Hydrogenation reaction using supported palladium Nano-particles

Thesis submitted in accordance with the regulations of the

University of Cardiff for the degree of

Doctor of Philosophy

By

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2014

بسم الله الرحمن الرحيم

***In The Name Of Allah, The Most Compassionate,
The Most Merciful***

Declaration

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To parents

To my wife

To my daughter Shadn and Lujain

To my sons Anas and Omar

To my brothers and sisters

Publications

1- **Obaid F. Aldosari**, Jennifer K. Edwards, Meenakshisundaram Sankar, Peter J. Miedziak, Sarwat Iqbal, David W. Knight and Graham J. Hutchings, *Solvent-free liquid phase hydrogenation/hydrogenolysis of cyclohexanol using supported Au:Pd catalysts,* Poster day in University of Cardiff, Cardiff, United Kingdom, May 2013.

2- Sarwat Iqbal, Xi Liu, **Obaid F. Aldosari**, Peter J. Miedziak, Jennifer K. Edwards, Gemma L. Brett, Adeeba Akram, Gavin M. King, Thomas E. Davies, David J. Morgan, David K. Knight and Graham J. Hutchings, *Conversion of furfuryl alcohol into 2-methylfuran at room temperature using Pd/*TiO_2 *catalyst*, Catalysis Science & Technology, 2014, DOI: 10.1039/c4cy00184b.

Acknowledgements

I would like to begin with praising and thanking God, Allah, the almighty for all his bounties upon me and for his assistance in my studies, as without Him this work would not have been achieved

I would like to greatly thank my supervisor, Professor Graham Hutchings, for all his guidance and support during my studies. I am also very grateful to Dr.Jennifer Edwards; Dr.Sarwat Iqbal, Dr.Gemma Brett, and Dr.Peter Miedziak for their guidance and support in resolving technical problems and revising my thesis. Thanks as well to all the technical staff in the Chemistry Department. I would also like to thank my co-supervisor Professor David W. Knight. My thanks also go to all the people in Lab. 0.90, Lab. 1.88 and 1.86 who helped me during my studies. Special thanks go to my friends Dr. Salem Bawaked, Dr. Mosaed Alhumaimess, Dr. Hamed Alshammari, and Dr. Moataz Morad who made this time enjoyable. I am grateful to my special friends Dr. Ibrahim Alhaidari, Dr. Raee Alqhtani, Dr. Ali Alotaify Mr. Mansour Aldosari, Mr.Abdullah Alfadil, Mr. Ali Almiman, Mr. Ibrahim Alsokiti and Mr. Abdullah Albahdil with whom I have spent a lovely time in the UK.

Thanks are due to my sponsor, the Ministry of Higher Education, in Saudi Arabia for their financial support and for giving me this opportunity to increase my knowledge.

Finally, great thanks are due to my parents, my sisters and brothers, and I would especially like to thank my wife, my daughters and my sons for their unlimited patience and sacrifices- without them I do not think I would have completed this journey successfully.

Abstract

Hydrogenation is one of the major processes used in commercial and academic applications in the manufacture of chemical intermediates; high tonnage products of high value, and useful chemicals, such as agrochemicals and pharmaceuticals. Free solvent hydrogenation of cyclohexanol using Au, Au:Pd and Pd/$Cs_xH_{0.5}PW_{12}O_{40}$ catalysts have been performed in the liquid phase. Reaction conditions, for example supports with/without Cs-salt loading, metal loading and/or ratio were varied to achieve ideal conditions. The Palladium supported on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is a successful catalyst for such hydrogenation, and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ has been shown to be the best of the supports investigated for the preparation of catalysts using the impregnation method.

Pd, Au and Au:Pd catalysts supported on TiO_2 have been used for the hydrogenation of furfuryl alcohol and furfural with H_2 at room temperature. The influence of the pressure, catalyst mass, support, Au:Pd variation, Pd loading and solvent have been investigated. In addition, Ru and Ru:Pd was studied with furfural, and also the effect of Ru:Pd ratios. The selective hydrogenation of both Furfuryl alcohol and Furfural into 2-methylfuran was investigated at room temperature using Palladium supported catalysts. This study has shown that Pd/TiO_2 catalysts can be very effective for the synthesis of 2-methylfuran at room temperature and low pressure hydrogen (1-3 bar). The effect of various reaction conditions (pressure, catalyst amount, and solvent) has been studied. Controlling the catalyst composition can control the selectivity to molecules with multiple functioning groups, and reaction conditions can promote or hinder the various reaction pathways, thus increasing selectivity to the desired hydrogenation yields.

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Chapter 1

Introduction

Chapter 1

1. Introduction:

1.1 Historical background:

The word "catalysis" was introduced for the first time by J.J Berzelius in 1836 when he described some improved chemical reactions.[1,2] G.G. Bond defines a catalyst, as "*a substance that increases the rate at which a chemical system approaches equilibrium, without being consumed in the process*"[3] Catalysis is an important topic in chemistry, whether it is for academic research or industrial research. Catalysis has other important applications such as its successful use in the control of pollution, known as green chemistry. It plays a major role in the production of a wide range of products, and is an essential part of the manufacturing process. Between 85-90% of chemical industry products are made via catalyst processes.[4] Catalysts are big business, and Europe had a turnover of 3.7 billion dollars reported in 1998 according to the British agency Frost and Sullivan.[5] In fact, catalysis represents about a quarter of the market in chemistry.[5] Recently, nanoparticle size metals have given rise to interest in a diverse range of fields, including catalysis. Owing to the large fraction of metal atoms that are exposed to the surface, the use of metal nanoparticles as nanocatalysts allows mild reaction conditions and high catalytic efficiency in a wide range of chemical transformations.[6]

1.1.1 Definitions of catalyst and catalysis:

Substances that change the rate of a reaction, without being consumed by the reaction, are referred to as catalysts. Catalysis is the word used to describe the action of the catalyst. Catalysts work by providing a reaction pathway with an alternative mechanism and low activation energy barrier, or by inhibiting the one already present. However, the catalyst will not change the thermodynamics of the reaction or the equilibrium position, because the effect of the catalyst will be placed on both the forward and reverse reactions (i.e. increasing the rate constant of the reaction K_1 and K_2)[7], as shown below:

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$$

The rate constant k, is defined by the Arrhenius equation:

$$\boldsymbol{k = A \,.\, \exp^{(-Ea/RT)}}$$

Equation 1.1: Arrhenius equation

Where ***A*** is the collision frequency, ***Ea*** is the activation energy (KJ mol^{-1}), ***R*** is the gas constant (8.314 $JK^{-1}\ mol^{-1}$) and ***T*** is the temperature.

As a consequence, the rate of the reaction is increased. For example, a hypothetical exothermic chemical reaction, with or without a catalyst, that leads to the same product, is shown in Figure 1.1, where it can be observed that the uncatalysed reaction pathway has a much higher activation energy barrier than that of the catalysed reaction pathway.

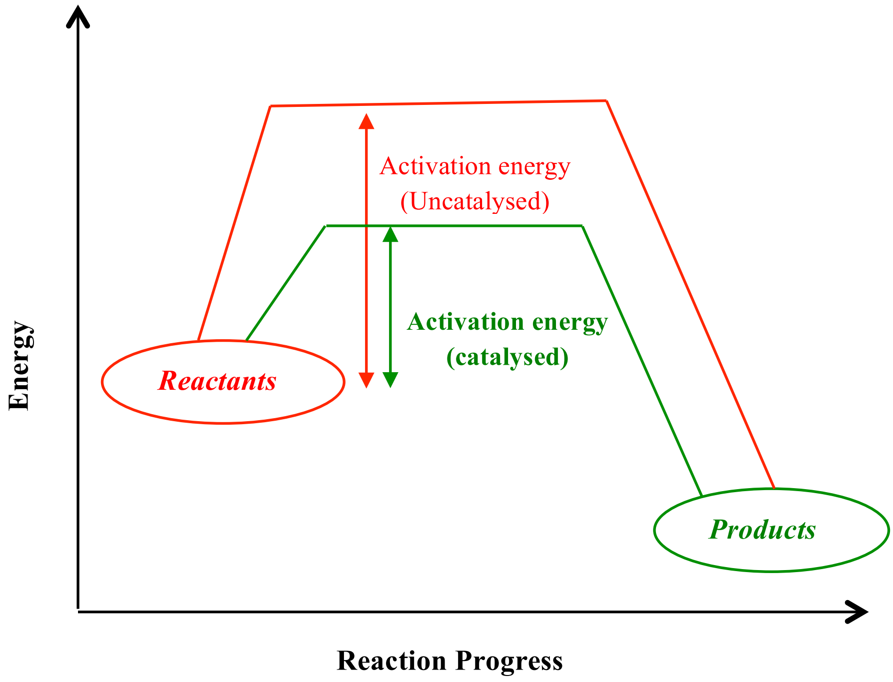


Figure 1.1: Generic graph for the effect of a catalyst on a chemical reaction.[4]

1.2 Types of Catalysis:

Overall, there are three types of catalysis: Biocatalysis where reactions are catalysed by enzymes; this is a fast reaction, sensitive, selective, and happens under mild conditions (section 1.2.1). Homogenous catalysis, where the catalysis is at the same phase as the reaction and no phase boundary appears to happen in the gas phase or liquid phase (section 1.2.2). Heterogeneous catalysis, where the catalyst and reaction mixture are in different phases (section 1.2.3).

1.2.1 Bio-catalysis:

Biocatalysts are a particular case in which enzymes, which are complex proteins, catalyse the reactions in living organs. Enzymes are efficient as catalysts often under mild conditions, and are often better than homogeneous and heterogeneous ones due to their high turn-over frequency, which is related to their high specificity.[8]

1.2.2 Homogeneous catalysis:

With homogeneous catalysis both the reactant and the catalyst have a similar phase, such as ozone destruction by chlorine radical.[7] The major advantage of homogeneous catalysis is that all of the active sites of the catalyst are reachable by the reactant, and hence greater selectivity can be obtained. However, due to the difficulty of separating the catalysts from the reaction mixture, some homogeneous catalytic processes cannot be achieved industrially.[9]

1.2.3 Heterogeneous catalysis:

Heterogeneous catalysis usually involves solids, where the catalyst and reaction mixture are in different phases. Usually the catalyst is solid while the reactant is liquid or gas, such as the production of ammonia from N_2 and H_2 using solid Fe catalysts.[7] The process of heterogeneous catalysis includes the adsorption of one or more of the reactions on to the surface of the catalysts at the active site, where one or more of the reactants adsorb the catalyst’s surface (Figure 1.2).

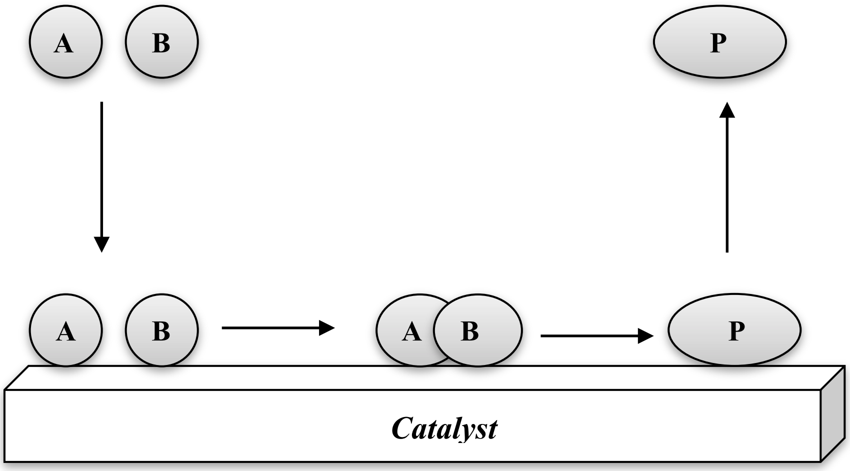


Figure 1.2 The general reaction steps for the heterogeneous catalytic reactions[4]

Heterogeneous catalysis has many features for example ease of separation; recovery, reused and a long life span. Heterogeneous catalysts can be recovered and reused and is mostly used in the petrochemicals industry because of there being no difficulty in catalyst separation and reusability.[8,10] Also, it can be used for the cleaning of waste and exhaust gas emissions as well as energy conversion in fuel cells.[11] Table 1.1 shows the main variations between homogeneous and heterogeneous catalysis.

Table1.1 The main differences between heterogeneous and homogeneous catalysis [12].

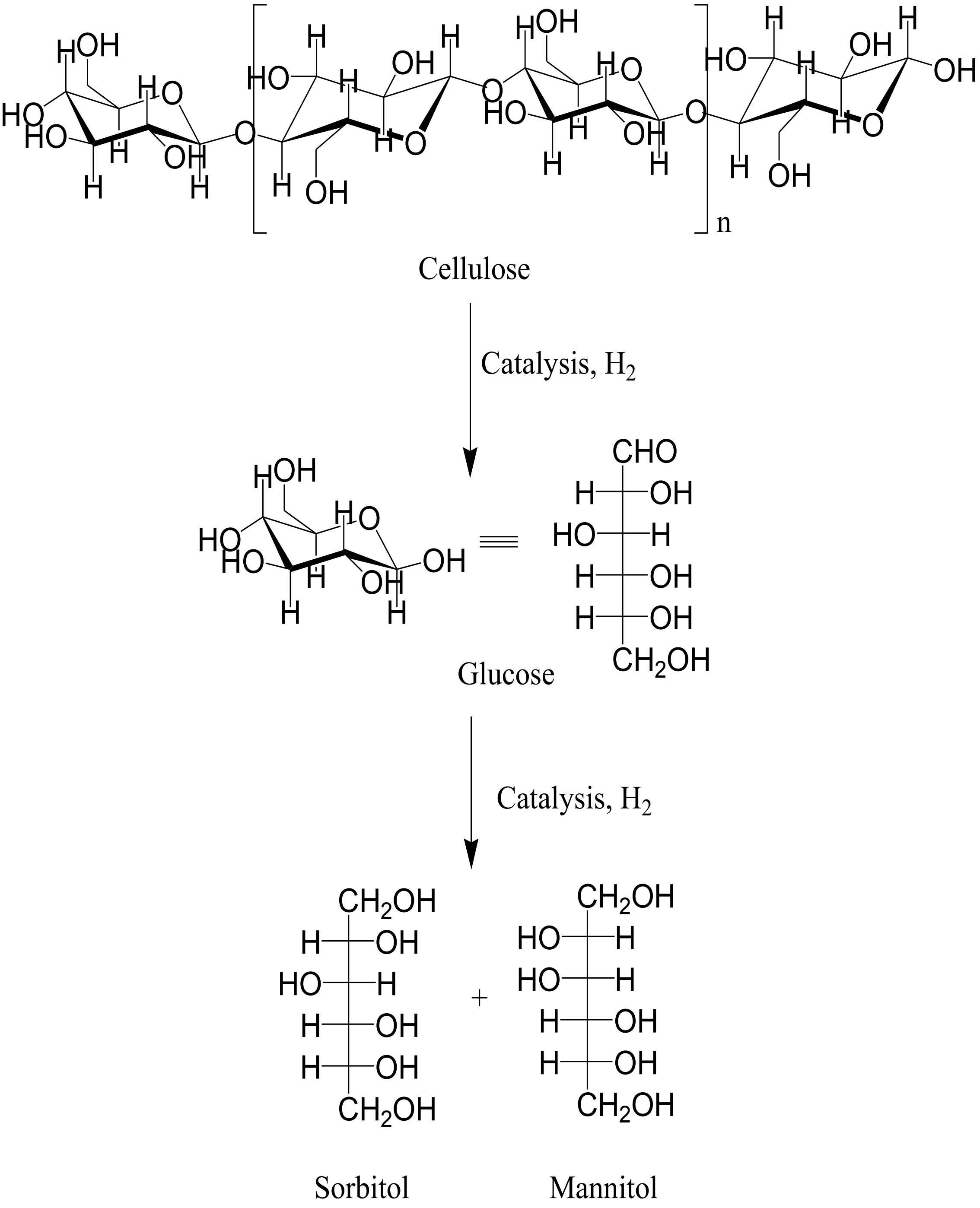
	Homogeneous	**Heterogeneous**
Catalyst phase	Complex catalyst	Solid
Activity	High	Changeable
Selectivity	High	Changeable
Stability	Decomposes at high temperatures	Stable at high temperatures
Recovery	Difficult and expensive	Easy
Application	Limited	Wide

1.3 Literature on hydrogenation and hydrogenolysis of biomass:

Hydrogenation -to treat with hydrogen- is a chemical reaction between hydrogen and another compound. The activation of H_2, has an important role in the valuation of biomass, due to biorenewable feedstock, and contrary to petroleum based feedstock, it contains high concentrations of oxygen.[13]. The reactions of choice aim to increase the H/O and H/C ratio of these biomass derived oxygenates with hydrogenolysis or hydrogenation.[14] Typically, the catalysts of choice for hydrogenation reactions are metal catalysts, for example RANEY Ni or supported monometallic noble metal catalysts.[13] In general, for hydrogenation reactions, supported bimetallic catalysts containing Pd:Pt and Pd:Ru are known to be superior catalysts with excellent catalytic activities, compared to their monometallic analogues, due to the synergistic effect between the two metals.[13] For example, Pd based bimetallic catalysts used for the hydrogenation of alkynes, alkadienes to alkenes, and nitriles to amines. Rh-based bimetallic catalysts can be used for the hydrogenation of alkenes. Moreover, Pd:Pt supported on solid acids is used for hydrogenation of aromatics.[13,15-17] In addition to their excellent catalytic activities, these catalysts have been utilised to avoid some of the less propitious features of monometallic catalysts, for example deactivation and leaching. The latest studies on the efficient use of bimetallic catalysts have involved aromatic hydrogenation by Pd:Pt supported on solid acids,[15-17] such as alkenes hydrogenation by Rh based bimetallic catalysts, such as Rh:Sn (rhodium takes the prize for ethene hydrogenation, but nickel is the most active base metal)[18] alkynes hydrogenation; alkadienes to alkenes by Pd based bimetallic catalysts like Pd:Au and Pd:Pt;[13,15] nitriles hydrogenation to amines by Pd based bimetallic catalysts, and hydrogenation of CO to methanol over Pd based alloys such as Pd:Li[19] as catalysts.[15-17] In recent studies, metallic catalysts have been used for the substrates of biorenewable hydrogenation and other petroleum fields where it may possibly be further utilised. For example the progress of bimetallic or alloy catalysts set by mixing two metal within a catalyst. Catalyst has been enhanced in the area of petroleum refineries. Bimetallic catalyst has very important in petroleum refineries, particularly in increasing the octane number of gasoline and that controlled the replacement of the hazardous tetraethyl lead.[13,14]

