Powder Diffractogram (XRD) Analysis

X-ray diffraction (XRD) analysis were further conducted using the XRD D8 instrument. X-ray diffraction is classified as non-destructive analysis in which the sample is scanned and subsequently reclaimed for further characterization or catalysis. The x-ray source, a form of Cu radiation for all powder characterization, involves photoemission, where vacancies or holes are generated in the core electron level and they are filled by electrons from a higher energy level. The change in energy results in emission of an x-ray. The resulting radiation can then be angled towards the sample via adjusting the prisms within a monochromator. Ideally, the powdered sample used should be finely grounded to provide a smooth surface. However, there will most certainly be a variation in the range of sizes within the grounded material. Regardless, sufficiently large array of crystallites with the correct orientation will be capable to generate constructive interference is explained in Bragg's Law, where it can be inferred that refraction angles are observed only if the interplanar distance is equal to an integer multiplied by the x-ray wavelength.

The main limitation to detection of crystallite structures is the dependence on crystallinity of the supporting material. This is particularly prominent for particles within the nanoscale, where the peaks displayed will show some degree of broadening. This is due to destructive interference which was not removed from the signal produced thus diminishing any constructive interference leading to the peak. The issue is usually circumvented by the monitoring multiple crystal planes and taking an average of their crystallite size.

In this study, the diffraction peaks were measured at 28 °C using Cu K radiation at an X-ray wavelength (λ) of 1.5406. Bragg's angle range was set from10 to 80° with a 1° step size and a 1 s/step acquisition time at 40 kV and 40 mA. Equation (3.2) was used to calculate the lattice strain of each catalyst.

Lattice strain =
$$\frac{1}{V_s} (d_{hkl}^2 \beta_{hkl}^2 \cos\theta_{hkl}) + (\frac{\varepsilon_a}{2})^2$$
 Equation (3.2)

Where:

 d_{hkl} =Apparent lattice distance between <h k l> planes, V_s=Apparent volume-weighted average size ϵ_a = Measure of apparent strain related to root-mean-square strain

The degree of crystallinity can also be calculated with the following equation:

Degree of crystallinity = $\frac{\text{Area of crystalline peaks}}{\text{Area of crystalline and amorphous peaks}} \times 100$ Equation (3.3)



Figure 3.4 : X-ray Powder Diffractogram (XRD); XRD D8

3.3.7 High Resolution Transmission Electron Microscope (HRTEM)

High-resolution transmission electron microscopy (HRTEM) analysis was carried out for each sample using the JEOL JEM-3010 model. Samples were dispersed in ethanol and then deposited on carbon-supported grids (300-mesh) and were then dried at room temperature. Images were processed by using ImageJ version 1.41 software. The principle of electron microscopy is centered on the process in which a beam of electrons is passed through a thin layer of sample deposited on a carbon coated grid which results in electron absorption leading to an image shown on a fluorescent screen; this image can then be magnified and focused for detailed analysis. The main limitation of this analysis is the electron beam itself which if held in position for an extended period of time, may lead to the sintering, agglomeration or generally an overall deformation of the samples.

3.4 Tandem Hydrogenation-Esterification of Furfural and Acetic Acid

3.4.1 RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg Catalysts Performance

Prior to the reaction, a set of computational data was obtained as follows. COSMOthermX acts as a quantum chemical and thermodynamic suite in this analysis. This was used to analyze the polarities of furfural, acetic acid, furfuryl alcohol, and hydrogen, individually as they interact with each other and/or with copper metal surface. The procedure was carried out using COSMO-RS implementation which is based on BP-TZVPC30-1401-ctd procedure of parameterization. Each of the components of the tandem reaction and Cu⁰ was constructed and then optimized on the Tmolex platform using the def-SV(P) as a basic building set for all of the relevant atoms, at the hartree-Fock (HF) levels. The COSMO-files were then generated at DFT levels using the Becke-Perdew functional with consideration into the def-TZVP for the atoms. The resolution of identity standard approximation was also included as a factor in the consideration. The job function for the molecules was used to generate the individual σ -profiles/surface.

The experimental run of the activity of the catalysts was investigated for the hydrogenation-esterification of furfural in an automated 100 mL capacity stainless steel autoclave reactor. Before the commencement of the reaction, the H₂ cylinder set at 30 bar dosing pressure was connected to the reactor. The reactor was sealed and purged with inert N₂ and then H₂ to exclude air. In a typical experiment, 0.1 g of the activated catalyst was placed in a catalyst bulb and fixed on the catalyst bulb holder. This was followed by loading into the reactor, 20% (v/v) furfural and acetic acid in ethanol solvent. Afterwards, the reactor was heated and allowed for isothermal stabilization to obtain the desired set point reaction temperature and H₂ pressures (Halilu et al., 2016a). After completion of the reaction, the autoclave was cooled to 35 °C and depressurized to atmospheric pressure.

The performance of RHSiO₂-Cu-Al-Mg was compared to the catalysts previously used in the past researches, specifically Pd/Al-SBA-15 and Pd/C-Al₂ (SiO₃)₃. These two catalysts were compared based on their respective conversion and selectivity values as reported in their respective articles.

In regards, to process variation parameters, the following variation statement can be applied for each catalyst within the same batch. The temperature was varied from 100 to 250 °C with increments of 50 °C (four data points); pressure was varied from 10 to 40 bar with increments of 10 bar and finally reaction time was studied from 1 h to 4 h with increments of 1 h.

3.4.2 RHSiO₂-M (Pd, Cu, Ni)-Al-Mg Catalysts Performance

In an automated 100 mL stainless steel autoclave reactor, the activity of the catalysts was evaluated for the hydrogenation-esterification of furfural. The H₂ cylinder was connected to the reactor before the start of the reaction at a fixed-bar dosing pressure. To keep air out, the reactor was sealed and purged with inert N₂ and subsequently H₂. 0.1 g of activated catalyst was inserted in a catalyst bulb and set on the catalyst bulb holder in a typical experiment. Following that, 20 % (v/v) furfural and ethanoic acid in ethanol solvent were loaded into the reactor. After that, the reactor was heated to allow for isothermal stabilization of the reaction temperature and H₂ pressures to the required setpoints. The autoclave was cooled to room temperature and depressurized to atmospheric pressure when the reaction was completed. An extra calculation was done for this section to calculate the Goldschmidt constant for the acidic sites in the catalyst using the following equation:

$$K_{\text{Goldschmidt}} = \frac{(a+r)\ln(a/(a-x))-x}{rt}$$
 Equation (3.4)

Where:

- a = Original concentration of furfural,
- x = Concentration of furfuryl acetate,
- t = Reaction time
- r = Ethanol solvent constant at varying reaction temperatures.

3.4.3 Catalyst Performance of RHSiO₂-Cu-Al-Mg Synthesized at Varying pH

Similar to the previous two subsections, the activity of the catalysts was investigated for the hydrogenation-esterification of furfural in an automated 100 mL capacity stainless steel autoclave reactor. Before the commencement of the reaction, the H₂ cylinder set at 30 bar dosing pressure was connected to the reactor. The reactor was sealed and purged with inert N₂ and then H₂ to exclude air. In a typical experiment, 0.1 g of the activated catalyst was placed in a catalyst bulb and fixed on the catalyst bulb holder. This was followed by loading into the reactor, 20% (v/v) furfural and acetic acid in ethanol solvent. Afterwards, the reactor was heated and allowed for isothermal stabilization to obtain the desired set point reaction temperature and H₂ pressures (Halilu et al., 2016a). After completion of the reaction, the autoclave was cooled to 35 °C and depressurized to atmospheric pressure. Table 3.2 and 3.3 show the detailed operation limits of the Autoclave Reactor.



Figure 3.5 : Stainless steel autoclave reactor

Condition/Variables	Туре	Limits	Units
Experiment ID			
Catalyst Mass	Real	0-10	gram
Catalyst ID	Text	0-15	characters
Reactant Mass	Real	0-10	gram
Reactant ID	Text	0-15	characters
Gas ID	Text	0-15	characters
Leak Check Conditions			
Set point pressure	Real	0-250	bar
Time	Integer	0-60	minute
Reaction Conditions			
Set point temperature	Real	0-250	°C
Set point pressure	Real	0-250	bar
Stirring	Boolean	On-off	N/A
Stirring speed	Integer	0-1500	rpm
Reaction time	Integer	0-500	minute

Table 3.2 : Operation limits on autoclave reactor (a)

Condition/Variables	Туре	Limits	Units
Post Processing Conditions			
Reactant melting point	Real	0-250	°C
Product flash point	Real	0-250	°C
End point temperature	Real	0-250	°C
Stirring	Boolean	On-off	N/A
Stirring speed	Integer	0-1500	rpm
Purge time	Integer	0-60	minutes
Alarm Conditions			
Temperature High alarm	Real	0-300	°C
High alarm set point	Real	0-250	°C
High High alarm	Real	0-300	°C
Low alarm	Real	0-300	°C

Real

Real

Real

Real

Real

Low Low alarm

High High alarm

Low Low alarm

Low Alarm

Pressure High alarm

Table 3.3 : Operation limits on autoclave reactor (b)

°C

bar

bar

bar

bar

0-300

0-270

0-270

0-270

0-270

3.4.4 Product Analysis

Gas chromatography (GC) measurements on an Agilent 6890N with 5973 MSD, autosampler, and HP-5 capillary column (1.5 m 30 m 530 m) were used to analyze the reaction product. The conversion of furfural, products selectivity and their respective TOF values were calculated using Equations (3.5), (3.6) and (3.7) respectively (Chen et al., 2002; Sitthisa & Resasco, 2011a):

Conversion (%)

 $=\frac{m(\text{reactant})_{\text{in}} - m(\text{reactant})_{\text{out}}}{m(\text{reactant})_{\text{in}}} \times 100$ Equation(3.5)

Selectivity (%) = $\frac{m(product)}{\sum m(products)} \times 100$

Equation (3.6)

 $TOF = \frac{m(product)}{amount of metal active sites \times reaction time}$

Equation (3.7)



Figure 3.6 : Gas Chromatography with Flame Ionization Detector; Agilent 6890N with 5973 MSD

The data from every characterization, COSMO-RS simulations, Goldschmidt analysis and the overall performance of each individual catalyst from each batch allowed for the elucidation of a general mechanism for our multifunctional catalyst system.

3.4.5 Reusability analysis of multifunctional catalysts

The catalyst batches used in the previous runs were separated from the reaction mixture via centrifugation and washed three times using ethanol. Each of the catalysts were then dried at 80 °C for 12 hours before being reused as described above with respect to each catalyst batch. The clean catalysts can then be subjected to OHE reactions of furfural with each runs selected to be conducted at 150 °C and 20 bar for the duration of 4 hours each. The collected sample was then analyzed using GC-FID instrumentation similar to the previous runs. The reusability of each catalyst can be defined as the overall furfural conversion with respect to the first runs conducted using the same respective catalysts.