1.3.1 Hydrogenation of carbohydrates:

Aldehydes and ketones are compounds, which include carbonyl functional groups (C=O) such as glucose and xylose, which can be hydrogenated to form alcohol groups, (O-H) to obtain sugar alcohols such as sorbitol and xylitol using metallic catalysts. Naturally, they are present in some fruits and vegetables in minuscule amounts and are commercially formed through the hydrogenation of glucose, mannose and xylose[13,14] China alone is currently producing the most commonly used sugar alcohols in the world, such as sorbitol and xylitol, at more than 700000 tonnes per annum and this figure has been increasing annually.[13,20] Approximately 50% of the total global production of sugar alcohols is carried out in China, and this is causing a significant amount of research to focus on this field in this particular area. RANEY Ni suffers from deactivation because of the Ni leaching, which requires purification of the alcohols; however, it has long been used as the commercial catalyst in this transformation.[14] In addition, a second non-metal has been incorporated into the catalyst in an attempt to avoid this leaching.[13] The hydrogenation of glucose to sorbitol by Ni:B alloy has not indicated any large Ni leaching, and additionally, activity was improved compared with the monometallic RANEY Ni catalyst, as reported by Li et al.[13,21] The monometallic Ni/SiO_2 compared with the Ni:B alloy supported on SiO_2 has shown moderate activity, and the Ni:B alloy activity is found to be higher than that of the RANEY Ni catalyst. The researchers have attributed this to the amorphous phase of the catalyst being important for improved activity. The higher activity of this alloy catalyst has been attributed to a combination of two reasons structural advantages and the electronic state on the surface. Analyses of the amorphous catalyst have shown shorter Ni:Ni bond distance and a lower Ni coordination number compared to the crystalline catalyst prepared from calcination of the amorphous material. In other words, furthering the high dispersion of prepared Ni:B amorphous catalyst, its high activity was mainly attributed to its favourable structure and the electronic interaction between metallic Ni and the alloying B in the Ni:B alloy, which made it Ni electron-rich.[21] The presence of boron produces an influence of electrons and then weakens the glucose adsorption during the carbonyl functional group (C=O). Subsequently, more hydrogen can be adsorbed on the surface of the catalyst Ni:B, and therefore higher hydrogenation activity was observed.[21] Another amorphous Ni:P alloy catalyst was investigated for the hydrogenation of glucose to sorbitol by Li et al.[22] The active surface area of the catalyst was increased and thus had improved catalytic activity *via* RANEY Ni for making the alloy. The surface area of the RANEY Ni:P alloy catalysis was observed to be lower than the RANEY Ni catalyst, even though the TOF (turnover frequency 0.4 s^{-1}) of the RANEY Ni:P alloy catalyst was found to be higher than previous catalysts reported. The higher catalytic activity has been attributed to be the formation of a Ni:P alloy at the surface.[22] Gallezot et al. modified a RANEY Ni catalyst with metals including Mo, Cr, Fe and Sn, instead of metalloids such as B or P, and investigated them for the hydrogenation of glucose.[23] The rate of hydrogenation of glucose was increased through the loading of Cr onto the Ni catalyst and the substantial enhancement in the hydrogenation rate of glucose was attributed to the united effect of being thermodynamically stable, and the reduced Ni atoms and low valent Cr^{3+} ions on the surface of the catalyst (surface area increased and provided more space for the interaction on the surface of the catalysts via a nucleophilic attack on the carbon atom by hydride ions). The Cr^{3+} ions were used as Lewis acid sites where the glucose molecules were adsorbed via the C=O bonds during the donation of the lone pair of electrons on oxygen. This polarises the C=O bond, while at the same time H_2 becomes separated at the closest Ni atoms, and the aldehyde group of the glucose is reduced by the nucleophilic attack of the C=O bond. The activities of the catalytic process decreased when Cr integrated with the Ni catalyst, and this decrease implies that the remnants of organic material adsorbed caused poisoning of the active sites.[23] The hydrogenation of glucose to sorbitol by a Co:B alloy catalyst, as a replacement for the Ni based alloy catalysts was reported by Li et al.[24,25] Previous studies indicate that the monometallic Co catalysts were found to be less active compared to the Co:B alloy catalysts, and alloy catalysts were detected having an impact on the success of being reused five times with no deactivation or leaching of the metal ions.[24] The reactions of Ni or Co based alloy catalysts achieved higher activity, but most of the deactivation problems of these catalysts is from metal leaching into the reaction solution, which until now has not been solved. In contrast, cobalt, platinum, palladium, rhodium and ruthenium based catalysts have been used as alternatives to Ni catalysts. Ruthenium based catalysts have been shown to be active catalysts for hydrogenation, with the advantage of the ruthenium catalysts being that they do not leach into the reaction medium.[26-29] Ruthenium supported on carbon appears to be an attractive alternative to RANEY Ni catalysts because the Ru/C catalysts show higher activity, do not leach into the reaction solution and it has been shown to be stable.[13,29,30] The stability of Ru/SiO_2 has been revealed under glucose hydrogenation conditions by using in situ X-ray absorption spectroscopy and electron microscopy, and it has been predicted that the sintering of Ru catalysis is caused by deactivation, according to a study by Maris et al.[31] The ruthenium nanoparticles in aqueous glucose solution stabilised against sintering for a short reaction time and the ruthenium nanoparticles started growing, resulting in catalyst deactivation with reactions over a long time.[13,29,30] Many ruthenium based catalysts used for the hydrogenation of sugars have been explored.[32] The stability and the catalytic activities of Ru based alloy catalysts are substantially higher than their Ni analogues for the hydrogenation of glucose.[31,32] The reasons are attributed to the favouring of the ruthenium based amorphous alloy based catalysts over the RANEY Ni catalyst and monometallic ruthenium catalysts,[32] similar to those prepared for Ni based catalysts by Li et al.,[21] *firstly*, because of their amorphous nature, short range ordering with long range disordering; *secondly*, the highly coordinatively unsaturated ruthenium sites in the alloy; and *finally*, by alloying ruthenium with a non-metal such as B or P, where the B or P sites are electron deficient, whilst the ruthenium sites are slightly electron rich. Both the electron rich state of the ruthenium sites, and the electron deficient state of the non-metal sites, results in the adsorption of glucose on to them being weaker and this makes them stiable for hydrogen adsorption. Mishra et al.[33] have attempted, relatively successfully, to study the impact of both Ni and Ru in Ru/NiO-TiO_2 catalysts for the hydrogenation of D-glucose to D-sorbitol through the hydrogenation of sugar monosaccharides to sugar alcohols, and this has gained great attention. These sugars are obtained through the acid hydrolysis of polysaccharides.[19] Recently, these two reactions have been mixed in one reaction using both acid functionality in addition to metal sites (Scheme 1.1).[34,35] This cascade reaction leads to decreasing the reaction time, and a reduction in the consumption of raw materials, energy and solvents, reducing the waste formed. Several monometallic (Pd, Pt, Rh and Ru) supported nanoparticle based catalysts have been tested for the one reaction conversion of cellobiose (glucose dimer) to C6 alcohols, as reported by Yan et al.[36] In addition, Ru on poly(N-vinyl-2-pyrrolidone) was found to be active and completely selective for sorbitol, whilst the selectivity to sorbitol decreased to approximately 26% due to the formation of 3-b-D-glucopyranosyl-D-glucitol when the pH of the solution was increased to seven. However, under basic conditions (pH=10), the selectivity of sorbitol decreased to 24% due to the formation of dideoxyhexitol and another C6-alcohol.[13,36]



Scheme 1.1: Hydrogenation of cellulose into sugar alcohols in one reaction.[34]

Table 1.2: Hydrogenation of biomass using mono and bimetallic catalysts:

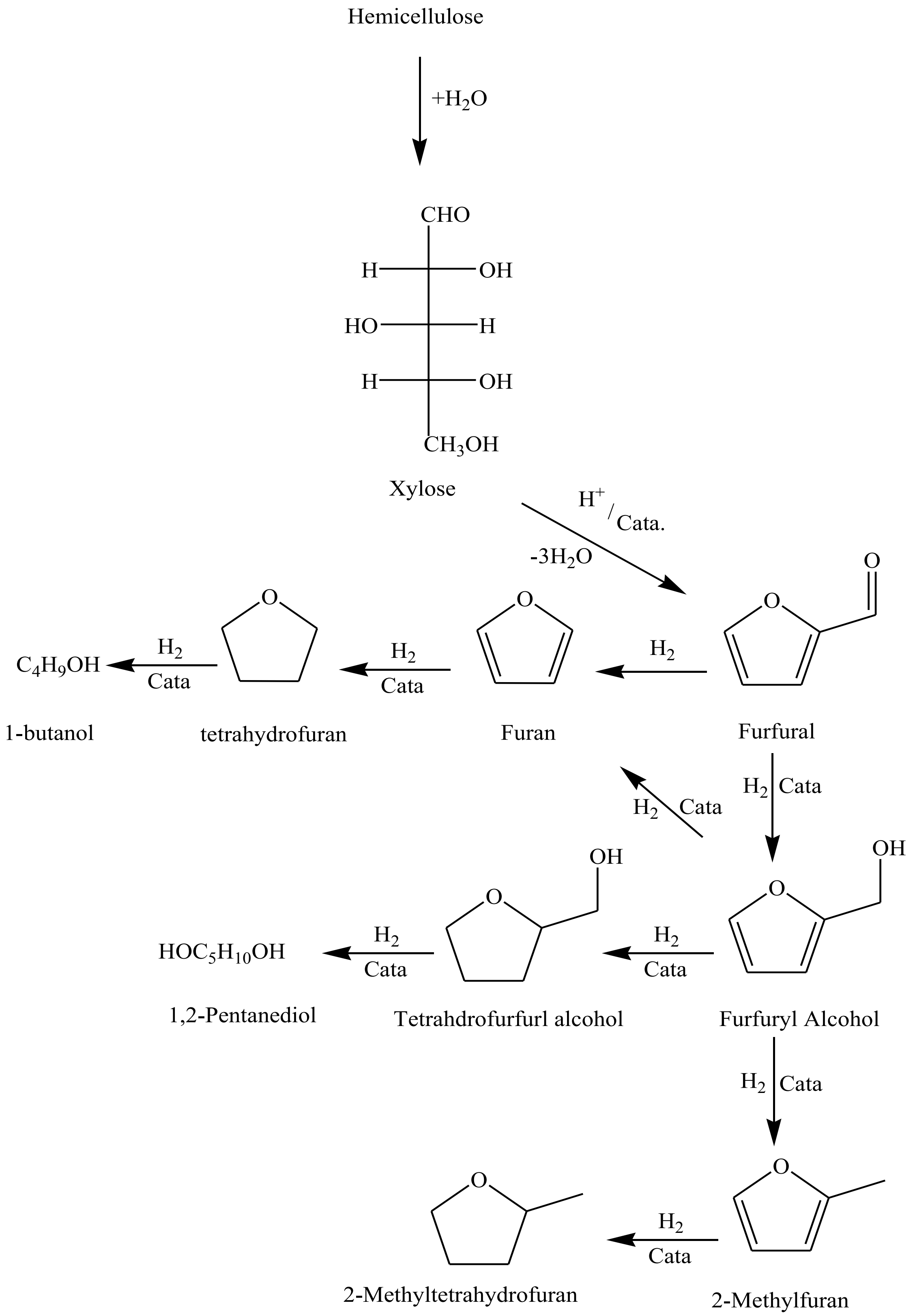
Catalyst	Substrate	T(°C)	P(bar)	t(h)	Conv.(%)	Ref.
Ni:B/SiO_2	glucose	100	400	6	30	[21]
10%Ni/SiO_2	glucose	100	400	6	8	[21]
RANEY Ni	glucose	120	40	2	38	[37]
Ni:B	glucose	120	40	2	85	[37]
$Co_{75.4}B_{24.6}$	glucose	120	40	6	89	[25]
$Co_{73.7}Cr_{1.5}B_{24.8}$	glucose	120	40	6	91	[25]
$Co_{74.8}Mo_{0.5}B_{24.7}$	glucose	120	40	6	92	[25]
$Co_{74.7}W_{1.2}B_{24.1}$	glucose	120	40	6	97	[25]
$Ru_{88.9}B_{11.1}$	glucose	80	40	2	95	[38]
$Ru_{86.8}Cr_{2.6}B_{10.6}$	glucose	80	40	2	99	[38]
$Ru_{86.7}Cr_{3.0}B_{10.3}$	glucose	80	40	2	100	[38]
$Ru_{93.2}P_{6.8}$	Maltose	90	20	2	98	[39]
$Ru_{88.9}B_{11.1}$	Maltose	90	20	2	45	[39]
1% Pt:5%Ni/MC	Cellulose	245	60	0.5	100	[40]
1% Pd:5%Ni/MC	Cellulose	245	60	0.5	100	[40]
1% Ru:5%Ni/MC	Cellulose	245	60	0.5	100	[40]
1% Rh:5%Ni/MC	Cellulose	245	60	0.5	100	[40]
1% Ir:5%Ni/MC	Cellulose	245	60	0.5	100	[40]
1% Ir/MC	Cellulose	245	60	0.5	90	[40]
5% Ni/MC	Cellulose	245	60	0.5	86	[40]
1% Ir/MC+5% Ni/MC[a]	Cellulose	245	60	0.5	92	[40]
2% Ir:5% Ni/MC	Cellulose	245	60	0.5	99.5	[40]
3% Ir:5% Ni/MC	Cellulose	245	60	0.5	100	[40]
4% Ir:4% Ni/MC	Cellulose	245	60	0.5	100	[40]
1% Ir/AC	Cellulose	245	60	0.5	66	[40]
5% Ni/AC	Cellulose	245	60	0.5	59	[40]
1% Ir:5% Ni/AC	Cellulose	245	60	0.5	79	[40]

a) Physical mixture. MC= mesoporous carbon AC= activated carbon

This example provides an indication of the required durability level of supported metal catalysts. As an alternative method, the one step method of cellulose converting to sugar alcohols (sorbitol and mannitol) using acidic oxides as supports for monometallic catalysts such as Pt/γ-Al_2O_3, Pt/SiO_2–Al_2O_3 has been reported by Fukuoka et al.[34] They claim the yield for sugar alcohols was 30% at 190°C in 24h. Accordingly, bi-functional catalysts have been studied for the one step synthesis of sugar alcohols. In other examples, a mixture of Ru/C and $H_4SiW_{12}O_{40}$,[41] Ru/C nanotubes,[42] reformed Ni/C nanofibres,[43] and Pt/C black[44] have been used. A range of studies have attempted to facilitate the hydrolysis of cellulose through the modification of the support material, but at the present time, it has not been widely studied. Pang et al.[40] have reported on Ni bimetallic catalysts, including Pt, Pd, Ru, Rh and Ir supported on mesoporous carbon (MC) for the formation of hexitols from cellulose directly; in the one-pot conversion of cellulose it can be observed that the best result achieved is an overall hexitol yield of more than 57% (1%Ir–5%Ni/MC). In contrast, 5%Ni/MC and 1%Ir/MC yielded hexitol of around 10% and 5% consecutively under the same reaction conditions. In addition, a physical mixture of the two monometallic catalysts was found to be less active than the bimetallic catalysts. Nickel bimetallic catalysts have also been investigated and found to show stability for more than three reuses with the same activity. Summary data for the hydrogenation of glucose, monosaccharides and polysaccharides *via* monometallic, bimetallic and related catalysts are shown in Table1.2, and it can be observed that the investigation of the catalysts in the hydrogenation of biomass reactions is limited.[13]

1.3.2 Alcohol and Aldehyde hydrogenation:

Renewable biomass refers to sustainable sources of energy and organic carbon. It has been the primary industrial and consumer feedstock throughout human history. Over the last century, coal, natural gas and petroleum have grown to dominate the renewable biomass as resources, supplying approximately 85% of energy and 95% of organic chemicals. However, it is said that after two decades petroleum production is unlikely to meet the growing needs of humanity; likewise, natural gas resources will be increasingly inaccessible.[45-48] Moreover, consumers and governments, concerned about CO_2 emissions and other environmental impacts, are demanding renewable power and products. The advances in conversion technology are many, and biomass resources have the potential to regain their central position as feedstocks for civilization, particularly as renewable carbon sources for transportation fuel and bulk chemicals.[49] One of the most important current discussions in the chemical industry concerns petroleum and the manufacture of carbon-based compounds. The increasing cost and decreasing supply of oil has resulted in a focus on potential routes for producing solvents, fuels, and bulk chemicals from biomass as an alternative. Biomass mainly consists of fatty acids, lignin, lipids, proteins and carbohydrates. It is an alternative and the most attractive feedstock, as it is the only widely available carbon source, apart from coal and oil.[14,50] In recent years, there has been increasing interest in biomass technology, and many studies have been published describing the relative advantages of applying different forms of chemical production to natural sources.[51,52] It is an important subject matter concerning the recent requirements for energy to meet a diverse range of needs that will progressively replace dependence on fossil fuel resources.[53] One primary renewable feedstock consists of furan derivatives which are considered to be important intermediates as a result of their rich chemistry and typical ease of formation from carbohydrates.[14] Carbohydrates, in particular, show promise because they are the largest natural source of carbon.[50] Recently, improvements have been made in the conversion of carbohydrates into furan derivatives in the form of furfural and furfuryl alcohol.[53] One of the methods used to obtain fuel from this renewable feedstock resource is from its pre-treatment through hydrolysis of the cellulosic and hemicellulosic components to produce sugar alcohols, such as sorbitol, xylitol, mannitol, lactitol or maltitol, which are consequently converted into fuel components via chemical reactions.[52] Industrially, furfuryl alcohol is prepared through the hydrogenation of furfural using catalysts. There are two routes used to make furfuryl alcohol through hydrogenation of furfural: liquid phase and vapour phase hydrogenation.[54,55] In vapour phase hydrogenation, depending on the type of catalyst used, hydrogenation of furfural can produce different products, for example 2-methylfuran and tetrahydrofurfuryl alcohol, in addition to furfuryl alcohol. In the liquid phase, hydrogenation, high temperatures and high pressure are required, and products from ring-opening are formed.[55] Scheme 1.2 shows a typical way to form furfuryl alcohol and the possible pathway for reactions of both it and furfural. Recently, furfuryl alcohol has been reported to be excellent as a starting material for the manufacturing process (as mentioned in chapter four) including its derivatives such as an important chemical intermediate for the manufacture of fragrances, vitamin C, and lysine.[55]



Scheme 1.2: Reaction pathway proposed in the literature for furfuryl alcohol hydrogenation.[55,56]

Hence, this study will discuss in brief the main transformation of furfuryl alcohol to the primary types of derivatives, including 2-methyltetrahydrofuran, 2-methylfuran, tetrahydrofurfuryl alcohol and 1,2-pentanediol, which can be obtained under green conditions such as: low pressure, low temperature and green solvent. These compounds show a variety of applications in the chemical industry, such as furfural, furfuryl alcohol and attractive biofuels like 2-methylfuran, and 2-methyltetrahydrofuran.[57-59] They are important starting materials for manufacturing in the production of resins.[55] Historically, perhaps the first report of forming furfuryl alcohol as a primary product through the hydrogenation on furfural, was written by Padoa and Ponti back in 1906: they passed the vapours of furfural with hydrogen over a nickel catalyst at 190°C.[60,61] according to Kaufmann et al.[62] In 1931, Adkins et al. studied the hydrogenolysis of furfuryl alcohol to 1,2 and 1,5-pentandiols over copper chromite. The reaction was carried out in the liquid phase and under the drastic conditions of 11.5h, 175°C, 100 to 150 barg H_2. A large amount of catalyst was used 3g. However, the yield was only 70% and there was a 10% yield of tetrahydrofurfuryl alcohol and methyltetrahydrofuran.[63] The main problem with copper chromite catalysts is their toxicity, which causes severe environmental pollution.[55] Dunlop et al,[61] discovered a new process for transforming furfural and furfuryl alcohol into tetrahydrofurfuryl alcohol with very high yields, *via* hydrogenation in the presence of nickel-based catalysis. The hydrogenolysis of furfuryl alcohol was carried out in the vapour phase, at temperatures of between 120-150°C and a pressure of 2 to 3 barg.[64] Furfuryl alcohol can be converted by catalytic hydrogenation into tetrahydrofurfuryl alcohol using noble metals (Ni, Ru, Rh, Pd and Pt) as supported catalysts, in addition to mixtures formed with a copper supported catalyst.