Figure 3.7 : Work flowchart

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characterizations of Multifunctional Catalysts

4.1.1 Reducibility of Multifunctional Catalysts

4.1.1.1 Reducibility of RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg

The reducibility of each batch of multifunctional catalysts were measured in direct relation to the temperature at which they were reduced. The higher the temperature required for reduction to take place, the lower the reducibility of the catalyst. As shown in Figure 4.1 (a), the RHSiO₂-Cu catalyst was reduced at the highest temperature, at approximately 630 °C. For RHSiO₂-Cu-Al catalyst, it was reduced at lower temperature in two steps, represented by peaks centered at ~319 °C and ~490 °C. The RHSiO₂-Cu-Al-Mg catalyst was reduced in a single phase similar to RHSiO₂-Cu, indicated by a single peak at ~300 °C. These observations indicated first and foremost that despite the variation in the magnitude of the reduction temperature, the catalysts have reducible Cu-metallic functions, which is essential in the first hydrogenation portion of the OHE reaction. The Cu reducibility has been suggested to be influenced by its high dispersion in the SiO₂ matrix (Villaverde et al., 2013a; Villaverde et al., 2015), which was observed to be further improved after the addition of Al and Mg (Figure 4.1 (a) and Table 4.1). This observation was largely attributed to Al and Mg incorporation within RHSiO₂-Cu-Al-Mg which can affect the surrounding hydrogen potential surrounding Cu²⁺ species. This effect yielded a higher degree of distortion within the electron cloud in the metal oxide framework due to the different metals electrophilic nature hence easing the reduction of Cu²⁺ (B. Nagaraja et al., 2007). The increased dispersion of the main metal active sites which came with the addition of Al and Mg will be further discussed in Section 4.1.3 of this thesis. Suffice to say that one of the first observable effect in introduction of Al and Mg into RHSiO₂-Cu is the increase in reducibility of Cu due to the metal particles high dispersion within the structure of the support material.



Figure 4.1 : (a) Reducibility of multifunctional catalysts (b) Reducibility of support materials

Catalyst	Cu dispersion	Al dispersion	Mg dispersion
	(µmol/g)	(µmol/g)	(µmol/g)
RHSiO ₂ -Cu	1300.1		-
RHSiO ₂ -Cu-Al	1861.4	726.4	-
RHSiO ₂ -Cu-Al-Mg	2439.8	913.4	351.2

Table 4.1 : Dispersion of active metals in the catalysts

4.1.1.2 Reducibility of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg

The reducibility of each active metal species was analyzed via TPR analysis as shown in Figure 4.2. RHSiO₂-Cu-Al-Mg shows the highest reducibility indicated by the low temperature required at only ~400 $^{\circ}$ C. On the other hand, both RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg show a similar degree of reducibility with both catalysts requiring a temperature of approximately 650 $^{\circ}$ C to reduce the metals. To be more precise, the TPR profile of RHSiO₂-Ni-Al-Mg was indicative of reduction peaks for nickel occurring at 550 and 650 $^{\circ}$ C for N²⁺ to Ni⁺ and Ni⁺ to Ni⁰ reduction process, respectively. The TPR profile of RHSiO₂-Pd-Al-Mg also showed two peaks representing Pd²⁺ reduction to Pd⁺ and Pd⁺ reduction to Pd⁰ at 400 $^{\circ}$ C and 630 $^{\circ}$ C, respectively. These catalysts underwent a two-step reduction process, and the reduction of the single atoms occurred at a higher temperature than the conventional catalyst. Reduction at higher temperatures was due to the formation of a coordinated phase.

As observed in Table 4.2, RHSiO₂-Cu-Al-Mg showed the highest degree of Al and Mg dispersion compared to RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg. This increased the degree of distortion within the metal oxide framework, yielding a much higher degree of ease in reducing Cu²⁺ formed within RHSiO₂-Cu-Al-Mg. It was also interesting to note that when comparing data from Tables 4.1 and 4.2 that the catalysts with both Al and Mg components consistently showed higher level of dispersions compared to the ones with just Al or without either Al and Mg.



Figure 4.2 : TPR analysis of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg

Table 4.2 : Dispersion of active metals in the catalysts for Cu/RHSiO2-Al-Mg
Ni/RHSiO2-Al-Mg and Pd/RHSiO2-Al-Mg

Catalyst	Cu dispersion (µmol/g)	Al dispersion (µmol/g)	Mg dispersion (µmol/g)
RHSiO ₂ -Cu-Al- Mg	2637.8	903.6	361.2
RHSiO ₂ -Ni-Al- Mg	2321.9	958.9	351.0
RHSiO ₂ -Pd-Al- Mg	2337.5	983.3	354.2

4.1.1.3 Reducibility of RHSiO₂-Cu-Al-Mg (pH = 1, 3, 7 and 10)

The reducibility of the RHSiO₂-Cu-Al-Mg synthesized at varying pH was analyzed via TPR analysis as shown in Figure 4.3. RHSiO₂-Cu-Al-Mg 3 showed the highest reducibility requiring only ~300 °C followed by RHSiO₂-Cu-Al-Mg 1 which requires ~375 °C. RHSiO₂-Cu-Al-Mg 7 and RHSiO₂-Cu-Al-Mg 10 requires highest temperature at ~450 and 500 °C, respectively, implying a lower degree of reducibility. These results are in line with the observation from XPS analysis in which RHSiO₂-Cu-Al-Mg 3 demonstrated superior ease in reducibility of the Cu²⁺ to Cu⁰. We propose that this observation is once again related to the higher degree of Al and Mg incorporation within RHSiO₂-Cu-Al-Mg 3 which can be attributed to the surrounding hydrogen potential during synthesis. The degree of distortion within the electron cloud for a metal oxide during sol-gel synthesis is a direct product of the surrounding pH, in other words the hydrogen potential (Lesiak et al., 2014a). This is even more vital when considering the additional metals electrophilic nature which can ease the reduction of Cu^{2+} as demonstrated in the previous two subsections. It was previously discussed in Chapter 2 that [(OEt)₄SiOH]⁺ is the prevalent intermediate form prior to the condensation process to form silica support to encapsulate the metal components via formation of silanol bridges. The formation of sufficient amount of this intermediate requires an appropriate amount of proton from the surrounding. As was demonstrated by the data in Table 4.3, too high of an acidity, in this case at pH 1 lead to a lowered degree of metal component dispersion within the catalyst, however it was not as prevalent as increasing the pH up to 7 and 10 which proliferated the effect of the problem.



Figure 4.3 : TPR analysis of RHSiO₂-Cu-Al-Mg at pH 1, 3 7 and 10

Table 4.3 : Dispersion of active metals in the RHSiO2-Cu-Al-Mg cata	lysts
synthesized at different pHs	

Catalyst	Cu dispersion (µmol/g)	Al dispersion (µmol/g)	Mg dispersion (µmol/g)
RHSiO ₂ -Cu-Al- Mg 1	1837.5	603.5	267.3
RHSiO ₂ -Cu-Al- Mg 3	2439.8	913.4	351.2
RHSiO ₂ -Cu-Al- Mg 7	1237.8	513.3	294.2
RHSiO ₂ -Cu-Al- Mg 10	888.3	451.5	192.1

4.1.2 Acidity of Multifunctional Catalysts

4.1.2.1 Acidity of RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg

The NH₃-TPD profiles in Figure 4.4 indicated that the RHSiO₂-Cu catalyst showed a peak centered at ~ 287 $^{\rm O}$ C, indicating the presence of medium acid sites (Mallesham et al., 2014). RHSiO₂-Cu-Al catalyst contains both medium and strong acid sites represented by peaks at 216 $^{\rm O}$ C and 800 $^{\rm O}$ C, respectively. The presence of strong acid sites will impede the esterification of furfuryl alcohol (Wanjin Yu et al., 2011a). RHSiO₂-Cu-Al-Mg was observed to contain higher amount of medium acid sites centered at 324 $^{\rm O}$ C, with no peaks corresponding to strong acid sites. This observation was indicative of the role of Mg

addition in tuning the acidity of the catalyst. Similar to the effects observed in TPR analysis, the addition of Mg enhanced the formation of the metal oxide framework and the silica support via silanol bridges. Formation of such bonds has been observed to reduce the acidity of Al acid sites to a certain degree (Denardin & Perez-Lopez, 2019). Thus, the strong acidic sites formed in RHSiO₂-Cu-Al was reduced to medium strength in RHSiO₂-Cu-Al-Mg. The amount of the overall acidic sites for each of the catalysts, based amount of NH₃ gas adsorbed, followed this order: RHSiO₂-Cu (94.9 μ mol/g) < RHSiO₂-Cu-Al-Mg (203.6 μ mol/g) < RHSiO₂-Cu-Al (826.4 μ mol/g). These results are valuable, particularly for OHE of furfural, because strong acid sites tend to favor the formation of by-products rather than furfuryl acetate formation from furfuryl alcohol (Zhang et al., 2010).



Figure 4.4 : NH₃-TPD analysis of RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg

4.1.2.2 Acidity of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg

As indicated in Figure 4.5 (c), similar analysis of NH₃-TPD was conducted to three sample with different active metals to determine if the change in different metals will manifest as any form of changes to the overall acidity of the catalyst as a whole. The three

catalysts showed formation of similar acid sites of moderate strength indicated by the peaks at around 270 °C. The main difference between RHSiO₂-Cu-Al-Mg and the other two catalysts can be clearly seen with formation of strong acid sites at 790 and 820 °C for RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg, respectively. This observation can be related to the mechanism by which Si-O-Al linkages are formed within the structure of the catalyst. The process involves the replacement of one atom of Si (for a single Si-O-Si link) with Al to form the Si-O-Al linkage (Wang et al., 2015). Since, Pd and Ni have higher potential to accept electron due to their electronic configuration compared to Cu, they have higher tendency to form strong Si-O-Al linkages leading to strong acid site formations. This was further indicated to Al deposition as in Table 4.2, which indicate that said deposition was much higher in RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg (Bjelić et al., 2020).



Figure 4.5 : NH₃-TPD analysis of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg

To further understand the acidic sites in the three catalyst of different metals, Pyridine-FTIR of the catalysts were carried out. Figure 4.6 (a) and Figure 4.6 (b) show experimental and theoretical values of the pyridine FT-IR analysis of RHSiO₂- M (Pd,

Cu, Ni)-Al-Mg single-atom catalysts. The purpose here was to resolve the type acidity present in each of these catalysts. In Figure 4.6(a), the pyridine FT-IR spectra were shown to have the presence of both Brønsted and Lewis acid sites on the RHSiO₂- M (Pd, Cu, Ni)-Al-Mg single-atom catalyst surface. The Brønsted acid sites detected on RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg exhibited pyridine vibration centering at two frequency regions; 1) lower frequency of 1544, 1535, and 1529 cm⁻¹, and 2) higher frequency of 1632, 1621, and 1616 cm⁻¹. When compared to Figure 4.6 (b), these vibrations of pyridine adsorbed on the surface of characteristic the RHSiO₂- M (Pd, Cu, Ni)-Al-Mg single-atom nanoparticle catalysts were shown to be available with the inclusion of displacement vectors, dipole derivative unit vector. Although the pyridine ring does show certain displacement vectors, the primary vibration of pyridine occurred between the proton and the pyridine ring as indicated by the dipole derivative. The dipole derivative provides insight into the interaction between similar groups on adjacent molecules, which determined the band splitting in vibrational spectra, and permits calculation of the infrared IR intensities, which can serve as an independent test of force field. The theoretical information on this analysis validated the presence of Brønsted acid site culled from a transition dipole coupling accounts for pyridine mode adsorbed on Brønsted acid mode band splitting in spectra of pyridine. Apart from the Brønsted, there are several low-intensity peaks at 1439 cm⁻¹ for strong Lewis acidic site-bonded pyridine (Farneth & Gorte, 1995; Halilu, Hussein Ali, et al., 2019a; Hutchings & Lee, 1994; Sumiya et al., 2001).