Nickel supported catalysts are the most active and gave the best results: using 59%Ni/SiO_2-Al_2O_3 catalyst resulted in a 99% yield, selectivity to tetrahydrofurfuryl alcohol, and conversion of more than 99%. Furthermore, hydrogenation of furfuryl alcohol in the presence of this catalyst was shown to be the best route for the generation of tetrahydrofurfuryl alcohol. Nickel supported catalysts are most commonly used.[65] Group VIII (Pd, Rh and Pt) supported catalysts are less efficient than such nickel-supported catalysts.[65] In addition, for group VIII supported catalysts, the reactions were carried out in the liquid phase and strong conditions for temperature and pressure were usually required.[64,65] The hydrogenation reactions were carried out in an autoclave to transform the furfuryl alcohol into tetrahydrofurfuryl alcohol over a nickel supported catalyst. The reaction conditions studied involved a hydrogen pressure of around 40 barg, temperatures of 180°C and a stirring rate of 1000 rpm. Within 3.5h, the conversion of furfuryl alcohol into tetrahydrofurfuryl alcohol in the presence of the catalyst was more than 99.9%, with selectivity above 98.3%.[47,66] The liquid phase hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol over various ruthenium-supported catalysts (5%Ru/TiO_2, 5%Ru/Al_2O_3 and 5%Ru/C) was conducted in a slurry reactor. The optimum conditions for this hydrogenation of furfuryl alcohol were revealed to be a hydrogen pressure of 27 barg at a temperature 60°C using a 5%Ru/TiO_2 catalyst in the presence of 2-propanol as a solvent. The conversion was approximately 95% and the selectivity to tetrahydrofurfuryl alcohol was more than 97% after 2h.[47,67] In 2011, Sitthisa, et al[68] investigated the gas phase hydrogenation of furfuryl alcohol under conditions of 250°C, with hydrogen pressure during the reaction at one bar over Ni-Fe/SiO_2 bimetallic catalysts. In addition, the main products of furfuryl alcohol hydrogenolysis over the monocatalyst Ni/SiO_2 were 2-methylfuran and furan. However, when the loading of Fe as a bimetallic catalyst was increased, the yield of 2-methylfuran increased and that of furan decreased. Similar products were achieved when hydrogenolysis of furfural or furfuryl alcohol was performed; the important change was the low conversion of furfural into 2-methylfuran, compared to that from furfuryl alcohol. A much higher yield of 2-methylfuran was achieved from furfuryl alcohol compared to furfural in all of the catalysts (comprised of 5%wt Ni:Fe/SiO_2), but the change becomes even more marked as the Fe/Ni ratio increases.[68] Zhang et al (2012)[47] describe the hydrogenation of furfuryl alcohol carried out at 120°C and hydrogen pressure of 30-60 barg for 4h in an aqueous phase over Ru-supported catalysts and MnOx supported Pd, Pt and Rh catalysts. A high selectivity for hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol was achieved with Pd/MnOx and Rh/MnOx catalysts, but a high selectivity for 1,2-pentanediol was displayed over the Ru/MnOx catalysts. The MnOx in the Ru/MnOx catalysts increased the selectivity of 1,2-pentanediol, and also suppressed the polymerisation of the furfuryl alcohol. The formation of 1,2-pentanediol was shown to increase at a higher temperature, low pressure and with water as a solvent. For example, the yield of 1,2-pentanediol was up to 42.1% over the Ru/MnOx catalyst at 6h, 150°C and 15 barg. However, up till now, few examples are available in the literature where bimetallic or metal-metalloid alloys have been used for the hydrogenation/hydrogenolysis of furfuryl alcohol, although there are many potential possibilities for their effective utilisation in biomass valorisation (Table 1.3).

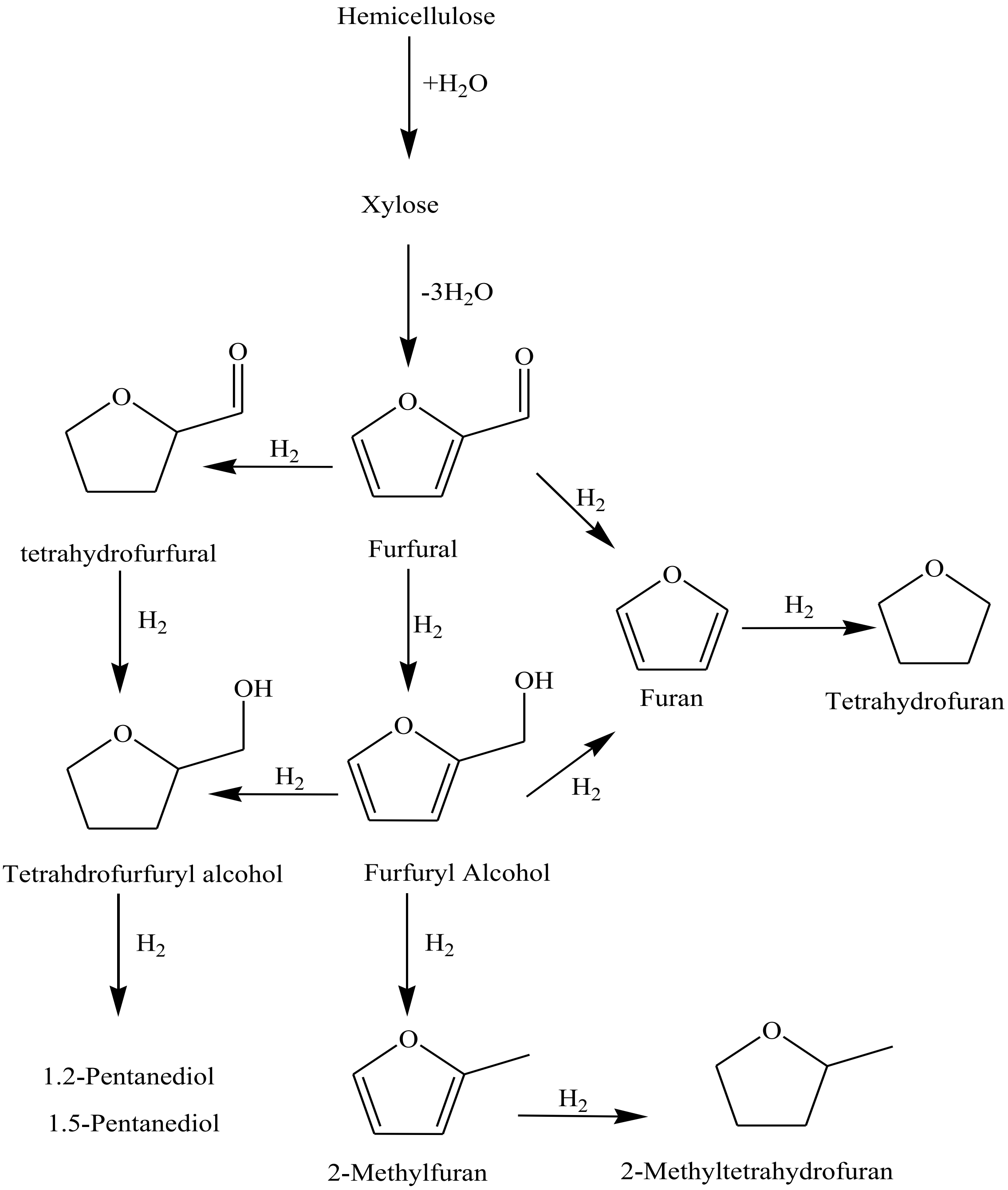
Table 1.3: Hydrogenation/hydrogenolysis of furfuryl alcohol using alloy catalysts:

Catalyst	Phase	T(°C)	P(bar)	t(h)	Conv.(%)	Selec.(%)	Ref.
$Cu_2Cr_2O_5$	liquid	175	100-150	11.5	70 % (Yield)	Pediols	[63]
59%Ni/SiO_2-Al_2O_3	vapour	120-150	20-30	1.5	>99%	THFA 99%	[64,65]
Ni-Cu	liquid	40	130	3	>99%	THFA 98.3%	[64,65]
Ni supported	liquid	130	50	3.5	99%	THFA 97%	[65]
Ni-Fe/SiO_2	gas	250	1	0.1	80% (Yield)	2-MF	[68]
5%Rh/C	liquid	120	20	26 min	53%	THFA 57%	[65]
5%Pd/C	liquid	120	20	1/3	29%	THFA 100%	[65]
5%Pd/C	liquid	130	50	1.5	81%	THFA 79%	[65]
5%Pd/$CaCO_3$	liquid	120	20	1/4	19%	THFA 100%	[65]
5%Pd/Al_2O_3	liquid	120	20	13 min	17%	THFA 100%	[65]
5%Ru/TiO_2	liquid	60	27.2	2	95%	THFA 97%	[47,67]
Ru/MnOx	liquid	120	60	4	100%	THFA 79%	[47]
Ru/MnOx	liquid	120	30	4	100%	THFA 79%	[47]
Ru/MgOx	liquid	120	60	4	63%	THFA 74%	[47]
Pd/MnOx	liquid	120	30	4	45%	THFA 100%	[47]
Rh/MnOx	liquid	120	30	4	32%	THFA 96%	[47]
Ru/$MgAlO_4$	liquid	120	60	4	100%	THFA 84%	[47]
Ru/NaY	liquid	120	60	4	100%	THFA 77%	[47]

THFA= tetrahydrofurfuryl alcohol, 2-MF=2-methylfuran, Pediols= 1,2 and 1,5-pentandiols.

Research into renewable biomass (celluloses and hemicelluloses) has reported a new development in reactions, whereby the process is carried out over solid catalysts and coupled with other reactions for better utilisation of the feedstock. The best source for pentose sugars is lignocellulosic biomass, and it does not compete with food supplies. In addition, current studies have shown that there is indeed promise for chemical transformation.[69] One of the most important current discussions in the chemical industry concerns petroleum and the manufacture of carbon based compounds. The increasing cost and decreasing supply of oil has resulted in a focus on potential routes for producing solvents, fuels, and bulk chemicals from biomass as an alternative. Biomass consists of fatty acids, lignin, lipids, proteins and carbohydrates. It is an alternative and the most attractive feedstock, as it is the only widely available carbon source, apart from coal and oil.[14,50] In recent years, there has been increasing interest in biomass technology, and many studies have revealed the relative advantages of applying different forms of chemical production to natural sources.[51,52] It is an important subject matter with regard to the recent need for energy to meet a diverse range of requirements that will progressively replace dependence on fossil fuel resources.[53] One of the methods used to obtain fuel from renewable feedstock source is by pre-treatment through hydrolysis of the cellulosic and hemicellulosic components to produce sugar alcohols, such as sorbitol, xylitol, mannitol, lactitol or maltitol, which are subsequently converted into fuel components via chemical reactions (for example: furfural, furfuryl alcohol, 5-hydroxymethylfurfural, 2-methyl-furan, 2,5-dimethylfuran and 2-methyltetrahydrofuran).[51,52,55,57,70,71]

Industrially, the most common chemical derived from lignocellulosic biomass is furfural[45,72] and this was first discovered by the Quaker Oats Company in 1921.[73,74] Furfural is formed from xylan contained in lignocelluloses through dehydration and hydrolysis and, thus, in turn, furfural can be converted into different components.[57] Commercially, furfural is considered to be a platform chemical and it has been applied to upgrading fuels, such as 2-methylfuran and 2-methyltetrahydrofuran[75,76] through hydrogenation and acid/base catalysed reactions (Scheme 1.3).[57,69,71] The literature mentions that furfural can be converted through catalytic hydrogenation (95%) to 2-methylfuran by using copper catalysts at high temperature (200–300°C), under the conditions of a H_2/furfural molar ratio of 5–8, using furfuryl alcohol as an intermediate.[77] In its liquid phase, furfural has been hydrogenated to furfuryl alcohol (yield, >96%) over copper chromite ($CuCr_2O_4{\bullet}CuO$). The reaction was conducted under high hydrogen pressure 69–104 barg and at 180°C.[78] Copper-chromite, Raney-copper and Cu/Al_2O_3 display similar behaviour, while copper-chromite is more stable and active. However, the catalyst deactivates rapidly and is regenerated at 400°C. $Cu_2Cr_2O_5/C$ was found to be selective for 2-methylfuran (yield, >95 %).[79] Recently, in its gas phase, the hydrogenation of furfural using a zeolite catalyst (Cu/Fe) obtained 99% conversion and 98% selectivity in 2-methylfuran at 252°C, one bar pressure;[80] also in the vapour phase and under these conditions, furfural was hydrogenated over the Cu-based catalyst.[81]



Scheme1.3: Reaction pathway proposed in the literature for the hydrogenation of furfural [13,69,74]

On the other hand, in the gas phase, to obtain 2-methylfuran, a rapid deactivation of the catalyst was observed, which means there is the need for a process at a lower temperature and in the liquid phase. However, hydrogenation of furfural into ethyl levulinate over copper-based catalysts, and following ethanolysis of furfuryl alcohol in the presence of a strong acid has occurred. Furfural was converted to furfuryl alcohol, followed by being converted to ethyl levulinate using several strong acids and zeolites as solid acid catalysts[82] Zheng el. al,[54] have reported that in the vapour phase, furfural was hydrogenated to 2-methylfuran and several furan products, including 2-methyltetrahydrofuran with a yield of 2-methylfuran over Cu/Zn/Al/Ca/Na catalyst of 87.0% at 250°C.[54] In the same way, 2-methylfuran (90%) and 2-methyltetrahydrofuran (82%) were achieved as a mixture of products from super critical carbon dioxide ($scCO_2$) mediated continuous hydrogenation by Pd/C and copper chromite as a commercial catalyst.[58]

A recent study has investigated the vapour phase conversion of furfural over Ni/SiO_2 and $Ni:Fe/SiO_2$ catalysts in the presence of H_2 at one bar in the 210-250°C temperature range. The bimetallic ($Ni:Fe/SiO_2$) catalyst formed 2-methylfuran (38%) as a major product via C–O hydrogenolysis of furfural, with furfuryl alcohol (31%) and furan (32%) as primary products through hydrogenation and decarbonylation over a monometallic nickel catalyst. In this case, the addition of Fe promoted C–O hydrogenolysis at high temperatures, and C=O hydrogenation at low temperatures, while suppressing the decarbonylation activity of the monometallic nickel catalyst. The differences in selectivity shown by this can be attributed to the stability of the surface species, which is less with pure Ni than Ni:Fe.[68] Hydrogenation of furfural using H_2 gas on metal catalysts generates mostly furfuryl alcohol. It can be used as a solvent, but is mainly used as a part in the manufacture of chemicals.[83] A metal catalyst is usually used in the hydrogenation of furfural because it is able to dissociate H_2; hence it is likely to ensure hydrogenation. The catalyst support choices are based on their ability to strew and stabilise metal particles, increasing the active surface area. Furfural contains an aromatic furan ring that can also be hydrogenated, in addition to the carbonyl group, as compared to other aldehydes.