The presence of Brønsted acidity confirms the catalyst's potential activity to promote the acid-driven second esterification step. Furthermore, other Brønsted frequencies such as $\approx 1550 \text{ cm}^{-1}$ (2), $\approx 1627 \text{ cm}^{-1}$ (3), and $\approx 1673 \text{ cm}^{-1}$ (4) are not associated with sole Brønsted vibration. These frequencies incorporate the vibration of the Brønsted acid through the stretching mode of other sections and the pyridine, through wagging and scissoring modes. Therefore, the RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg catalysts are confirmed with two active functionalities; the metal function and the acid functions. These functions are suitable to promote the hydrogenationesterification reaction.



Figure 4.6 : (a) Experimental pyridine IR analysis) (b) DFT-pyridine IR, showing the dipole moment and dipole derivative of pyridine adsorbed on Brønsted acid sites for single metal-doped RHSiO₂-M-Al-Mg (M = Cu, Ni, and Pd).

4.1.2.3 Acidity of RHSiO₂-Cu-Al-Mg at pH 1, 3 7 and 10

The strength and amount of acid sites available in each RHSiO₂-Cu-Al-Mg catalyst was analyzed by taking into account the temperature at which NH₃ gas was desorbed and the amount of said gas adsorbed by the catalysts, respectively (Figures 4.7 (a) and (b)). With regards to the strength of the acid sites available in each catalyst, RHSiO₂-Cu-Al-Mg 3 requires the highest temperature of ~315 $^{\circ}$ C to desorb the NH₃ gasses implying that its of relatively higher overall acidity (Halilu, Hussein Ali, et al., 2019b). This is followed by RHSiO₂-Cu-Al-Mg 10 which requires ~240 $^{\circ}$ C while both RHSiO₂-Cu-Al-Mg 1 and 7 requires ~215 $^{\circ}$ C. Similar trend can be said with regards to amount of acid sites available in each catalyst, with RHSiO₂-Cu-Al-Mg 3 indicating significantly higher amount at concentration of ~1851.7 µmol/g. The superiority in acidic amount of RHSiO₂-

Cu-Al-Mg 3 is a direct result of its synthesis pH. [(OEt)₄SiOH]⁺ intermediate is the backbone in formation of Si-O-Si which will yield Si-O-Al linkages as Al was introduced. As pH 3 was previously demonstrated to be the one most suitable for the formation of [(OEt)₄SiOH]⁺ intermediate by providing sufficient amount of proton, the result will be the significant number of acidic sites as shown.



Figure 4.7 : NH₃-TPD analysis of RHSiO₂-Cu-Al-Mg catalysts synthesized at pH 1, 3, 7 and 10; (a) analysis of acid site strength and (b) analysis of the amount of acid sites available

4.1.3 XPS Analysis of Multifunctional Catalysts

4.1.3.1 XPS Analysis of RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg

The elemental composition and their oxidation states in RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg catalysts were studied by XPS narrow-scanning (Figure 4.8). There was an obvious evidence of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ spin splitting in Cu that depends on chemical state and energy separation between $2p_{3/2}$ and $2p_{1/2}$ components (Figure 4.8 (a)). These features confirmed the presence of Cu²⁺ in the developed catalysts. The Cu $2p_{3/2}$ component occurs at 932.5 eV, 932.4 eV and 932.1 eV for RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg catalysts, respectively. As well, the Cu $2p_{1/2}$ component

appeared at 952.9 eV, 952.4 eV and 952.1 eV in RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg catalysts, respectively. It can be further observed that the binding energies for Cu 2p_{1/2} and Cu 2p_{3/2} components were reduced after Al and Mg were added. This is because the addition of Al or Mg to RHSiO₂-Cu tends to create more non-uniform electron cloud within the metal oxide framework, making the metal-oxygen bonds weaker. Moreover, Al³⁺ and Mg²⁺ species are more electrophilic than Cu²⁺, and they become more susceptible for O²⁻, resulting in an increased bond length and low binding energy. The presence of RHSiO₂ phase was confirmed from the strong Si 2p peak in Figure 4.8 (b) for RHSiO₂-Cu, RHSiO₂-Cu-Al, and RHSiO₂-Cu-Al-Mg catalysts, which is centred at 103.2 eV, 101.8 eV and 101.6 eV, respectively. Similarly, the decreasing trend in the binding energy of the Si 2p component after the addition of Al and Mg was a result of the non-uniformity of the electron cloud around Si due to its point charge contribution to the bonds with Al³⁺ and Mg²⁺. These observations were consistent with the literature reports (Chanquía et al., 2012; Huang et al., 2007). The presence of a peak at 74.2 eV indicated that Al³⁺ ion was coordinated with the SiO₂ support, forming Si-O-Al bridges (Figure 4.8 (c)). Meanwhile, the presence of Mg KLL auger peak (Figure 4.8 (d)) at 306.3 eV is a reflection of Mg 1s, and the confirmation of Mg forming a bond with O^{2} through the silica point charges. Similar results were reported for different types of silica materials (H. Zhang et al., 2013).



Figure 4.8 : XPS spectra of RHSiO₂-Cu, RHSiO₂-Cu-Al, and RHSiO₂-Cu-Al-Mg catalysts: (a) Cu 2p, (b) Si 2p, (c) Al 2p, and (d) Mg KLL auger peak.

4.1.3.2 XPS Analysis of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-

Mg

The XPS analysis was then repeated for the catalysts RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg. To avoid redundance, this paragraph will focus on the narrow scan analysis of the active metals; Cu, Ni and Pd as the same analysis of Si, Al and Mg are similar to the ones found in Fig 4.8 (b), (c) and (d) respectively. With reference to Figure 4.9 (a), similar observations were made for the state of Cu in RHSiO₂-Cu-Al-Mg where there was an obvious evidence of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ spin splitting in Cu that depends on chemical state and energy separation between $2p_{3/2}$ and $2p_{1/2}$ as in Figure 4.8 (a). As such we can confirm the presence of Cu²⁺ in the developed catalysts. The Cu $2p_{3/2}$ component was indicated by the peak at 932.3 eV in this case. On the other

hand, the Cu 2p_{1/2} component can be found at 952.5 eV. the oxidation state of copper in RHSiO₂-Cu-Al-Mg has been investigated to show a mixture of oxidation states including Cu⁰, Cu^{+,} and Cu²⁺, featuring spin splitting of Cu 2p_{3/2} at 932.3 eV and Cu 2p_{1/2} at 952.5 eV (Mondal et al., 2013). The presence of these oxidation states is not unfamiliar since the reduction of RHSiO₂-Cu-Al-Mg in a hydrogen environment before XPS analysis may not completely reduce the copper oxide to copper metal (Beerthuis et al., 2020). Moreover, since special precautions were not taken to protect the catalyst from the environment, the reduced copper metal can get easily oxidized by atmospheric oxygen Cu⁺ and Cu²⁺. Regardless, the pre-treatment procedure could produce Cu⁰ phase in the catalyst which is known to catalyse the desired hydrogenation reaction step. In the case of Ni as indicated in Figure 4.8 (b), the peak was formed at 854.2 eV which was indicative of NiO formation. It should be added that there is a slight shift towards 855.6 eV, which was reported to be indicative of Ni(OH)₂ bonding, thus leading us to believe that the metal was chemisorbed into the structure of the rice husk derived silica support, via bonding at the silanol bridges, similar to the case of RHSiO₂-Cu-Al-Mg previously. The deconvolution peaks confirmed the presence of Ni⁰ and Ni²⁺ oxidation states featuring 853.2 and 855.6 eV, respectively.(Grosvenor et al., 2006) Similarly, the prior reduction of RHSiO₂-Ni-Al-Mg catalyst before the XPS analysis did not completely reduce the Ni²⁺ into Ni⁰, or Ni⁰ in RHSiO₂-Ni-Al-Mg get oxidized by atmospheric oxygen. Narrow scan analysis of RHSiO₂-Pd-Al-Mg indicated PdO, similar to RHSiO₂-Cu-Al-Mg and RHSiO₂-Ni-Al-Mg. The deconvolution peaks for Pd⁰ and Pd²⁺ oxidation states at 336.3 eV and 340.7 eV were also observed (Rahul et al., 2015). Though there is Pd²⁺ phase due to incomplete reduction of RHSiO₂-Pd-Al-Mg or unavoidable oxidation of Pd⁰ to Pd²⁺, it is obvious that the Pd^{2+} has a low intensity as indicated by the broad binding energy. Generally, it is common for all the catalysts to contain zero oxidation states of the single atom catalysts. Other oxidation states such as Cu⁺, Ni²⁺, or Pd²⁺ do not affect the potential

activity of the catalysts during the hydrogenation step since the Cu⁰, Ni⁰ and Pd⁰ exist to promote hydrogenation.



Figure 4.9 : XPS analysis of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg.

4.1.3.3 XPS Analysis of RHSiO₂-Cu-Al-Mg (pH 1, 3, 7 and 10)

To allow better understanding on the influence of pH towards the surface acidity of the catalysts, XPS analysis was conducted on each of them. Figure 4.10 (a) shows the Cu 2p XPS of each RHSiO₂-Cu-Al-Mg indicating peaks centered at ~933 and 954 eV corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ respectively (Andas et al., 2013a). However, as the pH during synthesis increases it can be observed that these values increased as well. The shift for Cu $2p_{3/2}$ binding energy towards ~934 eV for catalysts formed in basic environment is highly indicative of the increasing presence of Cu²⁺ present in the CuO form, unlike the ones formed in acidic pH which contrarily points towards presence of Cu⁰ (Wu et al., 2005a).

On the other hand, both XPS analysis for Al (Figure 4.10 (b)) and Mg (Figure 4.10 (c)) indicate similar shifts towards higher binding energy as the acidity of the synthesis environment increases. In the case of Al 3p the shift indicates that acidic environment favours incorporation of the Al into the silica support to form aluminosilicate like structure (Gómez-Cazalilla et al., 2007). The trend observed for Mg KLL peaks indicate the presence of Mg^{2+,} with increasing tendency to be reduced to its metal form as pH increases. For Si 2p XPS, it can be seen that as synthesis pH increases the binding energy increases from ~102.5 to ~103.5 eV. This observation is an indicator that with increasing basicity, formation of metal silicate network is favored rather than formation of SiO₂ within the overall catalyst (Adam et al., 2010a; Adam et al., 2012b).



Figure 4.10 : XPS analysis of RHSiO2-Cu-Al-Mg catalysts synthesized at pH 1, 3, 7 and 10 for metals (a) Cu, (b) Al, (c) Mg and (d) Si respectively.

4.1.4 Crystallinity, Morphological and Surface Analysis of Multifunctional Catalysts

4.1.4.1 Crystallinity, Morphological and Surface Analysis of RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg

The degree of crystallinity of RHSiO₂-Cu-Al-Mg, RHSiO₂-Cu-Al, and RHSiO₂-Cu catalysts were estimated based on the presumption that the sharp peaks and the broad peaks originated from crystalline and amorphous phases, respectively. As shown in Figure 4.11 (a), each of the catalysts exhibited distinct XRD peaks, which corresponded to SiO₂, CuO, Al₂O₃ and MgO phases (Table 4.4). The degree of crystallinity for RHSiO₂-Cu-Al-Mg, RHSiO₂-Cu-Al and RHSiO₂-Cu catalysts was found to be 79.10%, 75.43% and 35.5%, respectively. This was a clear indicator that RHSiO₂-Cu-Al-Mg was more crystalline in its nature when compared to RHSiO₂-Cu-Al and RHSiO₂-Cu. The crystallinity of RHSiO₂-Cu-Al-Mg was close enough to that of RHSiO₂-Cu-Al, hence indicating that the process of adding Mg and/or Al improved the crystalline nature of the nanoparticles (Jun Wang, 2011; Wanjin Yu et al., 2011a). Figure 4.12 (b) showed the HRTEM image of RHSiO₂-Cu-Al-Mg catalyst, while the HRTEM images of RHSiO₂-Cu-Al and RHSiO₂-Cu were also presented alongside the former in Figure 4.12. The amorphous RHSiO₂ phase is not clearly distinct in HRTEM images of RHSiO₂-Cu-Al-Mg and RHSiO₂-Cu-Al catalysts (Figure 4.12). Therefore, it can be said that there was no visible distinction of CuO phase in RHSiO₂-Cu-Al-Mg and RHSiO₂-Cu-Al catalysts. This suggested that, there was a possible coordination of three metal matrixes in the developed catalysts (Pech-Canul & Makhlouf, 2000). This was unlike RHSiO₂-Cu nanocatalyst, which clearly exhibited an amorphous phase of silica indicating a clear distinction between CuO phases evenly dispersed on the RHSiO₂ surface. Furthermore, it can even be suggested that the low crystallinity of RHSiO₂ may be attributed to the existence of more amorphous phase of RHSiO₂ (Armelao et al., 2005). The fast Fourier

transformation pattern of RHSiO₂-Cu-Al-Mg nanocatalyst in various orientations can be indexed to a superlattice made of different sublattices (inset of Figure 4.11 (b)).



Figure 4.11 : (a) Power XRD analysis of RHSiO₂-Cu, RHSiO₂-Cu-Al, and RHSiO₂-Cu-Al-Mg catalysts (DC – degree of crystallinity) and (b) HR-TEM image and fast Fourier transformation (FFT) image of RHSiO₂-Cu-Al-Mg catalyst

The superlattice reflections were indicated by arrows, evidencing the likely formation and reorientation of defects aroused from Cu, Al and Mg functionalization into RHSiO₂. The FFT revealed that the sublattice of RHSiO₂-Cu-Al-Mg is made of closely packed monoclinic CuO (a=4.6837, b=3.4226, c=5.1288 and β =99.54), cubic (a=4.2121) and trigonal Al (a=4.785, and c=12.991) phases. Table 4.5 further provided an insight into the morphological properties of each catalyst based on BET analysis. In general, the three properties studied here, showed gradual increment as more metals were introduced into the overall structure of the catalyst. This observation further conformed to the idea that each of the metal components were chemically adsorbed into the structure of RHSiO₂ support which resulted in the changes to these surface morphological properties of the catalysts. Among the catalysts, the RHSiO₂-Cu-Al-Mg catalyst showed the highest BET surface area (156.11 m²/g, Table 4.5). This is due to the strong interaction of the components in the RHSiO₂-Cu-Al-Mg catalyst, preventing the surface area loss against higher calcination temperatures. All the catalysts showed type IV isotherms with H3 loop, indicating the presence of slit shaped pores (Figure 4.13) (Hillary et al., 2017).



Figure 4.12 : HRTEM analysis of RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg catalysts

Peak position	h	k	1	Peak
(2 Theta)				Assignment
17.9	1	1	0	Al
21.8	1	0	2	Si
23.6	1	1	2	Al
26.9	2	1	0	Al
28.3	2	0	2	Cu
31.3	3	0	0	Cu
36.2	2	2	0	Cu
40.2	2	1	3	Mg

 Table 4.4 : XRD analysis of the catalysts along with each peaks' assignments



Figure 4.13 : BET analysis of RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg.

 Table 4.5 : Textural properties of the catalysts RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg.

Sn.	Textural properties	RHSiO ₂ -Cu	RHSiO ₂ -Cu-Al	RHSiO ₂ -Cu-Al-Mg
1	Surface area (m^2/g)	46.58	73.32	156.11
2	Pore volume (cm^3/g)	0.21	0.30	0.39
3	Pore diameter (nm)	9.80	14.30	19.90

4.1.4.2 Crystallinity, Morphological and Surface Analysis of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg

Figure 4.14 shows the wide-angle powder X-ray diffraction (XRD) analysis of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg different single-atom transition metals-based catalysts ranging from 20° to 80° diffraction angle. The diffraction pattern and single-atom crystal analysis were done using high score plus software,

showing different crystal patterns. All the three RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg catalysts are crystalline with unique crystallographic planes featuring the single-atom Cu, Ni, and Pd dope RHSiO₂-Al-Mg catalysts. The RHSiO₂-Cu-Al-Mg has two significant diffraction peaks at 32.5° and 38.7° for the CuO phase, with (110) and (200) crystallographic planes, respectively (Library matching code: 01-072-0629). Similarly, the RHSiO₂-Ni-Al-Mg featured NiO phase with diffraction peak occurring at 37.8°, 43.4° and 79.6° indexed with (111), (200), and (222) crystallographic planes, respectively (Library matching code: 01-073-1519). The RHSiO₂-Pd-Al-Mg featured PdO phase with diffraction peak at 45.5°, indexed with (111) crystallographic plane (Library matching code: 01-075-0584). The crystallite size of RHSiO₂-Cu-Al-Mg single-atom catalyst at the (200) crystallographic plane was ~ 8.43 nm with ~ 0.094 % lattice strain. This implied that the overall crystal structure of RHSiO₂-Cu-Al-Mg is 99.906 % perfect after doping monoclinic (FM-3m space group) single-atom Cu crystal system on RHSiO₂-Al-Mg. Similarly, RHSiO₂-Ni-Al-Mg has a crystallite size of 43.8 nm at the (222) crystallographic plane with 0.124 % lattice strain. This XRD result indicates that the overall crystal structure of RHSiO₂-Ni-Al-Mg is 99.876 % perfect after doping cubic (fm-3m space group) single-atom Ni crystal system on RHSiO₂-Al-Mg. The RHSiO₂-Pd-Al-Mg has a crystallite size of 27.0 nm with 0.357 % lattice strain. This RHSiO₂-Pd-Al-Mg has the highest lattice strain with 99.643 % crystal structure perfection after doping tetragonal Pd single-atom on RHSiO₂-Al-Mg support material. In conclusion, RHSiO₂-Cu-Al-Mg has the highest crystallite size and lowest lattice strain. Contrarily, RHSiO₂-Pd-Al-Mg has the lowest crystallite size and highest lattice strain. The crystallite size of RHSiO₂-Ni-Al-Mg is smaller than that of RHSiO₂-Cu-Al-Mg catalyst and higher than that of RHSiO₂-Pd-Al-Mg catalyst. RHSiO₂-Pd-Al-Mg has the highest lattice strain with 99.643% crystal structure perfection after doping tetragonal Pd single-atom on RHSiO₂-Al-Mg support material. Comparatively, RHSiO₂-Cu-Al-Mg has

the lowest lattice strain, but the crystallite size is inconclusive as it's not clear if the value is for the whole grain size or the single-atom Cu catalyst. This is because the crystalline domain of RHSiO₂-Cu-Al-Mg grain particles are below 10 nm. Peak broadening is so significant for particles < 10 nm that signal intensity is expected to be low, resulting in peak overlap that makes it difficult to discern.



Figure 4.14 : Powder X-ray diffraction spectra of (a) RHSiO₂-Pd-Al-Mg, (b) RHSiO₂-Cu-Al-Mg, and (c) RHSiO₂-Ni-Al-Mg, and (d) crystallite size and lattice strain of RHSiO₂-(M = Cu, Ni or Pd)–Al–Mg bifunctional catalysts

N₂ adsorption-desorption experiments on the RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg single-atom catalysts indicated hysteresis loops with Type IV isotherm patterns as shown in Figure 4.16. In principle, the Type IV isotherm implied a hierarchical porosity of a wide range of different pore size distributions spanning micro-meso and macro-pore regimes (Svidrytski et al., 2020). Observing the hysteresis spectrum, RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg single-atom catalysts has the network of a mesoporous system larger than 4 nm in pore diameter size.

This implied the hierarchical porous structures of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg single-atom catalysts essentially availed adsorbent-adsorbate interactions at lower partial pressures within their mesopores. The surface area of each catalyst increases in the order of RHSiO₂-Ni-Al-Mg, RHSiO₂-Cu-Al-Mg, and RHSiO₂-Pd-Al-Mg as shown in Table 4.6. We hypothesized that this variation in the surface area though not very high can be attributed to the low lattice straining difference of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg single-atom catalyst crystal structures. However, the surface area does not form a pattern with the magnitude of the lattice straining. Also, due to the stronger interaction between Pd and the supporting metals, Al and Mg are both intercalated within the mesoporous structure, thus contributing to the high lattice strain. Moreover, this interaction increases the overall distribution of the active metal within the structure of the silica support, hence increasing surface area, pore-volume, and pore diameter. However, the difference between these values for all of the catalysts is not significant due to the similarity of their metal composition, with the difference being the minuscule difference in the interaction between the active single-atom and the support material.