Although carbonyl group hydrogenation is usually favoured because of the high stability of the aromatic furan ring, the unsaturated C=C bonds that have a strong interaction with the metal catalyst can still saturate the ring. Thus, selectivity of aromatic alcohol is dependent on the metal catalyst used. In addition, the electronic properties and geometrics of different metals can influence both hydrogenation activity and selectivity by influencing the type of adsorption intermediates. Several studies have discussed the differences detected in furfural hydrogenation on metals (such as: Cu, Ag, Au, Fe, Ru, Co, Ni, Pd, Pt). Copper is the most commonly studied metal as a catalyst for furfural hydrogenation.[54,84,85] Silver has also been investigated in a few reports, while so far, gold as a catalyst has not been reported.[86] Other metals are remarkably more active than the copper group metals, for example: silver. However, the copper group metals show significant selectivity to hydrogenation of the carbonyl group leaving the C=C double bonds in the furan ring unreacted. In addition, the most selective among all of the tested metal catalysts was found to be the copper catalyst. A yield of furfuryl alcohol from furfural hydrogenation (60%) has been obtained over monometallic Cu/SiO_2 catalysts.[84] Moreover, monometallic silver catalysts have been shown to hydrogenate the C=O group of furfural with excellent selectivity (79%) over

Ag/SiO_2, but not as high as that of the monometallic copper catalyst. Additionally, over $Rh:Sn/SiO_2$ the yield of hydrogenation of furfural to furfuryl alcohol was 91%.[86] Both liquid and vapour phases have been investigated with regard to furfural hydrogenation over Ni, Pd, and Pt metals (the group VIII) on different supports; and they all display activity and selectivity.[86] For example, Ni catalysts have been used at 100°C in the liquid phase with selectivity to furfuryl alcohol at over 95%.[87,88] Similarly, supported Pt catalysts doped with transition metal oxides have displayed high selectivity, such as selectivity to furfuryl alcohol over a $Pt/TiO_2/SiO_2$ catalyst which was around 94%, and over a $Pt/ZrO_2/TiO_2$ catalyst which was approximately 95%.[89] However, the selectivity to alcohols for group VIII metals drops with the appearance of other reactions at >200°C. On nickel catalysts, for example, at 230°C over a Ni/SiO_2 catalyst, selectivity to furfuryl alcohol was around 25%, therefore it is even in excess of hydrogen.[90] On palladium catalysts, for example at 350°C over Pd-Y catalysts,[85] selectivity to furfuryl alcohol was 1% only and at 230°C over Pd/SiO_2 catalyst,[91] selectivity was 14%. A decrease in selectivity has been observed at high temperatures for group VIII metals, which can be attributed to the appearance of ring opening and decarbonylation reactions. Furthermore, over group VIII metal catalysts the ring of furfural hydrogenation obtained the saturated alcohol due to the stronger interaction of the metal surface with the furan ring, compared to the copper group metals.[92] Therefore, Cu and Ag are the favoured catalysts for high selectivity to furfuryl alcohol from furfural, usually at high temperatures.

On the other hand, the essential activity for furfural hydrogenation is higher on for VIII metals than copper group metals, and this is attributed to the d-orbital being filled in the copper group thus reducing the bond strength.[93] In addition, Pd,[94] Pt and Ni have been investigated as the active metals in furfural decarbonylation.[90,95]For palladium metal, it has been found that the high decarbonylation activity may be modified by the incorporation of a second metal (alloy formation).[91] Although a Pd catalyst is relatively more active than other catalysts a Pd/C catalyst was found to lose most of its decarbonylation activity while a Pd/Al_2O_3 catalyst was observed to have faster deactivation.[93] The deactivation can be attributed to the deposition of carbon, which may possibly be due to side reactions, for example decomposition and/or condensation of furfural. Earlier investigations have observed, in the absence of hydrogen a fast loss in the activity of Pd/Al_2O_3, but the activity can be recovered by increasing the hydrogen pressure.[93,94] Hronec et al., have investigated the influence of solvents and Ni, Pt, Pd, Pt:Ru and Ru catalysts in the reaction of furfural under a hydrogen pressure of 30–80 bar, and reaction temperatures of 160–175°C. In water as a solvent, the main product of furfural hydrogenation is cyclopentanone, and the conversion was 96.5% over 5%Pt/C, at 160°C and 30 barg hydrogen pressure.[96]

Table 1.4: Hydrogenation/hydrogenolysis of furfural using alloy catalysts:

Catalyst	Phase	T(°C)	P(bar)	Yield (%)	Ref.
Copper-aluminium	Liquid	193	1	FA (90%)	[77]
Copper-aluminium	Liquid	253	1	2-MF (66%)	[77]
Copper Chromate	Liquid	250	1	2-MF (87%)	[77]
$CuCr_2O_4 \bullet CuO$	Liquid	<180	1	FA (96%)	[78]
$Cu_2Cr_2O_5/C$	Vapor	>200	1	2-MF (95%)	[79]
Zeolite Catalysis (Cu/Fe)	Gas	260	55	2-MF (98%)	[80]
Cu/Zn/Al/Ca/Na	Vapor	250	1	2-MF (87%)	[54]
Ni/SiO_2	Vapor	210	1	FA (31%) F (32%)	[68]
$Ni:Fe/SiO_2$	Vapor	250	1	2-MF (38%)	[68]
Cu/SiO_2	Vapor	230-290	1	FA (60%)	[84]
Ag/SiO_2 $Rh:Sn/SiO_2$	Gas	160 200	2	FA (67%) FA (91%)	[86]
Ni-Fe-B amorphous alloy	Liquid	100	10	FA (100%)	[87,88]
$Pt/TiO2/SiO_2$	Liquid	150	1	FA (64%)	[90]
Pd/SiO_2	Liquid	230	1	F (43%)	[91]
$Pd:Cu/SiO_2$	Liquid	250	1	F (75%)	[91]
Pt/C, Pd/C, Ru/C	Liquid	160-175	30	CPON	[96]

F= Furan, FA= furfuryl alcohol, 2-MF=2-methylfuran, 2-MTHF=2-methyltetrahydrofuran, Pediols=1,2 and 1,5-pentandiols, CPON= cyclopentanone.

1.4 The aims of the thesis:

The selective hydrogenation of alcohols and aldehyde are a promising and challenging topic in heterogeneous metal catalysis. The hydrogenation of alcohols and aldehyde will be studied using supported metal catalysts under a green oxidation system. Firstly, there will be an examination of the use of a HPA as support for Au, Pd and Au:Pd nanoparticulate catalysts for the hydrogenation of cyclohexanol and selective to cyclohexane, under mild conditions and optimisation of the reaction conditions, that is, the loading metal and Cs salt, and choice of metal. Secondly, it will show whether the functional group of the alcohols (OH) and aldehyde (C=O) can be reduced in furfuryl alcohol and furfural, and will also examine the impact of the mono and bimetallic system, namely gold:palladium and ruthenium:palladium, on the hydrogenation of furfuryl alcohol and furfural under ideal conditions. This is in addition to investigating the influence of the metallic ratio and loading, and monitoring the temperature, to support the influence of hydrogenation and therefore the choice of metal.

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Chapter 2

Experimental

Chapter 2

2. Experimental

2.1 Chemicals and solvents:

The organic and inorganic chemicals and catalysts used were purchased from Aldrich®, unless stated otherwise, and used as supplied without further purification: Cyclohexanol (ReagentPlus® 99%) furfuryl alcohol (98%), furfural (99%), 1,2-dichloroethane (98%), octane (98%), toluene (reagent grade, fisher), acetonitrile (HLPC, grade), n-hexane (anhydrous, 95%) $HAuCl_4.3H_2O$ (Johnson Matthey), palladium chloride (Johnson Matthey), platinum chloride (Johnson Matthey), titania (P25, Degussa), aluminum oxide (activity grade), graphite, activated carbon (Darco, G60), cerium(IV) oxide powder (<5 micron, 99.9%), cerium(IV) oxide (nanopowder <25nm, 99.9%), silicon dioxide (nanopowder 10 nm 99.5%), silicon dioxide (powder 35-70 micron, 99%), silicon dioxide (powder 5-15nm, 99.5%), carbon (G60, Johnson Matthey), ruthenium on carbon, rhodium 5% on alumina, ruthenium 5% on alumina, palladium 10% on activated charcoal, and palladium hydroxide 20% on carbon as commercial catalysts.

2.2 Catalyst preparation

2.2.1 Impregnation method:

This is a very simple method that can be applied with any support. In impregnation, a solution of the gold precursor fills the pores of the support.[1] The method is called incipient wetness when the required volume of gold solution used to fill the pores exactly.[1] However, sometimes an increased volume is used by adding a solvent, which is evaporated to increase the concentration of the solution in the pores. Usually, chloroauric acid ($HAuCl_4$) and gold chloride ($AuCl_3$) are used in these methods as the gold precursors.[1]

- ***Preparation of $Cs_nH_nPW_{12}O_{40}$:***

The appropriate amount of $CsNO_3$ (Aldrich) was dissolved in deionised water and added drop-wise to an aqueous solution of heteropoly acid ($H_nPW_{12}O_{40}$) containing the appropriate amount of acid while stirring. The resulting solution was continuously stirred while being heated at 80°C until it formed a paste. The resultant paste was then dried overnight at 110°C, followed by calcination at 300°C for 2h to form the final support.[2,3]

2.2.1.1 Metal loaded catalysts:

- ***Preparation of Au, Pd and Au-Pd catalysts by wet impregnation supported on heteropoly acid:***

Catalysts with metals on heteropoly acids were prepared using the wet impregnation method with aqueous solutions of $PdCl_2$ (Johnson Matthey) and

$HAuCl_4.3H_2O$ (Johnson Matthey). Catalysts comprising a range of 2.5wt%Au:2.5wt%Pd/support and 5wt%Au/TiO_2; 0.5wt%, 1.26wt% and 2.58wt% Pd/TiO_2 were prepared, as shown Table 2.1. The detailed preparation procedure employed is as follows: $PdCl_2$ was dissolved in water and stirred, heated and added to an aqueous solution of $HAuCl_4.3H_2O$. The solution was added to the support and the resulting paste that formed was dried in an oven at 110°C for 16h. The powder was calcined in static air at 400ºC for 3h at a ramp rate of 20°C/min.[4]

Table 2.1: Preparation of Au, Pd and Au-Pd catalysts by wet impregnation supported on heteropoly acid:

No.	Catalyst
1	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$
2	$Cs_{1.5}H_{0.5}PW_{12}O_{40}$
3	0.025%Au-0.0375%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$
4	0.05%Au-0.075%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$
5	2.5%Au-2.5%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$
6	5%Au/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$
7	1%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$
8	5%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$

- ***Preparation of Au, Pd and Au-Pd catalysts by wet impregnation on supports:***

Catalysts supported on titania (Degussa, P25) and silica (Aldrich) were prepared through the wet impregnation method using aqueous solutions of $PdCl_2$ (Johnson Matthey), and $HAuCl_4.3H_2O$ (Johnson Matthey). Catalysts comprising 5wt%Au/TiO_2;

0.5wt%, 1.26wt% and 2.58wt%Pd/TiO_2; and a range of 2.5wt%Au:2.5wt%Pd/support were employed, as shown in Table 2.2. The detailed preparation procedure was carried out as follows: $PdCl_2$ was dissolved in water and stirred, heated and added to an aqueous solution of $HAuCl_4.3H_2O$. The solution was added to the support and the resulting paste formed was dried in an oven at 110°C for 16h. The powder was calcined in static air at 400ºC for 3h at a ramp rate of 20°C/min.[5]

Table 2.2: Preparation of Au, Pd and Au-Pd catalysts via wet impregnation supported on a solid support:

No.	**Catalyst**
1	2.5%Au:2.5%Pd/Al_2O_3
2	2.5%Au:2.5%Pd/MgO
3	2.5%Au:2.5%Pd/Graphite
4	2.5%Au:2.5%Pd/CeO_2
5	2.5%Au:2.5%Pd/TiO_2
6	2.5%Au:2.5%Pd/SiO_2
7	0.5%Pd/TiO_2
8	1.26%Pd/SiO_2
9	2.58%Pd/TiO_2
10	5%Ru:Pd/TiO_2
11	5%Ru/TiO_2

2.2.2 Catalyst pretreatment:

- ***Reduction:***

The calcined catalysts (in static air at 400ºC for 3h at a ramp rate of 20°C/min) were reduced in 5%H_2/Air at 200°C for 3h at a ramp rate of 5°C/min.

- ***Oxidation:***

The calcined catalysts (in static air at 400ºC for 3h at a ramp rate of 20°C/min) were then reduced in 5%H_2/Air at 200°C for 3h at a ramp rate of 5°C/min, before being oxidised at 200°C for 3h at a ramp rate of 5°C/min in atmosphere.

2.3 Catalyst reaction studies:

2.3.1 Dehydration and hydrogenation of Cyclohexanol:

Dehydration and hydrogenation of cyclohexanol was carried out in an autoclave reactor (50ml) at a continuous pressure for nitrogen followed by hydrogen (1bar unless otherwise stated) (Figure 2.1). Typically, the supported catalyst (0.1g) was suspended in cyclohexanol (10g). The reaction mixture was stirred (1000 rpm) at 150°C for 6h. A sample of the reaction was taken for analysis after the reaction was completed. Analysis was carried out using gas chromatography (Varian 3800 fitted with CP wax column) and a flame ionisation detector. For quantification of the reactants consumed and products generated, 0.1µL of this mixture was injected into the GC and the products were identified through a comparison with standard samples.

2.3.2 Hydrogenation of Furfuryl alcohol:

Hydrogenation of furfuryl alcohol was carried out in a stainless steel autoclave reactor (50ml) and the liner made from Polytetrafluoroethylene (PTFE) at a continuously controlled pressure of hydrogen (3barg unless otherwise stated) (Figure 2.1). Typically, the supported catalyst (0.1g) was suspended in furfuryl alcohol (1g), various solvent 20ml such as; 1,2-dicloroethane, octane, toluene, methanol and acetonitrile. The reaction mixture was stirred (1000 rpm) at 25°C for 30min. A sample of the reaction was taken for analysis after the reaction was completed. After reaction, one layer was obtained for all the solvents. After that, a small amount of solution was taken from the mixture reaction of around 1-2 g before adding 0.1g of 1-propanol as internal standard and then using the centrifuge and injecting the sample in GC. Analysis was carried out using gas chromatography (Varian 3800 fitted with CP wax column). For quantification of the reactants consumed and products generated, 0.1µL of this mixture was injected into the GC and the products were identified through a comparison with standard samples.

2.3.3 Hydrogenation of Furfural:

Hydrogenation of furfural was carried out in a stainless steel autoclave reactor (50ml) and the liner made from the Polytetrafluoroethylene (PTFE) at a continuously controlled pressure of hydrogen (3barg unless otherwise stated) (Figure 2.1). Typically, the supported catalyst (0.1g) was suspended in furfural (1g), various solvent 15ml such as; 1,2-dicloroethane, octane, toluene and methanol. The reaction mixture was stirred (1000 rpm) at 25°C for 2h. A sample of the reaction was taken for analysis after the reaction was completed (Figure 2.2). After reaction, the octane layer was separated from the furfural layer before adding 15ml (because of change of liner size in the reactor) of 1,2-dichloroethane to the furfural layer to make sure all compounds were dissolved. After that, a small amount of solution was taken from the furfural layer and the octane layer, around 1-2 g and 0.1g of 1-propanol as internal standard to both the furfural layer and the octane layer prior to the centrifuge and injecting both samples in the GC separately.

Analysis was carried out using gas chromatography (Varian 3800 fitted with CP wax column). For quantification of the reactants consumed and products generated, 0.1µL of this mixture was injected into the GC and the products were identified through comparison with standard samples. Productivity was achieved in both the fufural layer and octane layer. Total molar of compound (A) equal molar amount of compound (A) in fufural layer and molar amount of compound (A) in octance layer.

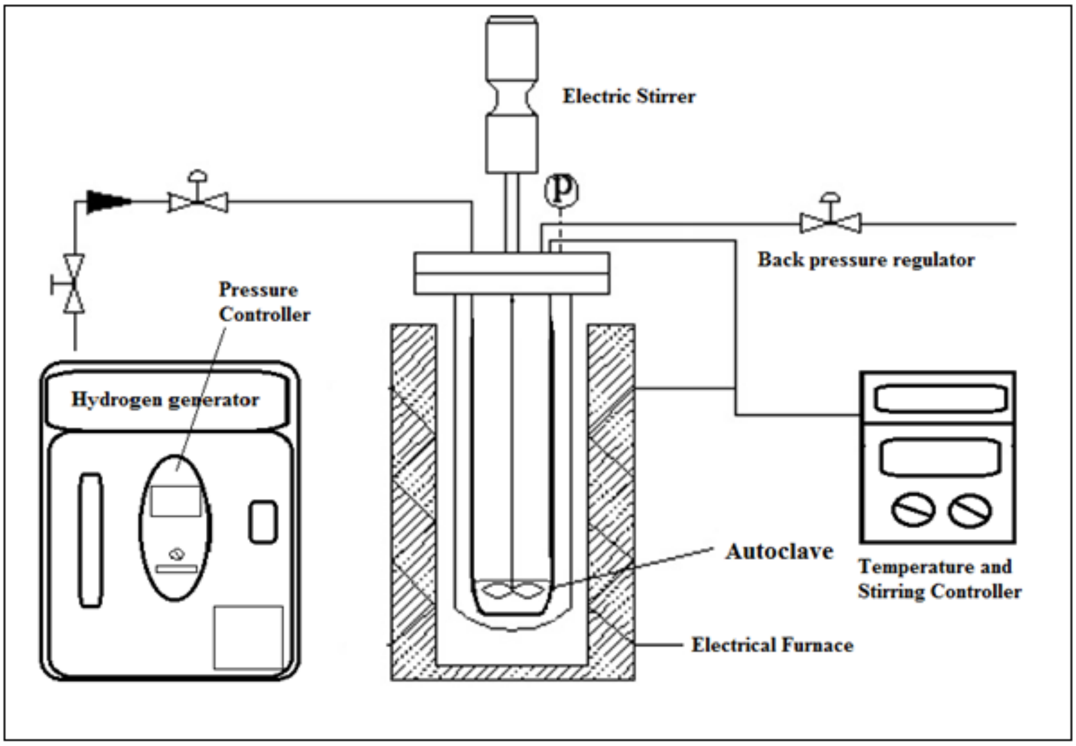

Figure 2.1. Schematic diagram of the Autoclave reactor used for the hydrogenation.