Figure 4.15 (a)-(c) show a series of HRTEM images of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg single-atom catalysts featuring Cu, Ni, and Pd phases doped on RHSiO₂-Al-Mg support material, irradiated by a high-energy electron beam (working at 200 kV). Fig 4.15 (a)-(c) also shows the corresponding fast Fourier transform (FFT) diffractograms from the grain region marked with crystallographic planes and d-spaces. Furthermore, 4.15 (a)-(c) illustrate the 3-D surface plot (3D-SP) of the RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg single-atom catalysts with color contrasts featuring the Cu, Ni, and Pd phases. In Figure 4.15 (a), at 50 nm resolution, the doping of the CuO phase can be spotted, and by increasing the resolution to 2 nm, the lattice fringes of Cu phase can be seen. The red-dotted line traced the grains of single-

atom Cu with d=0.275 for (110), d=0.232 nm for (111) crystallographic planes in cognizance to the XRD reports in Figure 5.14a. Moreover, through the BIJ plugin, the surface 3D optical surface algorithm in Java, interfaced with ImageJ was used as an extra command to visualize the 3D-SP1 inform of 3D image color contrast for RHSiO₂-Cu-Al-Mg single-atom crystal. The green-colored surface replicates the lattice fringes featuring single-atom Cu at different crystallographic planes. The purple-colored surface is attributed to the RHSiO₂-Al-Mg support material phase. Accordingly, at 50 nm resolution, Figure 4.15(b) shows the Ni phase, and by increasing the resolution to 2 nm, the lattice fringes of Ni phase can be spotted. The red-dotted line traced the grains of single-atom Ni with d= 0.120 for the (222) crystallographic plane in cognizance to the XRD reports in Figure 4.14 (a). The Ni phase can be spotted on the 3D-SP2 surface, while the purple color shows the RHSiO₂-Al-Mg phase. Furthermore, Fig 4.15(c) shows the morphology of RHSiO₂-Pd-Al-Mg at 50 nm, and by increasing the resolution to 2 nm, lattice fringes of the Pd phase are seen. The red-dotted line traced the grain boundary of the Pd phase doped on RHSiO₂-Al-Mg with d-space = 0.199 for (111), d-space = 215 for (110) crystallographic planes. The Pd phase can be spotted on the 3D-SP3 surface in green color, while the purple color shows the RHSiO₂-Al-Mg phase. To validate the presence of the single atoms, FFT analysis was conducted for spot containing d-space that correspond to Pd, Ni, and Cu phase. Accordingly, Figure 4.15(a)-(c) include the FFTs for Pd, Ni, and Cu phase single atoms in RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg indicated by FFT-1, FFT-2, and FFT-3, respectively. The FFTs show reflection of Cu, Ni, and Pd single atomic phases separated in an orderly fashion. Our approach of identifying the presence of single-atom could supplement the methods popularly used to identify single atoms such as high angle annular dark-field scanning
electron microscopy (HAADF-STEM) or the regular in situ/operando technique (Kottwitz et al., 2021; X. Li et al., 2019).



Figure 4.15 : High-resolution transmission electron microscope (HRTEM) images and particle size of (a) RHSiO₂-Cu-Al-Mg, (b) RHSiO₂-Ni-Al-Mg, and (c) RHSiO₂-Pd-Al-Mg bifunctional catalysts.



Figure 4.16 : BET hysteresis loop of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg

Table 4.6 : Textural properties of RHSiO₂-(M=Cu, Ni or Pd)-Al-Mg single-atom catalysts

Catalysts	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Diameter (nm)
Cu/RHSiO ₂ -Al-Mg	93.87	0.44	18.8
Ni/RHSiO ₂ -Al-Mg	93.32	0.42	18.6
Pd/RHSiO ₂ -Al-Mg	93.94	0.45	19.3

4.1.4.3 Crystallinity, Morphological and Surface Analysis of RHSiO₂-Cu-Al-Mg

(pH 1, 3, 7 and 10)

On the other hand, Figure 4.17 revealed that increasing the pH during synthesis will result in a lowered overall lattice constrain within the structure of the catalyst. In conjunction with HRTEM analysis of each catalyst as shown in Figure 4.18 (a-d), too much of lattice strain on the structure of the catalyst will cause it to collapse as in the case for RHSiO₂-Cu-Al-Mg 1(Gorrepati et al., 2010; Villaverde et al., 2013b). However,

without sufficient strain on the lattice arrangements, the structure relaxes and results in a less ordered arrangements of the metal particles within the SiO₂ support (Valliant et al., 2012). The XRD analysis further revealed that such decrease in lattice strain resulted in shifting of lattice arrangements from tetragonal (for pH 1,3 and 7) to monoclinic arrangement in RHSiO₂-Cu-Al-Mg 10. Interestingly, both the particle size and d-spacing increases when introduced to increasingly basic environment. This is most likely due to lower rate of flocculation among the silica nanoparticles in the basic medium (Gorrepati et al., 2010).



Figure 4.17 : XRD analysis of lattice strain for RHSiO₂-Cu-Al-Mg catalysts synthesized at pH 1, 3, 7 and 10

Catalyst	Crystal System	Particle size (nm)	d-spacing (nm)
RHSiO ₂ -Cu-	Monoclinic	11	0.465
Al-Mg 1 RHSiO2-Cu-	Monoclinic	13	0.471
Al-Mg 3			
RHSiO ₂ -Cu-	Monoclinic	20	0.501
Al-Mg 7 RHSiO2-Cu-	Tetragonal	23	0.512
Al-Mg 10	801101		

Table 4.7 : X-ray diffraction analysis on RHSIO2-Cu-Al-Mg nanoparticle atdifferent pH



Figure 4.18 : HRTEM images of RHSiO₂-Cu-Al-Mg catalysts synthesized at pH 1, 3, 7 and 10 indicated by (a-d) respectively.

4.2 Tandem Hydrogenation-Esterification of Furfural

4.2.1 COSMO-RS Analysis

COSMO-RS computations were conducted based on BP-TZVP-C30-1401-ctd parameterization in COSMOthermX to understand the realistic interaction of furfural and Cu⁰ on the surface of RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg catalysts. This

included in-situ esterification of furfuryl alcohol with acetic acid during the one-pot hydrogenation-esterification process. The interactions were estimated using the σ -profiles of the molecules (Figure 4.19). The σ -profiles were categorized into three regions; hydrogen bond donor (HBD) region ($\sigma < -0.82 \text{ e/nm}^2$), non-polarity region ($-0.8.2 \text{ e/nm}^2$ $< \sigma < +0.82 \text{ e/nm}^2$), and the region of hydrogen bond acceptor (HBA) ($\sigma > 0.8.2 \text{ e/nm}^2$) (Halilu, Hayyan, et al., 2019). Figure 4.19 (a) compared the σ -profiles of furfuryl alcohol's HBA, centered at 1.544 e/ nm², with that for acetic acid whose HBD centered at σ -surface with the charge density is either at -2.037 or -1.743 e/nm². By implication, furfuryl alcohol and acetic acid can interact at their respective σ -surface accrued to HBA or HBD, respectively. As shown in Figure 4.19 (b), hydrogen can interact with Cu⁰ due to the overlap of their σ -profiles at the non-polarity region. Furfural σ -profiles also have an overlap with $Cu^0 \sigma$ -profiles, suggesting their interaction. According to Figure 4.17 (c), σ -profiles of furfural whose non-polarity region centered at -0.7457 to 0.04121 e/nm², showed that furfural can interact with hydrogen whose non-polarity region centered at σ surface with the charge density is either -0.3802, -0.0987 or 0.237 e/nm². Similarly, based on Figure 4.19 (d), furfuryl alcohol can interact with hydrogen because they share an overlap of their σ -surface over the non-polarity region. These simulations provided valuable data in determining the functional groups involved in each hydrogenation and esterification reaction that took place inside a closed pressurized container. The data proved valuable in understanding the underlying mechanism involved in these tandem reactions.



Figure 4.19 : σ-profiles as a measure for the interaction between (a) furfuryl alcohol and acetic acid, (b) hydrogen and Cu metal, (c) furfural and hydrogen, and (d) hydrogen and furfuryl alcohol.

4.2.2 Tandem Hydrogenation-Esterification of Furfural Using RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg

The obtained COSMO-RS results were consistent with the performance of the catalysts investigated for OHE of furfural with acetic acid at 20 bar H₂ (Figure 4.20 a-c) and 40 bar H₂ (Figure 4.20 d-f) at 150, 200, and 250 °C. As shown in Figure 4.20 (a), the RHSiO₂-Cu catalyst is selective for the hydrogenation of furfural to furfuryl alcohol not to furfuryl acetate. This is because the RHSiO₂-Cu catalyst does not have sufficient amount of medium acid sites (Figure 4.4 to facilitate the esterification step further, and hence, no furfuryl acetate was produced. In contrast, the RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg catalysts were effective for both furfural hydrogenation and furfuryl alcohol

obvious because both RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg catalysts have sufficient amount of medium acid sites (Figure 4.4 (b)) that could facilitate the esterification reaction step. Due to the presence of strong acid sites in RHSiO₂-Cu-Al catalyst Figure 4.4, it showed lower activity towards furfuryl acetate formation compared to the RHSiO₂-Cu-Al-Mg catalyst in the OHE reaction of furfural. This is because the OHE reaction of furfural requires medium strength acidic sites. Thus, the addition of Mg to the RHSiO₂-Cu-Al catalyst regulated its acidity to the medium strength, thus the RHSiO₂-Cu-Al-Mg catalyst showed the highest selectivity to furfuryl acetate. The superior BET surface area (Table 4.5) and high dispersion of active metal in RHSiO₂-Cu-Al-Mg (Table 4.1) could also be the key reasons for its high catalytic performance in OHE of furfural. It was observed that the selectivity to furfuryl acetate over both RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg was decreasing as the reaction temperature was increased from 150 to 250 °C. irrespective of the hydrogen pressure. This trend was justified by the fact that in some cases, an increase in reaction temperature decreases the catalyst acidity and its proton availability for the reaction. Furthermore, at extreme temperature and pressure, the reaction path towards formation of products via cracking and hydrodeoxygenation begin to take precedence over products of hydrogenation and/or esterification (Tang et al., 2008a; Wanjin Yu et al., 2011e).



Figure 4.20 : OHE of furfural over (a) 5 wt.% RHSiO₂-Cu at 20 bar, (b) 5 wt.% RHSiO₂-Cu-Al at 20 bar, (c) 5 wt.% RHSiO₂-Cu-Al-Mg at 20 bar, (d) 5 wt.% RHSiO₂-Cu at 40 bar, (e) 5 wt.% RHSiO₂-Cu-Al at 40 bar, and (f) 5 wt.% RHSiO₂-Cu-Al-Mg at 40 bar. Error is ± 2% for all the experiments.

The RHSiO₂-Cu-Al-Mg catalyst shows a high efficiency in OHE of furfural with 24.5% and 75.1% selectivity to furfuryl acetate and furfuryl alcohol, respectively, outperforming various conventional noble metal-based catalysts, such as Pd/Al-SBA-15 and Pd/C-Al₂(SiO₃)₃ (Figure 4.21 (a)). The reusability test of the catalysts for OHE of furfural was carried out at 150 °C and 20 bar for 4 hours (Figure 4.21 (b)). It was observed that RHSiO₂-Cu-Al-Mg catalyst shows a lesser overall drop in furfural conversion of ~18% compared to that of RHSiO₂-Cu and RHSiO₂-Cu-Al each with drops of ~25%. The catalyst deactivation during the liquid-phase hydrogenation of furfural was most likely due to the leaching of the active metal components. We propose that these issues were not too prominent in case of RHSiO₂-Cu-Al-Mg catalyst, due to several innate characteristics of the catalyst. The high dispersion of Cu on the RHSiO₂ surface, along with the strong interaction of Cu with Al and Mg could prevent the leaching of the active metals during the reaction. The RHSiO₂ catalyst shows the highest TOF value compared to that of RHSiO₂-Cu and RHSiO₂-Cu-Al catalysts (Figure 4.21 (c)). This is attributed to superior BET surface area (Table 4.5) and high dispersion of active metal in RHSiO₂-Cu-Al-Mg catalyst (Table 4.1) (Jun Wang, 2011; Y. Tang et al., 2010b; Wanjin Yu et al., 2011a).



Figure 4.21 : (a) Comparison of the catalytic efficiency of 5 wt.% RHSiO₂-Cu-Al-Mg with 5 wt.% Pd/Al-SBA-15 and 5 wt.% Pd/C-Al₂(SiO₃)₂ catalysts for OHE of furfural at 150 °C, 20 bar, and 4 h, (b) repeated OHE of furfural over 5 wt.% RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg catalysts at 150 °C, 20 bar, and 4 h (error is ± 2%), and (c) TOF with respect to the production of furfuryl alcohol and furfuryl acetate (error is < 2%).

4.2.3 Tandem Hydrogenation-Esterification of Furfural using RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg

4.2.3.1 Effect of Reaction Time

Initially, the amount of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg catalysts each with known lattice strain was fixed at 0.1 g wherein the active singleatoms were 0.5 wt.%. The result for the effect of reaction time during hydrogenationesterification of furfural over the single-atom RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg are shown in Figure 4.22. The reaction period was from 1 to 4 h and the reaction conditions were maintained at 150 °C and H₂ 20 bars. In Figure 4.22 (a),

as the reaction time was increased from 1 to 4 h, all three single-atom catalysts show a similar increasing pattern in furfural conversion with different magnitude. For instance, conversion of furfural over RHSiO2-Cu-Al-Mg single-atom catalyst increased from 43.2 % in the first 1 h to 91.5 % after 4 h. On a similar account, conversion of furfural over RHSiO₂-Ni-Al-Mg increased from 40.3 % in the first 1 h to 87.6 % after 4 h. These results confirm that differences in the lattice strain of SACs does affect or change furfural conversion as reaction time elapsed. The conversion of furfural over RHSiO₂-Pd-Al-Mg increased from 48.2 % in the first 1 h to 87.1 % after 4 h. This shows that sufficient amount of lattice strain is the key in obtaining the maximum conversion of furfural. We postulated that too much lattice strain exerted too much steric hindrance within the structure of the catalyst thus preventing efficient contact between active sites and the reactant. However, the activity of the three single-atom catalysts shows the varying level of selectivity towards the formation of furfuryl alcohol and furfural acetate, as shown in Figure 4.22 (b) and Figure 4.22 (c), respectively. The RHSiO₂-Cu-Al-Mg shows 78.5 % selectivity to furfuryl alcohol as shown in Figure 4.22 (b), and 21.5 % selectivity furfuryl acetate as in Figure 4.22 (c) after 4 h of reaction. As for RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg, they show poor selectivity to furfuryl alcohol and furfuryl acetate. The poor activity of RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg as compared to RHSiO₂-Cu-Al-Mg is attributed to the single-atom crystal perfection. For instance, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg have 99.876% and 99.643% crystal perfection with 0.124 and 0.357% lattice strain. In contrast RHSiO₂-Cu-Al-Mg have the highest crystal perfection value of 99.906 % and the lowest lattice strain of 0.094 %. The production of furfuryl alcohol over the RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg confirmed the activity of the single-atom active sites in the bulk structure of RHSiO₂-Al-Mg support material. This implies that the 20-bar H₂ pressure and 150 °C temperature is sufficient enough to induce splitting of the hydrogen into proton and hydride wherein, the

hydride promoted the nucleophilic attack on the furfural to produce furfuryl alcohol similar to previous reports (Halilu et al., 2016c; Halilu, Hussein Ali, et al., 2019c). The reducibility of the single-atom catalyst phase discussed during the H₂-TPR analysis in Figure 4.2 further support this claim. Also, the production of furfuryl acetate, over the RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg confirmed that the activity of the single-atom active sites could promote the production of *in-situ* furfuryl alcohol, which served as an *in-situ* substrate for the esterification step. The esterification step was possible because the RHSiO₂-Al-Mg has a tuned Brønsted acidity, as confirmed by the pyridine-IR analysis discussed in Figure 4.6. Overall, 4 h tandem hydrogenationesterification reaction time over the RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg is suitable to produce high furfural conversion and selectivity toward furfuryl alcohol and furfuryl acetate, particularly for RHSiO₂-Cu-Al-Mg due to low lattice strain of the catalyst after doping. The three catalysts show similar conversion but RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg show much lower selectivity towards furfuryl alcohol and furfuryl acetate, implying the formation of products other than the targeted compounds. This can be attributed to Ni and Pd having much higher tendencies to convert products through cracking processes such as furan and methyl furan (Sitthisa & Resasco, 2011a). This is further outlined in Ni, showing decreasing furfuryl alcohol selectivity as reaction time increases which can be related to Ni favoring the formation of products via cracking and/or hydrodeoxygenation.



Figure 4.22 : Effect of reaction time for; (a) furfural conversion, (b) selectivity towards furfuryl alcohol, and (c) selectivity furfuryl acetate during tandem hydrogenation-esterification of furfural over RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg, and RHSiO₂-Pd-Al-Mg single-atom catalyst

4.2.3.2 Effect of Temperature

The effect of reaction temperature ranging from 100 to 250 °C was investigated to also check how the differences in lattice strain of the single-atom catalysts affect the Tandem hydrogenation-esterification of furfural to furfuryl acetate. A 4 h reaction time was chosen, and the results are presented in Figure 4.23 for furfural conversion, selectivity to furfuryl alcohol, and furfuryl acetate, respectively. The conversion of furfural over these catalysts is also dependent on the variation of temperature such that, it increases as temperature increases from 100 to 250 °C using all the catalysts. In Figure 4.23 (a), when the temperature increases from 100, 150, 200 to 250 °C, there is a different pattern of converting 5ml furfural for using 60 mg amount of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-

Mg and RHSiO₂-Pd-Al-Mg single-atom catalyst at 20 bar H₂ pressure. At 100 °C, furfural conversion was 88, 44, 55, and 66 % for RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg single-atom catalyst. This difference in conversion could be attributed to the disparity in the catalyst structural perfection induced by lattice strain. As the temperature increases further particularly for RHSiO₂-Cu-Al-Mg, the conversion of furfural converges to a constant amount such that a low temperature of ~ 150 °C is sufficient to induce higher catalyst activity. We believe this observation is attributed to the perfect crystal structure of RHSiO₂-Cu-Al-Mg. Considering that RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg have a lower relative perfect crystal structure, the conversion defines a linear pattern with increasing temperature such that higher temperature is required to induce the activity of the catalyst. Overall, the magnitude of the furfural conversion was higher for RHSiO₂-Cu-Al-Mg catalyst to the tune of 96.6 % for 250 °C after 4 h. In comparison, the conversion of furfural is higher for RHSiO₂-Cu-Al-Mg than RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg. The order of increment in conversion is relative to the temperature (100, 150, 200 and 250 °C) for the catalysts is as follows RHSiO₂-Pd-Al-Mg (45.3, 68.3, 88.1, 90.1 %) < RHSiO₂-Ni-Al-Mg (40.3, 48.7, 77.7, 87.6%) < RHSiO₂-Cu-Al-Mg (76.3, 91.5, 94.3, 96.6%). In Figure 5.7 (b), the selectivity to furfuryl alcohol declines when the temperature increases for all the three different single-atom catalysts and RHSiO₂-Cu-Al-Mg recorded the highest value at 100 °C. The decrease in selectivity to furfuryl alcohol at elevated temperature is attributed to its insitu consumption due to possible cracking to produce other related products. However, at mild temperature, the *in situ* produced furfuryl alcohol is available to be converted into furfuryl acetate, as shown in Figure 4.23 (c). Consequently, the highest selectivity to furfuryl acetate was 21.5 % for RHSiO₂-Cu-Al-Mg. Overall, 100 °C, 20 bars combinations for 4 h reaction gave the best furfuryl alcohol selectivity of ~85 % over RHSiO₂-Cu-Al-Mg.



Figure 4.23 : Effect of reaction temperature on; (a) Furfural conversion, (b) Selectivity towards furfuryl alcohol and (c) Selectivity furfuryl acetate during Tandem hydrogenation-esterification of furfural over RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg single-atom catalysts

4.2.3.3 Effect of Pressure

Figures 4.24 (a)-(c) show the effect of H₂ pressure in furfural conversion and selectivity to furfuryl alcohol and furfuryl acetate. The RHSiO₂-Cu-Al-Mg showed the highest value of conversion at 93.3 % at the highest tested pressure of 40 bar. This was followed by RHSiO₂-Pd-Al-Mg at 91.1% and then RHSiO₂-Ni-Al-Mg at 85.3%. In terms of selectivity, the general observation can be summarized to be that the relatively lower temperatures of 100 and 150 °C are much more favorable to the formation of the targeted products with RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg having the highest selectivity furfuryl alcohol and furfuryl acetate relative to the selectivity at 200 and 250°C. The highest selectivity was shown by RHSiO₂-Cu-Al-Mg at 150°C at 78.5 % of furfuryl

alcohol and 21.5% furfuryl acetate. Similarly, the selectivity towards the targeted product also favors shorter reaction times (1 and 2 h) for both RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg. However, the selectivity towards furfuryl alcohol and furfuryl acetate significantly dropped for these two catalysts past the 2 h reaction time. This is not the case for RHSiO₂-Cu-Al-Mg, which shows a steady increase in selectivity for both products as the reaction time increases. One particularly interesting point is the lack of any furfuryl acetate for RHSiO₂-Ni-Al-Mg at 3 and 4 h of reaction time. Contrary to the previous sets of data, with increased pressure during the reaction, the selectivity towards furfuryl alcohol for all three catalysts decreased. Regarding furfuryl acetate, the selectivity towards this product shows a similar decreasing trend with all three catalysts. RHSiO₂-Cu-Al-Mg still showed the highest selectivity at 21.5% for 20 bar of pressure while RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg showed zero selectivity towards furfuryl acetate at pressures of 30 and 40 bar. The selectivity to furfuryl alcohol is a confirmation that the catalysts are active to hydrogenate furfural through the participation of their active metals such as Cu, Ni, and Pd. In particular, these active metals were proven to be reducible from the TPR experiment. The selectivity to furfuryl acetate further confirmed that the catalysts are active with Brønsted acid sites to esterify the in-situ furfuryl alcohol. The presence of Brønsted acid sites was confirmed by the pyridine FTIR experiment in conjunction with the DFT IR calculation, and these sites are responsible for providing the proton needed to promote the esterification of furfuryl alcohol with acetic acid, thereby producing the corresponding furfuryl acetate.