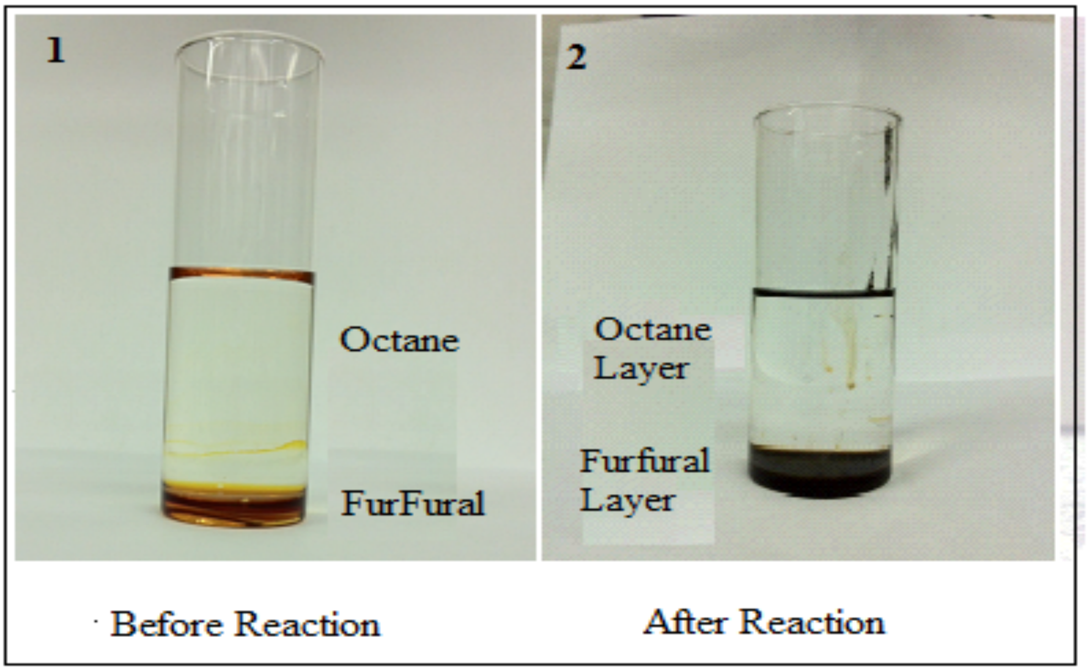

Figure 2.2. The Mixture of reaction.

2.4 Catalyst characterisation techniques:

Catalysis is a multidisciplinary area of science and is a mixture of basic and applied science with contributions from chemistry, physics and material science.[6,7] Characterisation techniques have been used in catalysis research, with the aim of understanding the catalyst composition and to show the microscopic mechanism after reactions are catalysed using various materials. In this chapter, the basic principles of some characterisation techniques involved in the research for this thesis are presented. Also, a brief description of the reactors used in the present research is given.

2.4.1 Powder X-ray diffraction (XRD):

Powder X-ray diffraction (XRD) is a method used for the determination of crystalline materials as it detects data about the crystal structure of the material according to its diffraction pattern. Thus, XRD can be utilised efficiently to analyse appropriate heterogeneous catalysts.[8] Bragg, William and Lawrence developed the Powder X-ray diffraction technique, and the simple equation for Powder X-ray diffraction is called Bragg's Law (Equation 1):

$$n\lambda = 2d \sin\theta \qquad \textit{(Equation 1)}$$

- θ = the diffraction angle.
- λ = the incident X-ray wavelength.
- d = spacings between atomic layers in the powdered sample.
- n = the order of the reflection (an integer value).

The X-ray diffraction equipment consists basically of an X-ray source; a detector used to detect the diffracted X-rays, and a sample holder. The generated X-rays required from the sample are reflected off the crystal plane with an angle that is equivalent to the glancing angle. The difference in length between the X-rays is AB+BC as shown in Figure 2.3; thus, it is equal to:

$$AB + BC = 2d\ Sin\theta^{[9]}$$

When the difference is equal to an integral number of a wavelength (AB + BC = nλ), the reflected waves interfere constructively and, therefore, the reflection is observed and detected, as it satisfies Bragg's law.[10,11]

In this study, the catalyst was ground up into a fine powder and then put on to a metal disc. Powder X-ray diffraction was carried out using a PANalytical X'Pert Pro with a CuKα X-ray source run at 40 kV and 40 mA fitted with an X'Celerator detector. Each sample was scanned from 2θ=10 to 80 at a certain time for 30 minutes. All the materials prepared and mentioned in this thesis revealed very well determined diffraction patterns. The results have been compared with each material in the literature.

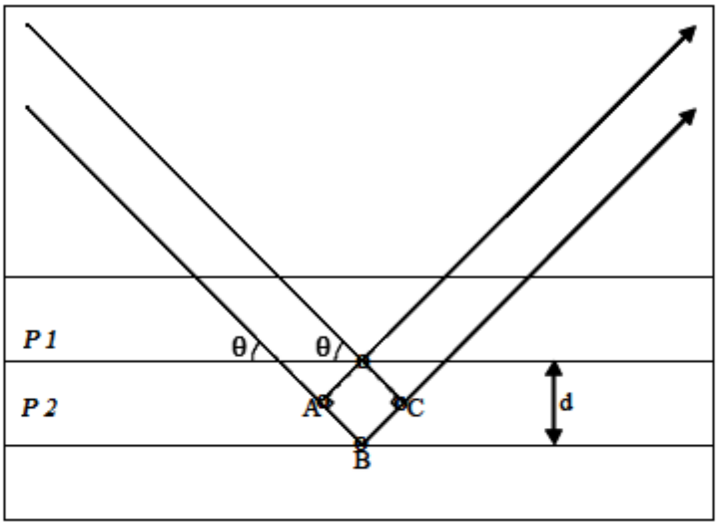

Figure 2.3. Bragg's Law of diffraction.[10-13]

2.4.2 X-ray Photoelectron spectroscopy (XPS):

In the 1960s, X-ray Photoelectron spectroscopy was developed by K. Siegbahn and in 1981 he was awarded the noble prize.[14] X-ray Photoelectron spectroscopy is an important and useful method for the characterisation of heterogeneous catalysts. This is a surface analysis method that can provide information about the element's oxidation state and composition. Based on the photoelectric effect, the surface of the sample was irradiated with X-Rays, before measuring the photo electrons emitted.[14] When an atom absorbs a photon of energy hν, a core or valence electron with binding energy E_b is ejected with kinetic energy E_k (Equation 2):

$$E_k = h\nu - E_b - \Phi \qquad \textit{(Equation 2)}$$

- Where, E_k is the kinetic energy of the photoelectron
- h is Planck's constant.
- ν is the frequency of the exciting radiation.
- E_b is the binding energy of the photoelectron with respect to the Fermi level of the sample.
- Φ is the work function of the spectrometer.

The XPS spectrum is usually binding energy versus a plot of the intensity of photoelectrons (Figure 2.4). The technique is highly surface specific; the electrons whose energies are analysed in XPS arise from a depth of no greater than about 5nm.[15] A set of binding energies is characteristic of an element, and XPS can be useful to analyse the formation of samples, considering the peak areas and cross sections for photoemission. Binding energy contains chemical information on oxidation state, because the energy levels of core electrons depend slightly on the chemical state of the atom. Chemical shifts are typically in the range of 0-3eV, and the most typical are Mg-Kα (1253.6eV) and Al-Kα (1486.6eV), which are produced from a standard X-ray tube, and the peak is detected in XPS spectra, corresponding to the bound core-level electron of the sample. The intensity of each peak is proportional to the abundance of the emitting atoms in the near surface region, while the precise binding energy of each peak depends on the chemical oxidation state and local environment of the emitting atoms. Moreover, XPS is able to provide information about the state of oxidation and chemical environment of a given element because of shifts in the binding energies.[14]

The XPS analysis work was performed by Dr. David Morgan from *the School of Chemistry, Cardiff University*. X-ray photoelectron spectra are recorded on a Kratos Axis Ultra DLD spectrometer operating a monochromatic AlKα X-ray source (75-150W) and analyser pass energies of 160 eV (for survey scans) or 40 eV (for detailed scans). Samples of the catalyst were mounted on double-sided adhesive tape with binding energies referenced to the C(1s) binding energy of adventitious carbon contamination (the carbon is from the tape) which was taken to be 284.7eV.[16]

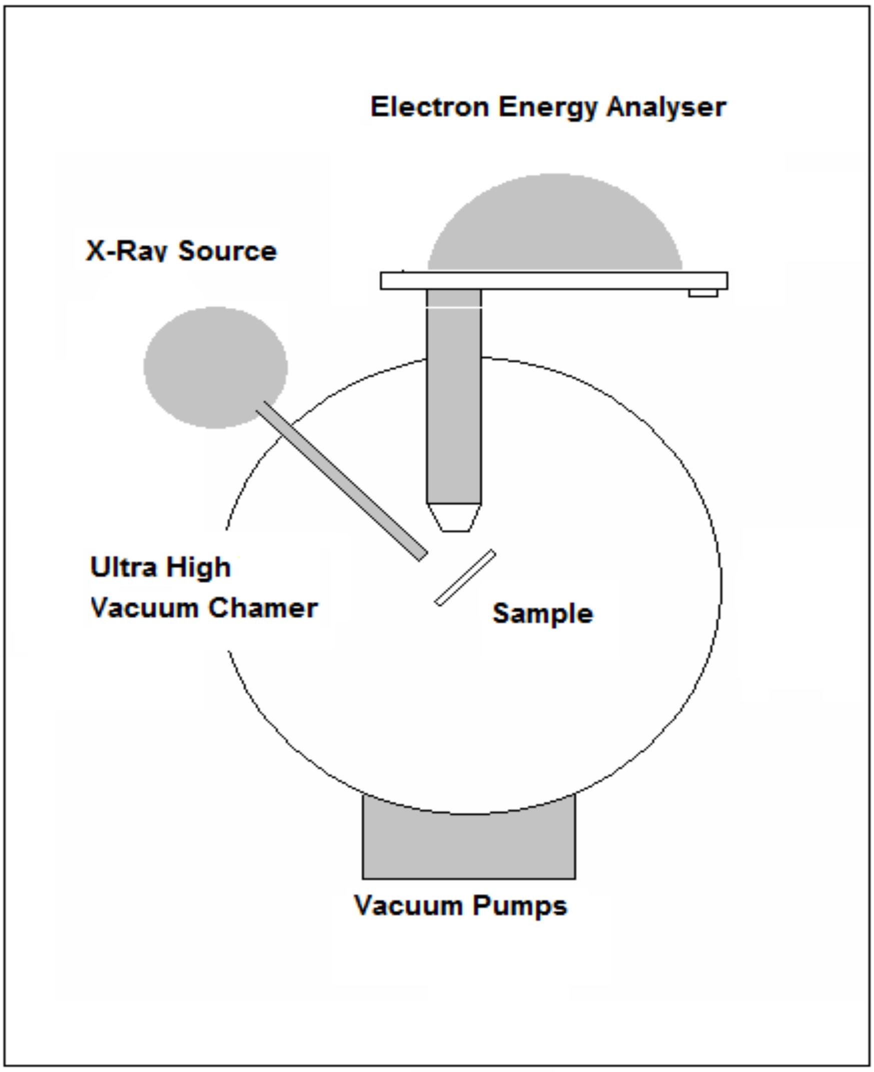

Figure 2.4. The basic set up for x-ray photoelectron spectroscopy.[16]

2.4.3 Surface area measurements (BET):

In 1938, Brunaure, Emmett, and Teller developed surface area measurements (BET). The BET technique is a form of analysis for the determination of the surface area of materials and the characterisation of catalysts because it is often the case that the more active the catalyst, the greater the surface area will be.[17] With this technique, the surface area of a material is based on the volume of the surface which adsorbs gas at a certain temperature and pressure. In general, the BET is used for N_2 adsorption and its concept depends on the BET equation (equation 3).

$$P/[V (P_0-P)]=[1/(V_m C)] + [(C-1)/(V_m C)*P/P_0]$$ [9,18] ***(Equation 3)***

- Where ***V*** is the volume of the adsorbed gas at pressure P.
- V_m is the volume of the monolayer of gas adsorbed.
- P_0 is the saturation vapour pressure of adsorbates at the temperature of adsorption.
- ***C*** is a constant, related to the heat of adsorption and condensation of gas.[9,18]

This equation gives a straight line when P/V (P_o-P) is plotted against P/Po, so Vm and C can be calculated accordingly. Once V_m and C are calculated, the surface area can be calculated from equation 4 by assuming every molecule of adsorbed N_2 is occupying σ=0.162 nm^2.

$$SA(m^2/g) = V_m \, Na \, \sigma / M \, Vo$$ ***(Equation 4)***

- Where ***SA*** is the surface area,
- ***Na*** is the Avogadro number (6.023 X 10^{23}),
- σ is the area of adsorbate = 0.162 nm^2 at 77 K.
- ***M*** is the sample weight.
- V_o is the molar volume of gas.[9,18]

The sample was performed for the BET analysis by degassing at 110 °C and after that linking to a Micromeritices Gemini 2360 Analyser automatic several point surface area analyser. During the analysis, the sample was left inside liquid N_2.

2.4.4 Temperature-Programmed Reduction (H_2-TPR):

Temperature programmed reduction (TPR) is a method used to determine the reducibility of the metal oxide species in the material.[19] Usually, the sample is heated regularly and a reducing gas mixture (often H_2 diluted in N_2 or Ar) flows over the sample. Through the gas flow over the sample, a thermal conductivity detector (TCD) measures the thermal conductivity changes of the consumed gas and records it as a signal. The thermal conductivity detector (TCD) signal refers to the concentration of hydrogen consumed (H_2 reacts with the O_2 present in the material). Temperature programmed reduction (TPR) is a useful method in catalysis through which different catalysts can be compared according to their reducibility profile in an attempt to explain differences in selectivity and activity which may be related to the surface structure.

$$MO + H_2 \longrightarrow M + H_2O$$

- Where MO is the metal oxide.

In this study, TPR analysis was carried out on a Quantachrome ChemBET instrument. Samples (0.9g) were pretreated under He for 1h at 100°C (ramp=20°C min^{-1}) prior to reaction to clean the surface. Analysis was carried out under 10%H_2/Ar (BOC 99.99%, 25ml min^{-1}) 30-850°C, 20°C min^{-1}.

2.4.5 Electron microscopy and High Resolution Transmission Electron Microscopy (HRTEM) and (SEM and TEM):

One of the main techniques in the characterisation of catalysts is scanning electron microscopy (SEM). Zworykin *et al.* have described the first modern scanning electron microscope (SEM).[20] Electrons are used in SEM as a replacement for light to manufacture images. Subsequently, it can present high quality images with detailed information about the morphology using SEM because of the massive depth of focus on the sample compared to optical microscopy.[21] Typically, a metallic filament cathode is heated in a vacuum by passing a voltage through it to generate an electron beam. It is accelerated during the column of microscopy by a powerful force conducted in the anode and the beam is focused, condensed and directed to a sample as a spot. Usually, Tungsten is used as a filament because of its low vapour pressure and high melting point. The collision between the sample and the incoming electron primary beam causes electrons to be reflected from the surface of the sample. The electrons reflected from the sample atom's nucleus have high electron energy and are called backscatter electrons. These electrons are detected by a backscatter detector and are used to show the contrast in chemical components. Secondary electron is as a result of the inelastic collision of the primary beam with the sample nucleus where energy loss takes place and to form an image of the surface, the electron is collected by a secondary electron detector. Both secondary and backscatter electrons are converted into a signal and view on screen as shown in Figure 2.5.[22]

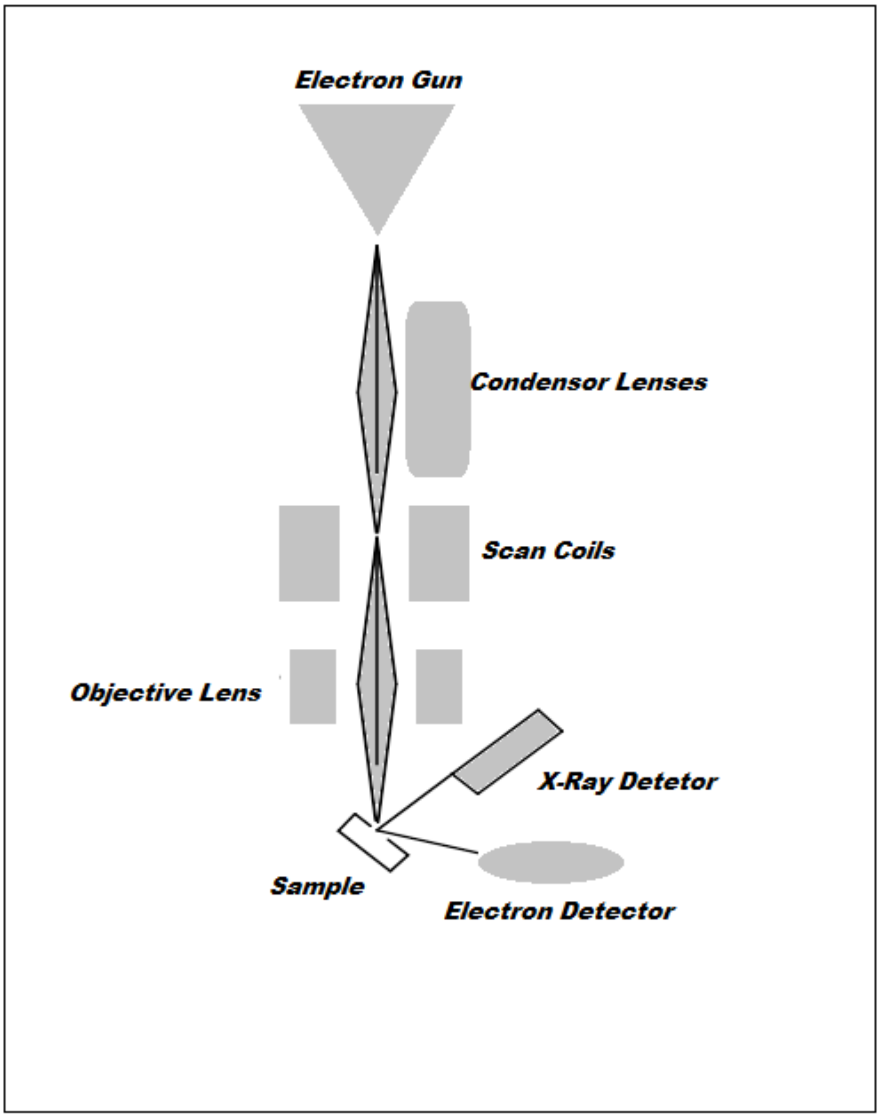

Figure 2.5. Schematic diagram of a scanning electron microscope (SEM).[23]

Transmission electron microscopy (TEM) is a useful technique in heterogeneous catalyst and it is used to determine of the size, composition and shape of the materials.[19] Electrons emitted from a gun on top of the unit proceed through electromagnetic lenses and are focused into a fine beam. Many types of electrons are reflected from the surface of the sample due to the hit between the sample and the beam causing them to produce and disappear as shown in Figure 2.6. The electrons are not reflected if they transmit over the sample and are hit by a fluorescent screen at the bottom of the microscope which creates the TEM image and can be studied by a camera (Figure 2.7). Dr. Thomas E. Davies from *Cardiff Catalysis Institute, School of chemistry*, *Cardiff University* obtained the TEM images.