Figure 4.24 : Effect of H2 pressure on; (a) Furfural conversion, (b) Selectivity towards furfuryl alcohol and (c) Selectivity furfuryl acetate during Tandem hydrogenation-esterification of furfural over RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg single-atom catalyst

4.2.3.4 Rate Constant of Limiting Reaction Step

To further elucidate the capability of each catalyst for the esterification step during the tandem reaction, we employed the Goldschmidt method to calculate the esterification reaction's rate constant concerning temperature and time. The metal function of the catalyst could promote hydrogenation steps, and the esterification step was taken as the limiting reaction. This step is limited by the amount of furfuryl alcohol produced and the availability of suitable acid sites. Therefore, as illustrated in Fig 4.25 (a), the esterification reaction is the highest at 150 °C, which is a relatively mild temperature. This observation further corroborates the decreasing selectivity towards furfuryl acetate once the reaction temperature exceeds 150 °C. Another observation of further interest lies in the

significantly higher rate constant of RHSiO₂-Cu-Al-Mg compared to RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg. Similar observations can be made when calculating the rate constant for increased reaction time. While all three catalysts show an increasing trend in the rate constant up to the 4 h mark, the change is much more significant in RHSiO₂-Cu-Al-Mg relatively.



Figure 4.25 : Limiting reaction rate constants influenced by (a) Effect of temperature and (b) Effect of time.

4.2.3.5 Turnover Frequency Analysis

Furthermore, the trends have shown regarding turnover frequency (TOF) as in Figure 4.26 of both furfuryl alcohol and furfuryl acetate conform to our previous observations. It should be noted that the production of furfuryl alcohol is less susceptible to changes in reaction temperature. This is because furfuryl alcohol is produced at a relatively high rate for both RHSiO₂-Cu-Al-Mg and RHSiO₂-Pd-Al-Mg. The same cannot be said for RHSiO₂-Ni-Al-Mg, which showed significantly low furfuryl alcohol production at temperatures 200 and 250 °C. These observations provided us an insight into the inner workings of the RHSiO₂-(M=Cu, Ni or Pd)-Al-Mg single-atom catalysts during the tandem hydrogenation-esterification reactions. First and foremost, the active metals Cu, Ni, and Pd play a significant role in producing in-situ furfuryl alcohol. As highlighted in

previous studies, each metal has a different degree of selectivity towards furfuryl alcohol, with Cu having the highest selectivity among these three metals towards this specific product. This is largely due to Cu having a preference to interact with the carbonyl group rather than the furan ring, which is in stark contrast to Pd and Ni, favoring the interaction with the latter. This study further elucidates on this matter in terms of ease of which each of the active metals undergoes reduction to form their metal counterparts, a necessary step to ensure high catalytic capability for the hydrogenation portion of the reaction. As shown previously in Figure 4.2, RHSiO₂-Cu-Al-Mg showed the highest degree of reducibility, which further enhanced its ability to catalyze the hydrogenation reaction of furfural to furfuryl alcohol. In terms of the esterification portion of the reaction, each catalyst's catalytic capabilities in descending order are as follows: RHSiO₂-Cu-Al-Mg > RHSiO₂-Pd-Al-Mg > RHSiO₂-Ni-Al-Mg. These results conform to our understanding that in the presence of Al and therefore acidic sites, Ni and Pd favor the formation of products in line with cracking of furfural such as furan. This is amplified in the presence of severe reaction conditions such as temperatures above 150 °C and pressures above 20 bar as discussed previously. From pyridine-FTIR analysis, it can be seen that Brønsted acidic sites rather than Lewis acid sites are the main source of protonation of furfuryl alcohol previously produced from the hydrogenation reaction. This ensures that Al is a viable source of a proton by forming the Al silanol bridge between Si and O atoms within the structure. Based on the data from the Goldschmidt method of analysis, RHSiO₂-Cu-Al-Mg was further confirmed to be superior to the other two catalysts in terms of its ability to catalyze the esterification portion of the reaction. This was further confirmed through similar observations in the trends for each catalysts' turnover frequency.



Figure 4.26 : Analysis of turnover frequency (TOF) of (a) furfuryl alcohol and (b) furfuryl acetate, respectively for all of the catalysts.

4.2.3.6 Reusability of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Cu-Al-Mg

The reusability of each RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg were analyzed with respect to their respective furfural conversions as shown in Figure 4.27 below. The run was repeated thrice in which after each run, the catalysts were recovered in method described previously. The catalyst all showed drops in conversion of furfural; however, the drops were less significant when compared to catalysts without Al and/or Mg. This was consistent in proving the impact that the strong interaction of the active metal components with Al and Mg had in preventing the leaching of the active metals during the reaction. Interestingly, RHSiO₂-Cu-Al-Mg maintained a higher degree of conversion of furfural and we attributed this to the effect lattice strain remaining prevalent as discussed in the previous sections. It should also be mentioned that this is also a direct effect of Ni and Pd having affinity towards formation of products through cracking or hydrodeoxygenation mechanism, which compared to furfural and furfuryl acetate are more prone towards coke formation on the surface of the catalysts (Ambursa et al., 2017).



Figure 4.27 : Reusability tests of RHSiO₂-Cu-Al-Mg, RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg.

4.3 Tandem Hydrogenation-Esterification of Furfural using RHSiO₂-Cu-Al-Mg Synthesized at pH 1, 3, 7 and 10

4.3.1 Overall Tandem Hydrogenation-Esterification of Furfural Analysis

The catalytic performance of each RHSiO₂-Cu-Al-Mg catalysts for one-step hydrogenation-esterification of furfural was analyzed and the results provided in Table 4.8. Generally, catalysts synthesized in basic environment showed lower conversion of furfural (less than 50%) compared to the ones synthesized in acidic medium. RHSiO₂-Cu-Al-Mg 3 recorded the highest conversion at 91.5% while a significant drop should be noted for RHSiO₂-Cu-Al-Mg 1 at only 69.1%. This is highly related to the degree of Cu⁰ species available on the catalyst surfaces which is especially important for the first phase of the hydrogenation of furfural. In terms of selectivity, RHSiO₂-Cu-Al-Mg 1, RHSiO₂-Cu-Al-Mg 7 and RHSiO₂-Cu-Al-Mg 10 showed relatively similar selectivity towards both furfuryl alcohol and furfuryl acetate. This is very much due to their similar acidity profile as demonstrated in Figure 4.7 (a). However, RHSiO₂-Cu-Al-Mg 10 shows slightly higher selectivity towards furfuryl acetate and this is likely due to the higher amount of

acid site available compared to RHSiO₂-Cu-Al-Mg 1 and 7; which relates to better in-situ conversion of furfuryl alcohol to furfuryl acetate (Y. Tang et al., 2010a; Wang et al., 2011). The selectivity towards furfuryl acetate is much higher in RHSiO₂-Cu-Al-Mg 3 at 21.7% and this is related to the availability of stronger acid sites in the catalyst which allowed for more efficient conversion of furfuryl alcohol to furfuryl acetate (Wanjin Yu et al., 2011b). It should also be noted that RHSiO₂-Cu-Al-Mg 3 showed better performance in hydrogenation-esterification of furfural even when compared to other catalysts from previous studies. This is very much due to the addition of MgO into the structure of the catalyst which not only regulates the acidity of the catalyst but provider of hydrogen spillover onto the Cu active sites which further promotes the efficiency of hydrogenation of furfural. Based on these observations, it should be noted that while each of the catalysts possess acid sites with medium strength (due to the regulatory effect of Mg), aside from RHSiO₂-Cu-Al-Mg 3 the remaining three catalysts exhibited insufficient acidity to reliably convert furfuryl alcohol to furfuryl acetate.

CATALYST	FURFURAL CONVERSION	SELECTIVITY (%)	
		FURFURYL	FURFURYL
	(%)	ALCOHOL	ACETATE
RHSiO ₂ -Cu-Al-	69.1	95.8	4.2
Mg 1			
RHSiO ₂ -Cu-Al-	91.5	78.5	21.5
Mg 3			
RHSiO ₂ -Cu-Al-	47.2	95.1	4.9
Mg 7			
RHSiO ₂ -Cu-Al-	49.3	94.3	5.7
Mg 10			

 Table 4.8 : One-step hydrogenation-esterification of furfural to form furfuryl alcohol and furfuryl acetate

4.3.2 Reusability of RHSiO₂-Cu-Al-Mg for Tandem Hydrogenation-Esterification of Furfural Analysis

The reusability of each catalyst was tested for a total of three more cycles (Figure 4.28). The reaction conditions were set to be 3mmol of furfural, 150 °C, 20 bar, 300 rpm, 100 mg of each catalyst and 4 h of reaction time. After each cycle, each of the catalyst was washed with acetone and methanol to remove any remaining reactants and products, before they were subsequently dried in an oven at 100 °C for up to 12 hours. The results were similar for each catalyst in that they show decreased conversion of furfural consistently from the first to the third cycle. However, the decrease while not negligible is much lower than expected especially compared to previously applied silica based catalysts (Jun Wang, 2011; Tang et al., 2008b). The decrease in activity requires further understanding and is still being investigated.

The superiority of pH 3 in terms of reusability compared to catalysts synthesized at other pHs are reflectively of the well-ordered section as reflected in the HRTEM results in Figure 4.18. It has been shown that the presence of lattice fringes creates defects within the structure of the catalysts, which allows for more efficient removal of coke deposits during the cleaning process in between runs. Furthermore, during the reaction itself the presence of such defects facilitate transport of the reactants from the active metal to the acid sites and finally into the surrounding solvent, thus further preventing overwhelming coke deposition (Halilu et al., 2016c).



Figure 4.28 : Reusability of RHSiO₂-Cu-Al-Mg catalysts for one-step hydrogenation-esterification of furfural. Reaction conditions: 3mmol of furfural, 150 °C, 20 bar, 300 rpm, 100 mg of each catalyst and 4 h of reaction time.

4.3.3 Discussion on Structure-activity relationships of RHSiO₂-Cu-Al-Mg

The performance of supported metal nano catalysts hinges heavily on several factors including particle size, the overall structure of the nanoparticles, the active metal's oxidation state and presence of interface between the metal and support (Nakagawa et al., 2013b; Pang & Medlin, 2011; Sitthisa & Resasco, 2011b; L. Zhang et al., 2013b). The latter is of particular importance in a bimetallic or in this case trimetallic catalyst, in which these metal nanoparticles are dispersed in the supporting material.

In this study, RHSiO₂-Cu-Al-Mg 3 outperforms the other catalysts in terms of the onestep hydrogenation-esterification of furfural (Table 4.8). There were a few main factors that contribute to the superiority of RHSiO₂-Cu-Al-Mg 3. The structural defects within the MgO and SiO₂ combined with the presence of Cu⁰ largely present in RHSiO₂-Cu-Al-Mg 3 favor the hydrogenation of furfural to furfuryl alcohol while acid sites due to the presence of Al³⁺ with sufficient strength and amount converts the furfuryl alcohol to furfuryl acetate in tandem (Halilu et al., 2016b). The oxygen vacancies within MgO further enhanced the adsorption of H_2 gas and splitting them creating spill over towards the activated furfural which facilitates hydrogenation process (Hillary et al., 2017; Sudarsanam et al., 2019).

XPS analysis on the samples synthesized at varying pH elucidated the presence of not just Cu^{2+} but Cu^0 in RHSiO₂-Cu-Al-Mg 1 and RHSiO₂-Cu-Al-Mg 3 (both were synthesized in acidic medium). The latter distinguished itself by having a large number of oxygen vacancies in the SiO₂ and Mg-O interface which may have been the determining factor in the its ~24 % increase in furfural conversion (Villaverde et al., 2013b; Vorotnikov et al., 2012b). In terms of overall hydrogenation-esterification process, as indicated in NH₃-TPD analysis of RHSiO₂-Cu-Al-Mg 3, the catalyst provided sufficient acidity, presumably of medium strength, at large enough concentration of 1851.7 µmol/g which can more efficiently convert furfuryl alcohol to furfuryl acetate.

The effect of pH during synthesis of catalyst can also affect the structure of the overall catalyst. The XRD analysis revealed that the decrease in lattice strain causes lattice arrangements to change from tetragonal for RHSiO₂-Cu-Al-Mg 1,3 and 7 to monoclinic arrangement in RHSiO₂-Cu-Al-Mg 10. As observed in Figure 4.18, RHSiO₂-Cu-Al-Mg 3 contains atomic particles in a more orderly manner (layers of atom stacked on one another) compared to the other catalysts. We believe this arrangement further contributed to its catalytic performance by providing sufficient surface defects within the structure (Kasatkin et al., 2007). The sufficient lattice strain also allowed for a strong interaction between the active metals and support which further strains the metal increasing its catalytic performance. Hence, the importance of pH regulation can be inferred here as sufficient lattice strain is required to prevent collapse of the structure as observed in RHSiO₂-Cu-Al-Mg 1.

4.4 Proposed Mechanism for Tandem Hydrogenation-Esterification of Furfural

The pathways for the hydrogenation-esterification of furfural to furfuryl acetate alcohol over the RHSiO₂-Cu-Al-Mg, compared to RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg catalysts, were presented in Scheme 1. There are two steps; 1) The hydrogenation step, and 2) The esterification step. Considering the first hydrogenation step, the singleatoms of Cu, Ni, and Pd metal dissociated hydrogen molecule (H₂) into proton and hydride differently irrespective of their lattice strain, and this was demonstrated by the H₂-TPR experiment. The hydride (H⁻) formed is a nucleophile capable of attacking the C (Sp^2) -O carbonyl carbon in furfural to promote nucleophilic reduction reaction. In essence, the positive character of the carbon in furfural increases due to the electronegativity difference between the carbon and oxygen availing the attack of hydride (H⁻). Consequently, there is possible electron transfer from the HOMO of the H^- nucleophile into the LUMO of the electrophile (C(Sp²)-O carbonyl carbon). By implication, the electron pair in H⁻ –HOMO interacted with the antibonding π electron in LUMO of C(Sp²)-O forming a δ bond. In terms of geometry, this electron movement from H^- –HOMO causes the trigonal C (Sp²)-O carbon in carbonyl to change to tetragonal C (Sp³)-O hybridized state in furfuryl alcohol. Mostly, this will be propagated by an additional protonation step inducing a mesomeric effect that results in forming *in*situ/ex-situ furfuryl alcohol due to the single-atom metallic catalysis. The formation of furfuryl alcohol is supported by the Monte Carlo statistical mechanic fact that conformational equilibrium of furfural avails its carbonyl group to rotates along the furan ring, thereby exposing $C(Sp^2)$ -O carbonyl carbon functionality to the single-atom catalysis (Halilu et al., 2016c). Therefore, during the Tandem reaction, furfural adsorption occurs at the terminal oxygen atom of the furfural furan ring by non-covalent interaction with the Brønsted acid or Lewis site. This mechanistic observation is strictly possible because the SACs support surface is non-reducible at the 250 °C/40 bar H₂ pressure as

confirmed by the H₂-TPR analysis. Therefore, the mechanism for hydrogen consumption to promote the production of nucleophilic H⁻ on the surfaces of SACs is energetically impossible to occur via hydrogen spillover. We have confirmed the non-reducibility of Fe₃O₄, SiO₂, and their hybridized state of Fe₃O₄-SiO₂ previously, particularly under the hydrogenation condition up to 250 °C and 20 bar H₂ pressure (Halilu et al., 2016c). In this present mechanism, the RHSiO₂-Al-Mg support material is also confirmed to be nonreducible up to 250 °C, ascertaining the absence of any likely hydrogen spill over. Significantly, there should not be a hydrogen spill over for the mechanism described for the tandem reaction to be valid.

In the second esterification step, the *in-situ* furfuryl alcohol through the activity of RHSiO₂-Cu-Al-Mg, compared to RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg is facilitated by the presence of Brønsted acid sites as shown in Figure 4.6. Initially, the Brønsted acid on RHSiO₂-Cu-Al-Mg, compared to RHSiO₂-Ni-Al-Mg and RHSiO₂-Pd-Al-Mg catalysts promoted the reaction with furfuryl alcohol to produce a complex of the form $R - OH_2^+$. Therefore, the complex further promoted an esterification reaction with acetic acid to produce furfuryl acetate. This reaction was observable because we ensured the absence of moisture in the reacting system else, the complex $R - OH_2^+$ will react with water to form R-OH and H_3O^+ as described in Fig 4.29.

The mechanism proposed here are reflective of the RHSiO₂-M-Al-Mg multifunctional catalysts, irrespective of their synthesis during pH. Regardless of the pH, we have established that the active metal, Cu is present and chemisorbed within the silica support with similar oxidation state, Cu⁰ during the reaction. Hence, it is within reasonable conjecture to assume that mechanism will be the same disregarding the difference in synthesis pH as all the components of the reaction are kept the same, to the best of our ability.



Figure 4.29 : Proposed tandem hydrogenation esterification reaction of furfural over RHSiO₂-(M=Cu, Ni or Pd)-Al-Mg single-atom catalysts.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study reported the development of rice husk derived silica (RHSiO₂) RHSiO₂-Cu, RHSiO₂-Cu-Al and RHSiO₂-Cu-Al-Mg catalysts using an efficient one-pot sol-gel method. A promising strategy was proposed to successfully modulate the acidity of RHSiO₂-Cu-Al catalyst using Mg functionalization. Among the catalysts tested, the RHSiO₂-Cu-Al-Mg catalyst showed better activity in one-pot hydrogenationesterification of furfural with a higher selectivity to furfuryl acetate (24.5%), outperforming various conventional noble metal-based catalysts, such as Pd/Al-SBA-15 and Pd/C-Al₂(SiO₃)₃. Optimum amounts of acid-redox sites, superior BET surface area, and high dispersion of active metal were the key reasons for high performance of RHSiO₂-Cu-Al-Mg catalyst in one-pot hydrogenation-esterification of furfural.

Our results also provided evidence on how lattice strain in single-atom catalyst influences the tandem transformation reaction, particularly using furfural as substrate. Our findings count on the synthesis of suitable single atom catalysts (SACs) with tuned acid function, which promoted the second esterification step beside the single-atoms. Detailed characterization of the SACs enabled an accurate description of the properties of the SACs at length scales relevant to experiments. The results shed light on the importance of correlating changes in the lattice strain of SACs for the fundamental catalytic performance of tandem catalysis. They provided a foundation for the thoughtful account of the selectivity and performances required of SACs, owing to the low lattice strain. Future developments require robust evaluation of the synergy of SACs lattice strain-SACs performance. Given the rigor of high-pressure tandem reactions as reported herewith, exhaustive measurement cannot be established on individual lattice strainactivity correlation without further recommendations. The evidence for the role of lattice strain in bifunctional catalysts, which strongly influence the tandem catalytic hydrogenation-esterification of furfural was investigated for the first time. Lattice strain in bifunctional catalysts as low as 0.1% is sufficient to improve their activity toward viable tandem reaction through the metal and acid functions. The Cu active metal with a low lattice strain of 0.094% has low size distribution in the atomic regime, is classifiable as a single-atom bifunctional catalyst, and performed better. High lattice strain arises for Ni and Pd active metals such as 0.124%, and 0.357% arise from their high particle size distribution far from the atomic regime and not classifiable as single-atom bifunctional catalysts. The result confirmed that aside from ensuring concurrent metal and acid function in a bifunctional catalyst, the lattice straining effect is an intrinsic factor that determines the overall catalytic performance towards the production of furfuryl acetate. This study lay a foundation for investigating the relationship between the lattice strain parameters of bifunctional catalysts and their impact on tandem reactions. This has great potential for scalable industrial production of fuel, fuel additives, or platform chemicals.

The effects of varying pH during synthesis of Cu-Al-Mg supported on rice husk silica on the structure, morphology and its catalytic properties were studied. XRD and HRTEM analysis of the catalysts revealed that as the pH is increased the lattice strain within the overall structure decreases, from 0.42 % (RHS-Cu-Al-Mg-1) to 0.12%(RHSiO₂-Cu-Al-Mg 10) which led to decrease in orderliness of the overall structure. The XPS data further revealed that the acidic condition favors the formation of Cu⁰, while basic condition favors formation of Cu²⁺ in the catalyst, which is the result of the reducibility of the catalyst as shown by the TPR analysis. The strength of acid sites available due to addition of Al³⁺ is also affected as the interaction between Al³⁺ the other components is affected by the pH which controls the rate of aluminosilicate precipitation. These factors combined to reveal that at pH 3 the conditions of the final catalyst product facilitates both hydrogenation and esterification reaction resulting in the highest conversion of furfural at 91.5%. **Objectives Achieved:**

- Multifunctional metal catalyst supported on rice husk derived silica were successfully synthesized with two variations in synthesis parameters: a) active metal introduced; b) pH during synthesis.
- The multifunctional metal catalyst supported on rice husk derived silica was characterized in terms of surface properties, reducibility, crystallinity and morphology including the batches from the said variation in parameters.
 - pH 3 provided the ideal condition to synthesize the final catalyst product which facilitated both hydrogenation and esterification reaction resulting in the highest conversion of furfural at 91.5%.
- 3. The performance of the multifunctional metal catalyst supported on rice husk derived silica in hydrogenation of furfural; hydrogenation esterification reaction using in-situ furfuryl alcohol and acetic acid.

- Among the catalysts tested, the RHSiO₂-Cu-Al-Mg catalyst showed better activity in one-pot hydrogenation-esterification of furfural with a higher selectivity to furfuryl acetate (24.5%), outperforming various conventional noble metal-based catalysts, such as Pd/Al-SBA-15 and Pd/C-Al₂(SiO₃)₃.

Cu showed the highest selectivity among the three tested active metals towards reduction of furfural. This is largely due to Cu having preference to interact with carbonyl group rather than the furan ring which is in stark contrast to Pd and Ni which favors interaction with the latter.

5.2 Suggestion for Future Works

- 1. Further optimization of the synthesis parameters of the RHSiO₂-Cu-Al-Mg catalyst which include:
 - a) Temperature during sol-gel formation
 - b) Calcination temperature programming
 - c) Metal loading ratio (Cu:Al:Mg)
- 2. Development of method to further improve control the strength of acidic sites in the catalyst.
- 3. Testing the RHSiO₂-Cu-Al-Mg catalyst at a larger scale for improvement and enabling application for industrial processes.

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