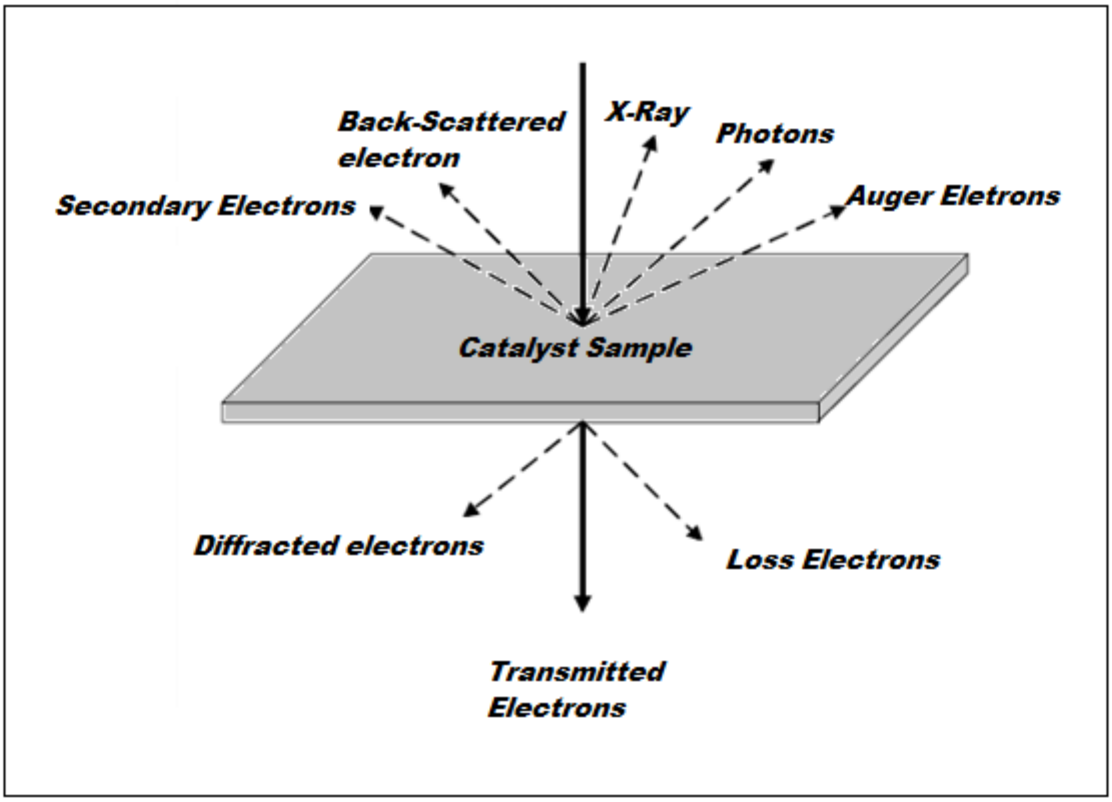

Figure 2.6. Interactions between electrons and the sample.[13,24]

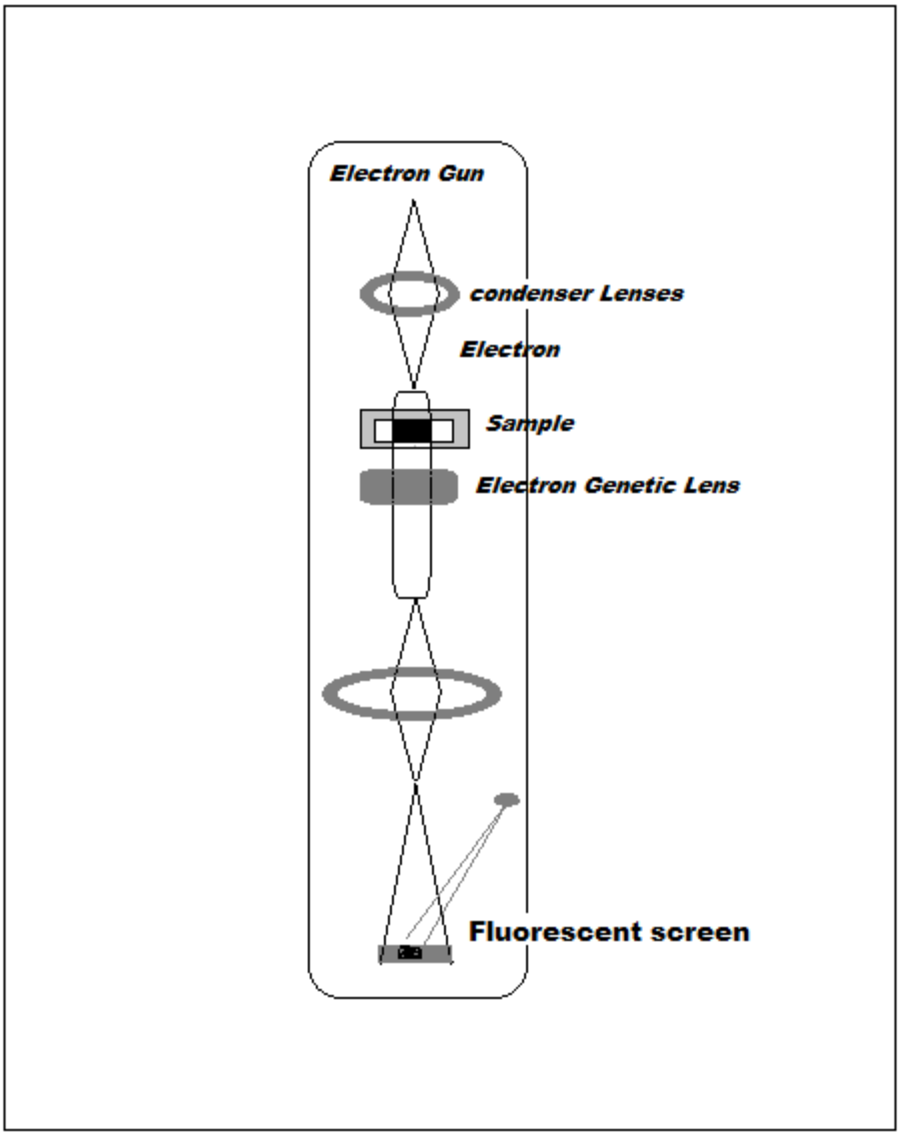

Figure 2.7. Schematic diagram of transmission scanning microscope (TEM).[23]

2.4.6 Gas Chromatography (GC):

Gas chromatography is commonly used in both industrial and academic laboratories. It is used for separating the components of mixtures and then identification and quantification. A GC contains an injector port; a carrier gas as mobile phase; columns as stationary phase, and detectors as shown in Figure 2.8. The samples are injected into the injection port, which is typically held at a high temperature to vapourise it. A carrier gas in the gas phase (for example argon, helium or nitrogen) transports the compounds, over the column to a suitable detector. The length, wall composition, and the polarity of the column separate the components and they elute thereafter (Figure 2.8).

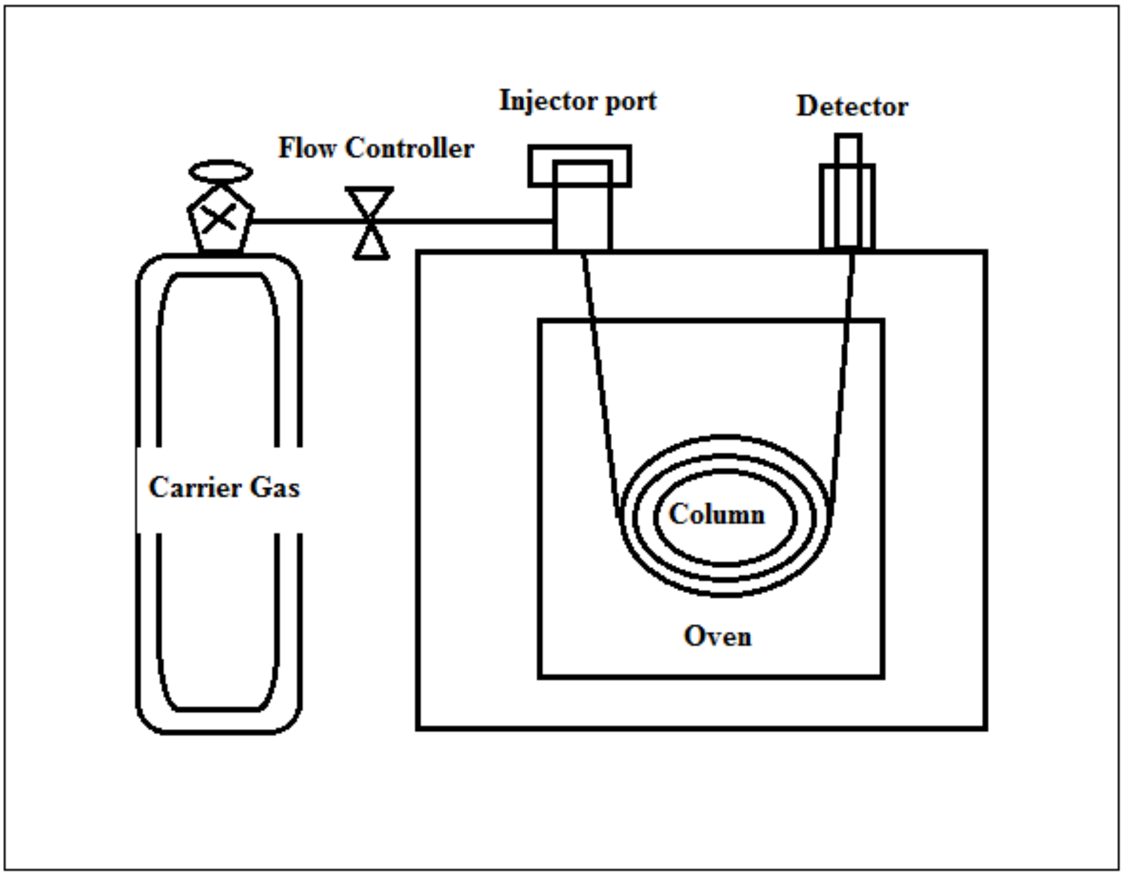

Figure 2.8. Schematic diagram of gas chromatography (GC).[25]

The separation happens because of the interaction between the sample components and the column. It is packed by an inert surface that acts as a stationary phase. Usually, two types of columns are used for separation in GC: packed and capillary.[16] The packed column contains an inert solid material covered by liquid as a stationary phase with typical length (1.5-10m) and internal diameter (2-4 mm). The capillary column is built up of a tube of capillary, and the inner wall is lined with a layer of material for example polyamide. Typically, the capillary tube is diameter (50-500 μm) and length (5-200m). Capillary columns are the most widely used columns in GC due to their high separation power. Once the sample components are separated, they are analysed and registered by a detector and then quantified by the user. The two most common detectors used in GC are the flame ionization detector (FID), and the thermal conductivity detector (TCD). The TCD is created for the detectable difference between the thermal conductivity of two streams; the primary is a carrier gas as a reference, and the secondary contains the carrier gas and the compound. The TCD contains tungsten-rhenium filaments formed as a Wheatstone bridge. One of the properties that must be provided by the carrier gas is high thermal conductivity, for example He, and the gas flows across the filaments to remove the heat. When a sample with lower thermal conductivity arrives from the column to the sample filaments, a change in thermal conductivity is detected due to variations in voltage. The flame ionization detector (FID) including the column is linked with a jet chamber (stainless steel). Once the carrier gas comes from the column to the chamber it is then mixed with hydrogen and air and combusted at the tip of the chamber. The molecules, which ionise are attracted and recovered by a metal collector electrode at the side of the flame. An amplifier changes the electron to millivolts. The

FID is insensitive to molecules like NO, NO_2, CO_2, CO, O_2 and N_2 but it is highly sensitively to hydrocarbons. For both detectors TCD and FID, the peak area was modified by a response factor to obtain the correct count.[25] The FID detector is more sensitive than the TCD but the TCD is suitable for all compounds. Hence it is commonly used for the analysis of gases, for example for components containing O_2, CO, CO_2, N_2, NO, NO_2[25]

Typically, the supported catalyst (0.1g) was suspended in the sample (1g), in solvent and hydrogen at 25°C. The reaction mixture was stirred (1000 rpm), and a sample of the reaction was taken for analysis after the reaction was completed. Analysis was carried out using gas chromatography (Varian 3800 fitted with CP wax column) and a flame ionisation detector. Hydrogenation of the samples was performed in an autoclave reactor.

2.4.6.1 Calculations of response factors for each compound:

The response factor (RF) of product is calculated from the ratio of a known amount of product and a constant amount of internal standard (1-propanol). Different concentration solutions were made up of all the different products. The different concentration solutions were injected for GC calibrations. The signal area of each compound is shown as a peak. The calibration curve can be found from the ratio between the calibration concentrations of each compound and normalised based on the area of the standard; this is used to calculate the response factor, as shown Figure 2.9.

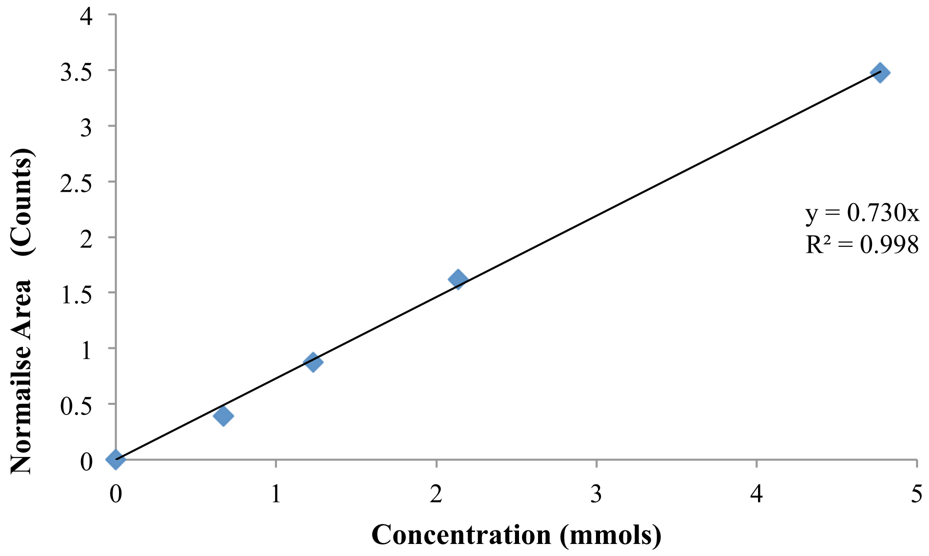

Figure 2.9. Example of calibration curve line in GC for 2-methylfuran.

Calculations of conversion and selectivity have been made with these formulae:

- *Conversion (%) =*

[[Moles of Feed in – Moles of Feed out] / Moles of Feed in] x 100

- *Selectivity to A (%) =*

[[Moles of Product A Formed] / Total moles of all Products Formed] x 100

2.4.7 Gas Chromatography Mass Spectroscopy (GC-MS):

Gas chromatography mass spectroscopy is a technique used to identify compounds after separation from a reaction mixture by gas chromatography mass spectroscopy. After separating the molecules by the GC an electron is accelerated through an electric field and an interaction between electrons leads to either negative or positive radicals. The positive radical (loss of an electron) is used more widely than the negative radicals (adding an electron). Ions are separated based on the mass to charge ratio using either a Period of flight analyser or Quadrapole analyser.

A period of flight detector is determined by calculating the time for the transfer of ions from the source to the detector while the quadrapole analyser is created out of four rods. Ions are quantified by separation through either an electron multiplier or a Faraday cup. A Faraday cup detects charged molecules either a (-) or (+). When (-) and (+) charge reach a ground electric plate they are neutralised. Molecules which have higher energy hit the cup and create a shower of secondary electrons and they are shown due to the shape of the Faraday cup then the signal is amplified. Secondary electron is used to magnify the signal in the electron multiplier. The first dynode is moved from ions, which cause the emission of the second electrons. This will increase speed through the electric field to strike the second dynode because of signal magnification to 10^6 times.[26]

2.4.8 Thermogravimetric analysis (TGA):

Thermogravimetric analysis (TGA) can be used to record the weight change with temperature or time due to decomposition or dehydratation in an atmosphere of N_2, H_2, He, air, or other gases.[27] The sample is constantly weighed as it is heated to elevated temperatures. Change in weight is as a result of the split or the formation of various bonds at high temperatures. The TGA analysis was carried out in a SETARAM Labsys thermogravimetric analyser. A basic technique for achieving a TGA pattern is as follows. 50 mg of a sample of catalyst is placed into an aluminium oxide pot for analysis. The analysis was performed in air. The temperature programme that was used was to have an isothermal time period at 25°C for 5 minutes, then a temperature ramp to 20°C/min.[27]

5.3 References:

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Chapter 3

Hydrogenation of Cyclohexanol

Chapter 3

3. Cyclohexanol hydrogenation:

3.1 Introduction:

The consumption of fossil energy to produce chemicals and fuel requires the utilisation of non-renewable resources on a large scale. Hence, the use of technologies which are effective yet not harmful to the environment have become a very important issue, and the use of hydrogenative treatment offers promising potential for future biomass reactions. This idea is presently being discussed in the context of the conversion of carbohydrates and sugar alcohols, and has huge possibilities with regard to the transformation of the extra biomass derivatives, as well as hemicellulose and cellulose, into important platform chemicals. Recently, it has become possible to convert biomass into various compounds already integrated in fossil fuel based value chains; thus, hydrogenolysis bears the potential to bridge the technologies available and develop alternative refinery concepts. In 1912, the first hydrogenative treatment of sugars and sugar alcohols was reported, when an attempt was made to achieve sugar alcohols through the reaction of several carbohydrates with hydrogen at 84bar and 100–135°C.[1] In 1922, Cake mentioned the hydrogenation of glucose to d-mannitol and d-sorbitol on Pt black in the presence of KOH in aqueous solution.[1,2] In this chapter, a model of a reaction will be presented in order to investigate a heterogeneous catalysis through the hydrogenation of biomass-based substrates (Furfuryl alcohol and Furfural), with a focus on promising product ranges and suitable catalyst systems. In addition, dehydration and hydrogenation of cyclohexanol will be described over various catalysts. Moreover, solid catalysts, over recent decades, have been increasingly examined for their efficiency in the partial hydrogenation of alcohol. In recent studies with supported metal nanoparticles, it states that it is possible to produce very effective catalysts for the hydrogenation of alcohols using H_2 under relatively mild conditions.[3]

3.2 Alcohol dehydration and hydrogenation:

Dehydration is an elimination reaction of an alcohol; the elimination reaction involves the loss of an OH^- from one carbon atom and an H^+ from an adjacent carbon atom. Overall, this amounts to the elimination of a molecule of water, resulting in a π-bond formation of an alkene or alkyne. The loss of water from a molecule is called dehydration. In many cases, alcohol dehydration requires an acid catalyst, as shown in scheme 3.2[4]

Hydrogenation is a chemical reaction between hydrogen and another compound. The activation of H_2 plays an important role in the valorisation of biomass. The reactions of choice to increase the H/O and H/C ratio of the biomass derived are hydrogenolysis or hydrogenation. Typically, the catalysts of choice for hydrogenation reactions are catalysts of metal or supported monometallic noble metal catalysts. Recently, for hydrogenation reactions, supported mono/bimetallic catalysts have become known as superior catalysts with excellent catalytic capabilities. In addition to excellent catalytic activities, these catalysts are utilised to avoid some of the less propitious features of other catalysts.[1,5]

3.2.1 Cyclohexanol hydrogenation:

3.2.1.1 Introduction to HPA:

Heteropolyanions are polyoxometalate inorganic anions consisting of nanosized metal oxygen groups. These anions have physicochemical properties, particularly their multifunctionality and structural mobility, and are thus important in several disciplines. A general formula for heteropolyanions is $[X_xM_mO_y]^{q-}$ ($x \leq m$), where M is the addendum atom and X is the heteroatom (also called central atom when located in the centre of the polyanion). Mo(VI) or W(VI) are the most commonly used addendum atoms; on the contrary, V(V)or Nb(V) are used less frequently. A broad range of elements can be used as heteroatoms. These include P(V), As(V), Si(IV), Ge(IV), B(III), and so on. Generally, this anion is prepared by a self-assembly method in an acidic aqueous solution, as shown in the following equation:[6]

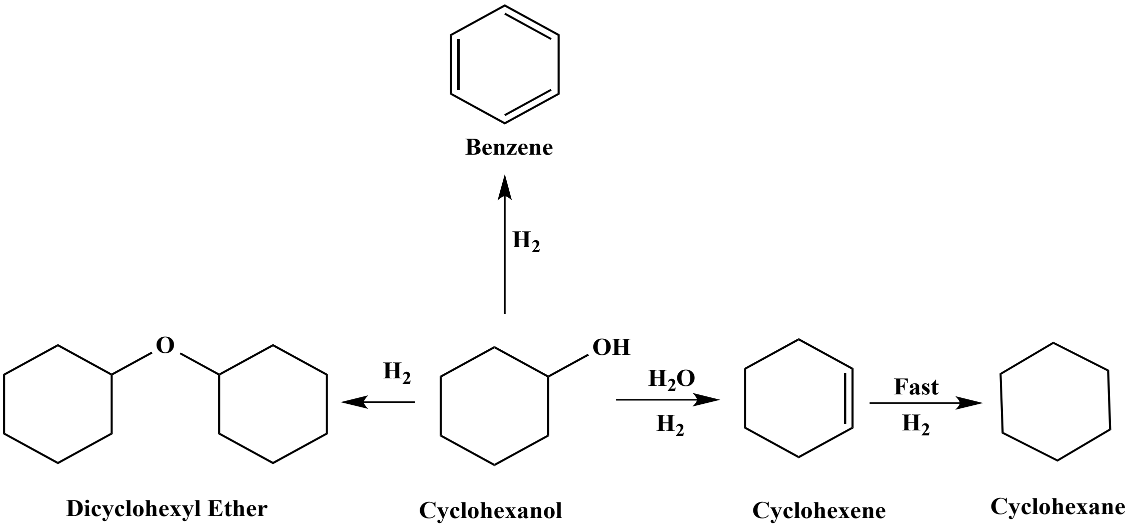
$$23H^+ + HPO_4^{2-} + 12WO_4^{2-} \longrightarrow [PW_{12}O_{40}]^{3-} + 12\,H_2O$$

In addition, the first heteropoly compounds were discovered by Berzelius in 1826.[7] These were ammonium 12-molybdophosphate. Then after approximately 70 years, heteropoly compounds were investigated, and around 750 such compounds were reported.[6] Since then, there have been many suggestions for the structure of heteropoly compounds. In 1933, Keggin succeeded in determining the structure of

$H_3PW_{12}O_{40}.5H_2O$ by using a powder X-ray diffraction technique.[8] By 1995, the X-ray structures of approximately 180 heteropoly compounds had been reported[6] Heteropoly acids (HPA) possess good thermal stability and high acidity, but little work has been carried out to study developing them as catalysts for cascade organic synthesis, where the catalyst performs two or more reactions.

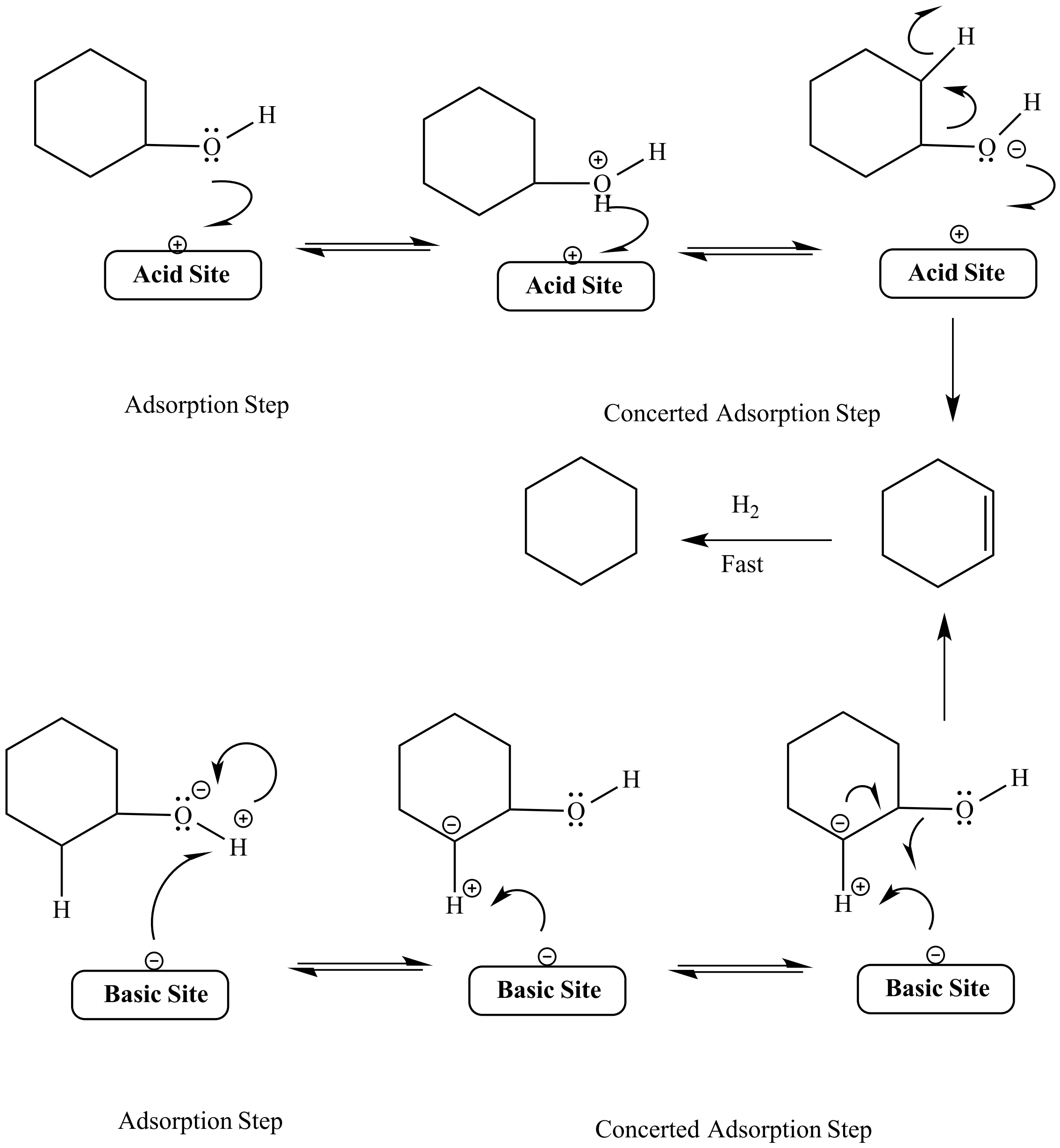
3.2.1.2 The aim of the work:

In this chapter, Pd and Au:Pd supported on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ are examined as catalysts for the conversion of cyclohexanol to cyclohexene; then in a second step, to achieve cyclohexane an industrially important reaction. The catalysts will be employed for liquid phase reactions, and the effects of varying reaction conditions will be discussed. The conversion of cyclohexanol to cyclohexane occurs through the dehydration of secondary group (OH^-) to cyclohexene, and after that the selective hydrogenation of the C=C bond on the cyclohexene ring, as shown in scheme 3.2.[4]



Scheme 3.1: Possible reaction pathways in the one-step conversion of Cyclohexanol.

In a final study, heteropoly acid catalysts have been investigated for the hydrogenation of cyclohexanol, in a reaction that takes place in the vapour phase for the dehydration of cyclohexanol to cyclohexene at 220°C for 5h over $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W); HPA catalysts reveal a continuous flow fixed-bed reactor at atmospheric H_2 pressure.[5] The aim of this work is to clarify how the dehydration and hydrogenation of furfuryl alcohol and furfural (Chapter 4) using heterogeneous catalysts takes place. Heteropoly acid catalysts have been investigated for the dehydration of cyclohexanol, as a model for furfuryl alcohol. The HPA were then ion exchanged with Au and Pd and the hydrogenation activity of these catalysts was investigated. Au and Pd were also impregnated into a HPA catalyst. The experimental process is explained in detail in chapter Two, but briefly summarised here for clarity. The reaction was carried out in a stainless steel autoclave equipped with a stirrer. Continuous stirring of the reaction mixture is important to minimise the heat and diffusion limitations between the bulk liquid phase and the catalyst particles. The catalyst was initially pretreated to a temperature of 400ºC in a furnace. The reaction mixture contained 10g of cyclohexanol and 0.1g of catalyst. The autoclave was pressurised with either N_2 or H_2 at 150°C. The reaction products were identified *via* a combination of gas phase chromatography coupled with mass spectroscopy (GC/MS) and by comparing the retention times of the reaction products with the retention times of the pure compounds. Dicyclohexyl ether was not available industrially and hence identified by NMR and GC/MS.



Scheme 3.2: Reaction mechanism for the dehydration of Cyclohexanol to Cyclohexane on a surface acid and basic site.[4]

3.3 Results and Discussion:

3.3.1 Study of support effect:

The HPA exhibits high catalytic activity in a wide range of reactions in heterogeneous systems. In general, the catalytic activity of solid HPAs is higher than that of conventional solid catalysts (e.g., mixed oxides and zeolites). Acidity and basicity behaviour are the main factors governing the acid catalysis of solid HPAs. The activity depends mainly on the size of the metal particles as the adsorption of H_2 occurs on the metals particles. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}$HPA) has a higher surface area which may possibly explain why higher activity was observed.[9] To study the influence of the support on a cyclohexanol reaction, Au, Pd and Au:Pd alloys metals were added to the HPA catalyst ($Cs_{2.5}$HPA). The reaction was carried out using either N_2 or H_2 at a temperature of 150ºC and resulted in a cyclohexanol conversion of 22% and 30% with N_2 while in the presence of H_2 it resulted in 10% and 29% that is with $Cs_{1.5}H_{0.5}PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ respectively in the absence of the metal. It is clear that the highest activity for cyclohexane was achieved with the support of the highest surface area, as shown in Table 3.3, ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$). The cesium salts of the tungstophosphoric heteropolyacid ($Cs_xH_{3-x}PW_{12}O_{40}$) have higher surface areas than hydrogen forms ($H_3PW_{12}O_{40}$), as shown in Table 3.3, which is close to the surface areas of the Cs salts[10]and for $H_3PW_{12}O_{40}$[11]. It can be seen that there was an increase in surface area with the increasing Cs content for $Cs_xH_{3-x}PW_{12}O_{40}$.

Table 3.1: Hydrogation of Cyclohexanol to Cyclohexane catalysed:

Catalyst	Conversion (%)	Selectivity %				
		Cyclohexene	Cyclohexane	Benzene	Dicyclohexyl ether	Unknown
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	30	85	0	0	15	0
$Cs_{1.5}H_{0.5}PW_{12}O_{40}$	22	84	0	0	16	0
0.025%Au-0.0375%Pd/ $Cs_{2.5}H_{0.5}PW_{12}O_{40}$	14	75	10	5	11	0
0.05%Au-0.075%Pd/ $Cs_{2.5}H_{0.5}PW_{12}O_{40}$	6	32	34	18	10	5
2.5%Au-2.5%Pd/ $Cs_{2.5}H_{0.5}PW_{12}O_{40}$	14	12	47	23	14	4
5%Au/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	3	5	56	34	2	3
1%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	25	20	49	23	8	0
5%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	27	1	63	30	6	0

Reaction conditions:- (10g, 0.1 mole) of substrate, 100mg of catalyst, autoclave reactor, 150ºC, 1000 rpm, 6h, 1bar N_2 constant pressure.

Table 3.2: Hydrogation of Cyclohexanol to Cyclohexane catalysed:

Catalyst	Conversion (%)	Selectivity %			
		Cyclohexene	Cyclohexane	Benzene	Dicyclohexyl ether
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	29	89	2	0	9
$Cs_{1.5}H_{0.5}PW_{12}O_{40}$	10	85	1	0	14
0.025%Au-0.0375%Pd/ $Cs_{2.5}H_{0.5}PW_{12}O_{40}$	15	66	17	6	10
0.05%Au-0.075%Pd/ $Cs_{2.5}H_{0.5}PW_{12}O_{40}$	14	29	49	13	8
2.5%Au-2.5%Pd/ $Cs_{2.5}H_{0.5}PW_{12}O_{40}$	16	20	57	10	12
5%Au/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	6	63	21	0	16
1%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	34	3	63	26	8
5%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	9	0	73	17	9

Reaction conditions:- (10g, 0.1 mole) of substrate, 100mg of catalyst, autoclave reactor, 150ºC, 1000rpm, 6h, 1bar H_2 constant pressure.

It should be noted that the relative activity over $Cs_xH_{3-x}PW_{12}O_{40}$ containing the lower concentration of Cs (two and below) is considerably lower owing to a much lower catalyst surface area, which is less than $2m^2/g$. When *x* is 2.5 then the catalytic activity reduces because of the lower surface acidity (the number of protons at the surface).[12] When Au, Pd and Au:Pd were added to the catalyst and used under the same reaction conditions (See Tables 3.1-3.2), the cyclohexanol conversion increased to 34% over 1%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as the catalyst; whilst there was high selectivity to cyclohexane (63%). However, over 5%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ the catalyst conversion was decreased to 9% and selectivity to cyclohexane was 73%. Palladium is known for its high activity in hydrogenation reactions[13,14] and the current results are also in agreement with the studies found in the literature. This is probably due to the palladium rich-H surface of the catalyst.[15] The highest selectivity was observed for 5%Pd/ $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and the selectivity was also clearly affected by the gold and palladium ratio, which suggests that the hydrogenation of cyclohexanol is dependent on the ratio of gold and palladium. Obviously, there is a variation between the results; particularly for 1% and 5%Pd loading, it seems the catalytic activity can be linked to the decrease in surface area by loading metals (decrease from 131 to 25 with loading Au:Pd and to 31 when loading Pd) as shown in Table 3.3, and that will be discussed further in a study of palladium's loading effect (section 3.3.3).

Table 3.3: Surface area of supports by BET method:

Support materials	Surface area (m^2/g)
$H_3PW_{12}O_{40}$	2
$Cs_{1.5}HPW_{12}O_{40}$	108
$Cs_{2.5}HPW_{12}O_{40}$	131
5%AuPd/$Cs_{2.5}HPW_{12}O_{40}$	25
5%Au/$Cs_{2.5}HPW_{12}O_{40}$	5
1%Pd/$Cs_{2.5}HPW_{12}O_{40}$	115
5%Pd/$Cs_{2.5}HPW_{12}O_{40}$	31

3.3.2 Study of the gold and palladium ratio effect:

To investigate the effect of Au:Pd ratios on the hydrogenation of cyclohexanol, the Au:Pd supported on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalysts were prepared using the impregnation method. The results show that the gold and palladium ratio affected the conversion and selectivity of the hydrogenation products. A reduced catalyst of pure gold supported on $Cs_xH_{0.5}PW_{12}O_{40}$ showed poor conversion. However, an addition of palladium along with gold showed a significant increase in the conversion and selectivity, as shown in tables 3.1 and 3.2. Sites of palladium are therefore much more active for hydrogenation than gold sites. Palladium has a rich-H surface for the catalyst[15] and hence is known for its high activity in hydrogenation reactions[13,14] and the current results are also in agreement with literature studies. The highest conversion and selectivity have been observed for the catalyst with pure palladium loaded catalyst, and the selectivity was also clearly affected by the gold and palladium ratio, which suggests that the hydrogenation of cyclohexanol is dependent on the ratio of gold and palladium.

3.3.3 Study of palladium loading effect:

Table 3.1 and table 3.2 show how the various Pd loadings affect the performance of catalysts. The highest cyclohexanol conversions of around 25% with N_2 and 34% with H_2 were obtained with the lower palladium loading of 1wt% under optimum reaction conditions. Lower conversion was observed when the catalyst with higher Pd loadings of 5wt% was tested at 1 bar H_2. This can be explained by the low surface area as well as lower dispersions, and hence larger average Pd particles. When palladium particle size increases, the average distance between the metal particles and the acid/base sites increases.[16] Chen et al. explain how Pd particles may aggregate when the Pd loading is at a higher level leading to the covering of basic sites on their Pd/hydrotalcite derived catalysts.[17] However, the selectivity to cyclohexane increases significantly with a Pd loading of 5wt%, which again can be explained by the more favourable conditions when the Pd acid/base site distance increases with higher Pd loading.

3.4 Catalyst characterisation:

Various catalysts were prepared and tested for the hydrogenation of the cyclohexanol reaction. The preparation procedure is explained in Chapter Two. So far, the 5%Pd/$Cs_{2.5}$HPA has been selected for this reaction because of the higher conversion of cyclohexanol when use N_2 gas while the 1%Pd/$Cs_{2.5}$HPA has been selected for this reaction because of the higher conversion of cyclohexanol when use H_2 gas. The 5%Pd/$Cs_{2.5}$HPA and $Cs_{2.5}$HPA catalysts have been characterised using scanning electron microscopy (SEM); X-ray powder diffraction (XRD) and surface area (BET). The results of the characterisation are presented in the following paragraphs.

3.4.1 Scanning electron microscopy (SEM):

The SEM image of the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}$HPA), 5%Pd/$Cs_{2.5}$HPA, $Cs_{1.5}$HPA, 1%Pd/$Cs_{2.5}$HPA, 5%Au/$Cs_{2.5}$HPA and 5%AuPd/$Cs_{2.5}$HPA prepared through the impregnation of the palladium metal (image 3.1) shows large metal particles. The SEM images show that the surface morphology of undoped $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Pd/Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalysts are indistinguishable. Moreover, the SEM images vary in morphology remarkably from the undoped $Cs_{2.5}$HPA to 5%Pd/$Cs_{2.5}$HPA catalyst. As with similar studies, a general decrease in the dispersion was recorded upon increasing the Pd loading.[18,19] This is described through the logical result of Pd group formation being more easily afforded with increasing Pd.[18]

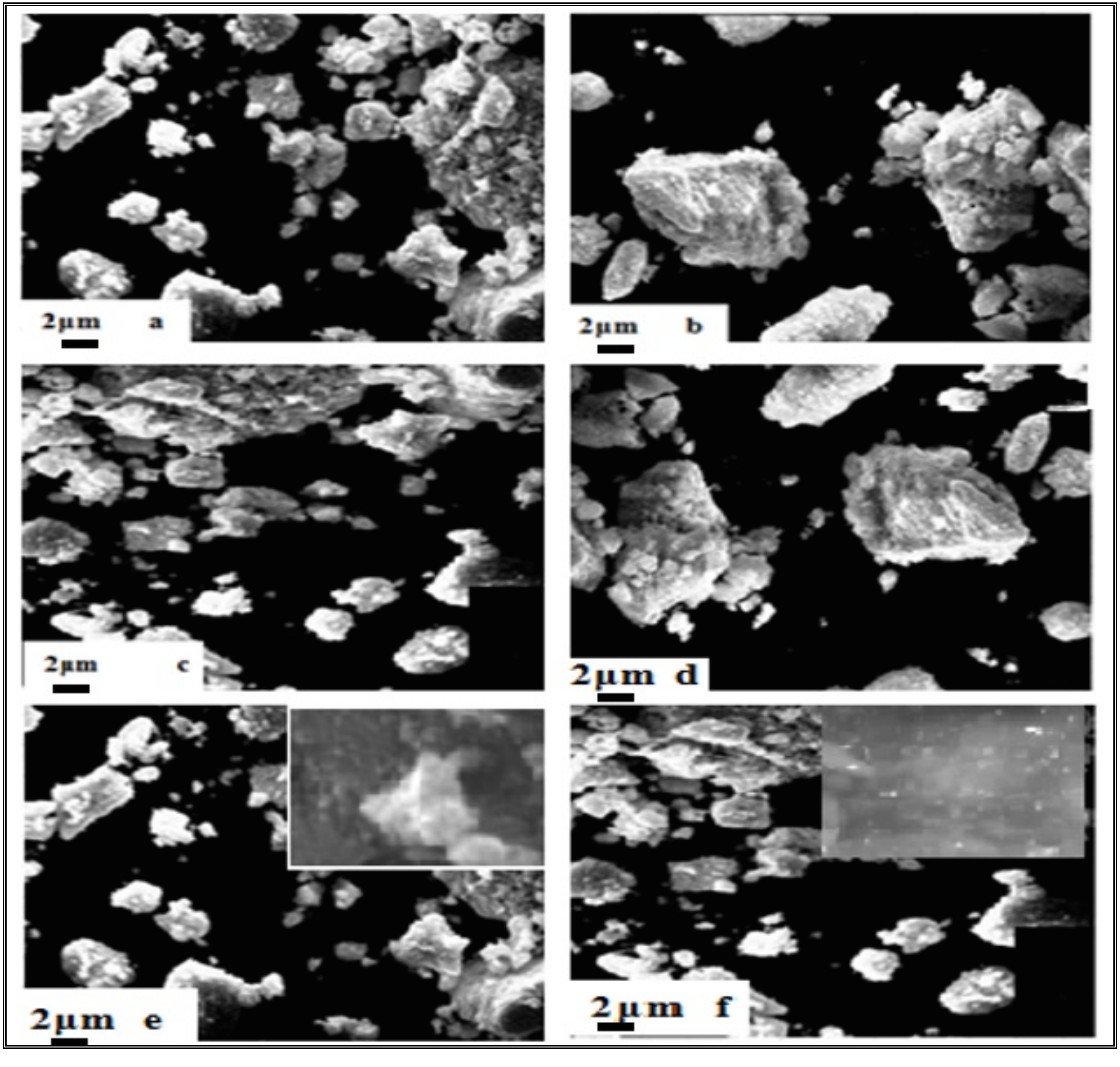


Image 3.1: an SEM image of catalysts prepared by the impregnation method: a) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, b) 5%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$. c) $Cs_{1.5}H_{0.5}PW_{12}O_{40}$, d) 1%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$, e) 5%Au/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and f) AuPd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$.

3.4.2 X-Ray Diffraction (XRD):

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is an ordered crystalline material with a proper crystallite size, as estimated from the XRD line width using the Scherrer equation by Okuhara *et al.*[20] The XRD pattern for $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is very similar to that of the parent heteropolyacid ($H_3PW_{12}O_{40}\cdot6H_2O$) except for the broadening of the sharp diffraction lines of the hexahydrate, due to the removal of water and crystallisation involved in the drying of the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.[20,21]

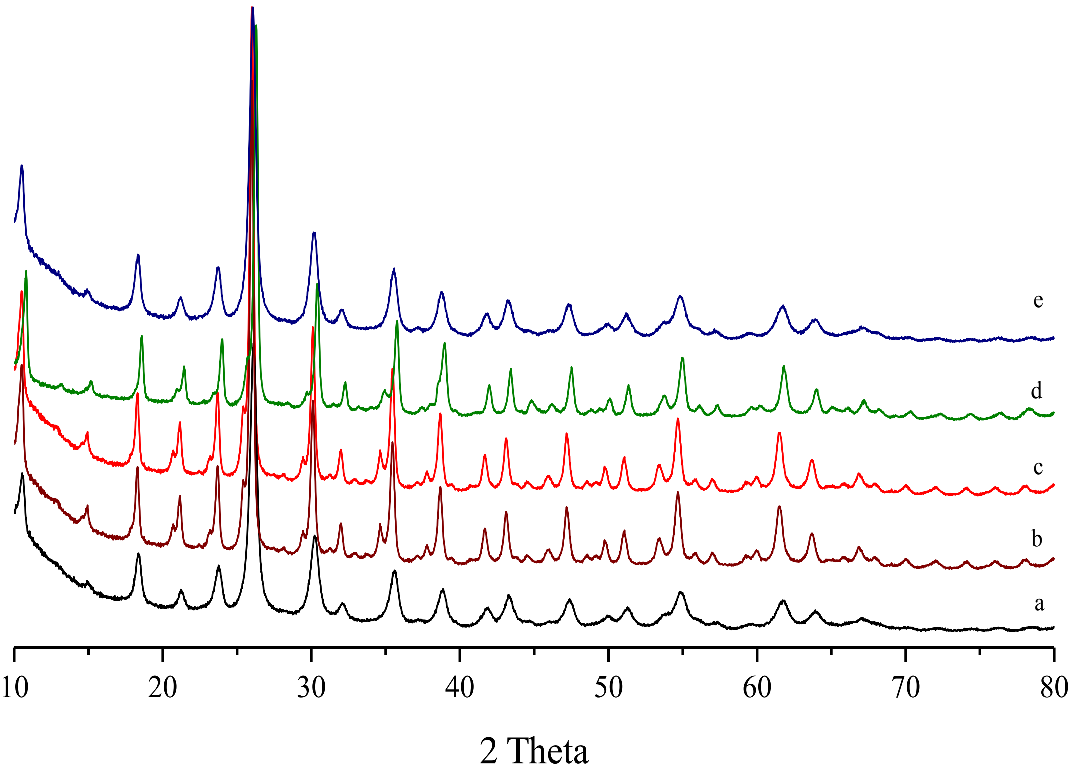


Figure 3.1: The XRD pattern of a) $H_3PW_{12}O_{40}$ b) $Cs_{1.5}H_{0.5}PW_{12}O_{40}$, c) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, d) 5%Au:Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and e) 5%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$.

The XRD diffraction patterns for $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and 5%Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ are achieved using the experimental process described in Chapter Two, and these are shown in Figure 3.1. The diffraction patterns compares well to those found for

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in the literature.[20,21] The main goal of the XRD analysis was to attempt to calculate the average particle size of palladium which is dispersed on the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ support using the Scherrer equation, a method detailed in a previous study of palladium nanoparticles in polyethylene glycol.[22] Palladium metal appears as diffraction lines at $2\theta=40.1, 46.6, 68.1^{o}$.

No change was observable in the diffraction pattern of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ upon the impregnation of palladium and the consequent pretreatment. More importantly, there was no diffraction line for Pd. This is an indication that the average particle size is less than 2nm.[23] This is also an indication of very high dispersion of metal on HPA.

In terms of Au:Pd alloy, corresponding peaks were clearly observed at 38.63°, 38.43° and 44.33°. A gold peak was present at 38.23° which is assigned. The peaks indicating the presence of metallic Pd were not observed, as all the catalysts were subjected to calcinations in static air at 400°C for 3 hours.

3.4.3 Temperature-programmed reduction (TPR):

TPR analysis has been used to investigate the reducibility of the $Cs_{2.5}$HPA, 5%Pd/$Cs_{2.5}$HPA and 5%AuPd/$Cs_{2.5}$HPA catalysts under different pre-treatment conditions. TPR analysis shows the catalyst calcined under static air was more reducible compared to the catalyst, which is oxidised by oxygen. This indicates that it has slightly more surface hydrogen available, which makes it suitable for the hydrogenation reaction (Figure 3.2). The TPR profiles of the $Cs_{2.5}$HPA, 5%Pd/$Cs_{2.5}$HPA and 5%Au:Pd/$Cs_{2.5}$HPA catalysts are compared in Figure 3.2. As previously observed, supported Pd is much more easily reduced. In fact, the reduction of 5%Pd/$Cs_{2.5}$HPA is around 100°C.

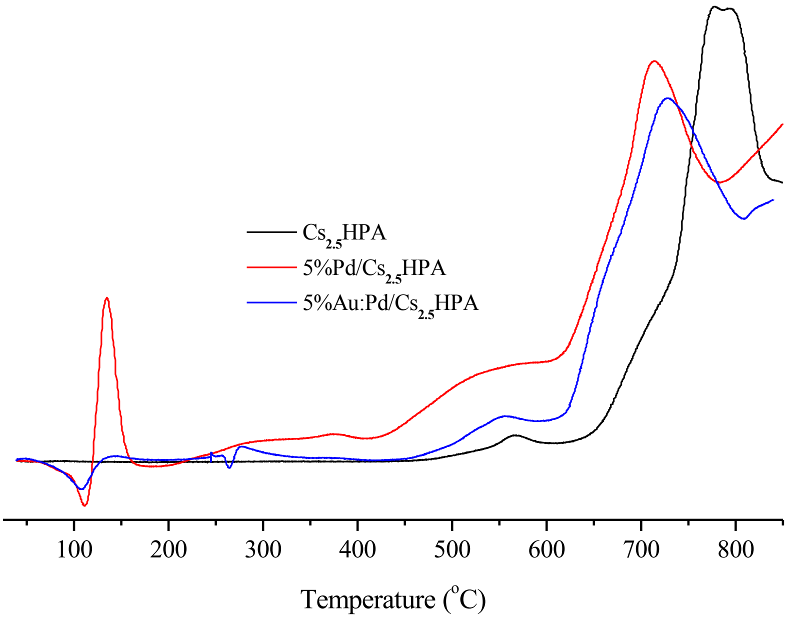


Figure 3.2: TPR measurements of the Cs2.5HPA, 5%Pd/Cs2.5HPA and 5%AuPd/Cs2.5HPA.

3.4.4 Surface area measurements (BET):

The surface areas and porosity of bulk heteropolyacids are very low, with surface areas typically in the range <10 m^2/g, reflecting their high solubility in water.[6,11] The porosity and the surface areas (50-200 m^2/g) can be increased significantly by replacing H^+ ions for large alkali metal, for example Cs^+, K^+, and Rb^+, via the addition of cation salts with the heteropolyacid. The surface areas of $Cs_xH_{3-x}PW_{12}O_{40}$ are changed from x=2 ($1m^2g^{-1}$) to x=2.5 ($130m^2g^{-1}$) and x=3 ($156m^2g^{-1}$). According to the TEM observation and nitrogen adsorption measurement[24], $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$ consist of very fine particles (8-10 nm in diameter) where the surface is covered by a monolayer of $H_3PW_{12}O_{40}$, and therefore, the pores are inter-particle, rather than intra-crystalline. Figure 3.1 is a diagrammatic representation of the bimodal pore size distribution in $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.[25] The BET and the pore size division for the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ used to produce the palladium doped $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalysts in this study are shown in Table 3.1. Table 3.3 is a summary of the data output from the BET for the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ materials and the palladium doped catalysts prepared in this study. The addition of palladium into the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ reduces the surface area to a small extent, and is confirmation of palladium on the surface of the catalysts. This has been observed in previous studies with Pt or Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ systems.[26,27] The highest loading had the biggest effect on the surface area, as can be expected.

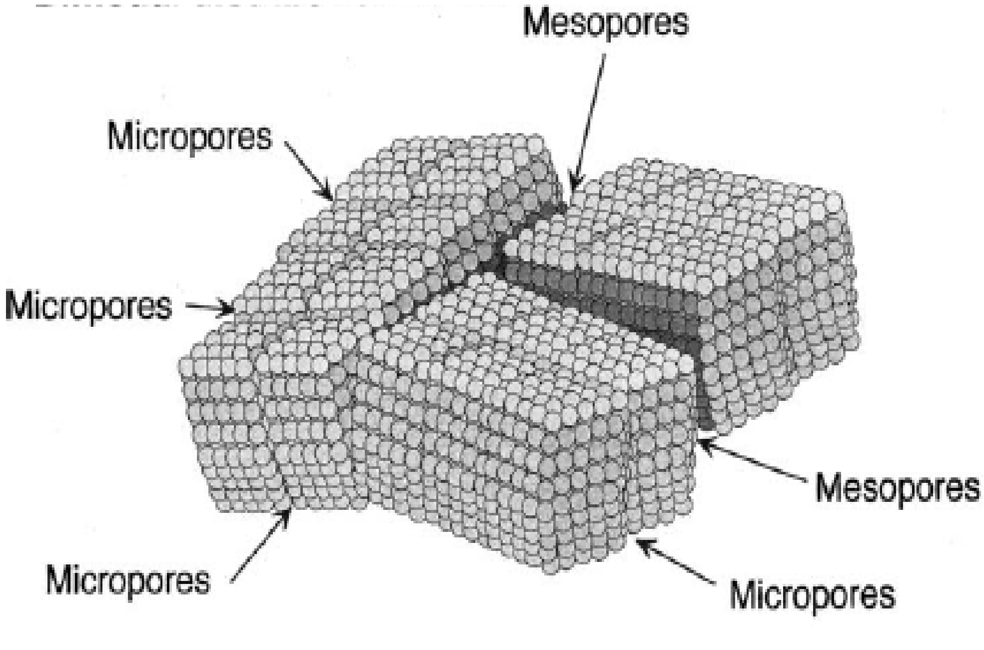


Figure 3.1: The bimodal pore size distribution in $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.[25]

3.5 Conclusions:

- Palladium supported on the heteropolyacid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ has been studied as a multifunctional catalyst for the conversion of cyclohexanol under mild conditions.
- The synergy of palladium and the Brønsted acid sites of the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ support were noted. A significant increase in the cyclohexanol conversion was also observed with the $Pd/Cs_{2.5}H_{0.5}PW_{12}O_{40}$.
- The Pd supported catalyst was more active for the direct hydrogenation of cyclohexanol, which led to high selectivity of cyclohexane and cyclohexene.
- In the presence of N_2 reactions, Pd loading of 5wt% at 150ºC was the optimum condition at a low N_2 pressure of 1 bar. A Cyclohexanol yield of 27% and selectivity to cyclohexane over 63% were reached.
- In the presence of H_2 reactions, a low Pd loading of 1wt% provided the optimum conditions at a low H_2 pressure of 1 bar. High cyclohexanol yields of up to 34% and selectivity of above 73% were obtained.
- The lower cyclohexanol conversions observed could be due to the following factors: (a) The significantly lower conversion of catalyst in N_2 gas when compared to the H_2 gas. (b) Lower catalyst deactivation (coke formation) which is generally associated with liquid reactions due to the solvation of strong acid sites. (c) Polar groups from compounds produced in the dehydration reaction and the reaction products, cyclohexene and cyclohexane, compete with the cyclohexanol molecules on the active sites, suppressing the activity of the strong sites.[28]

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Chapter 4

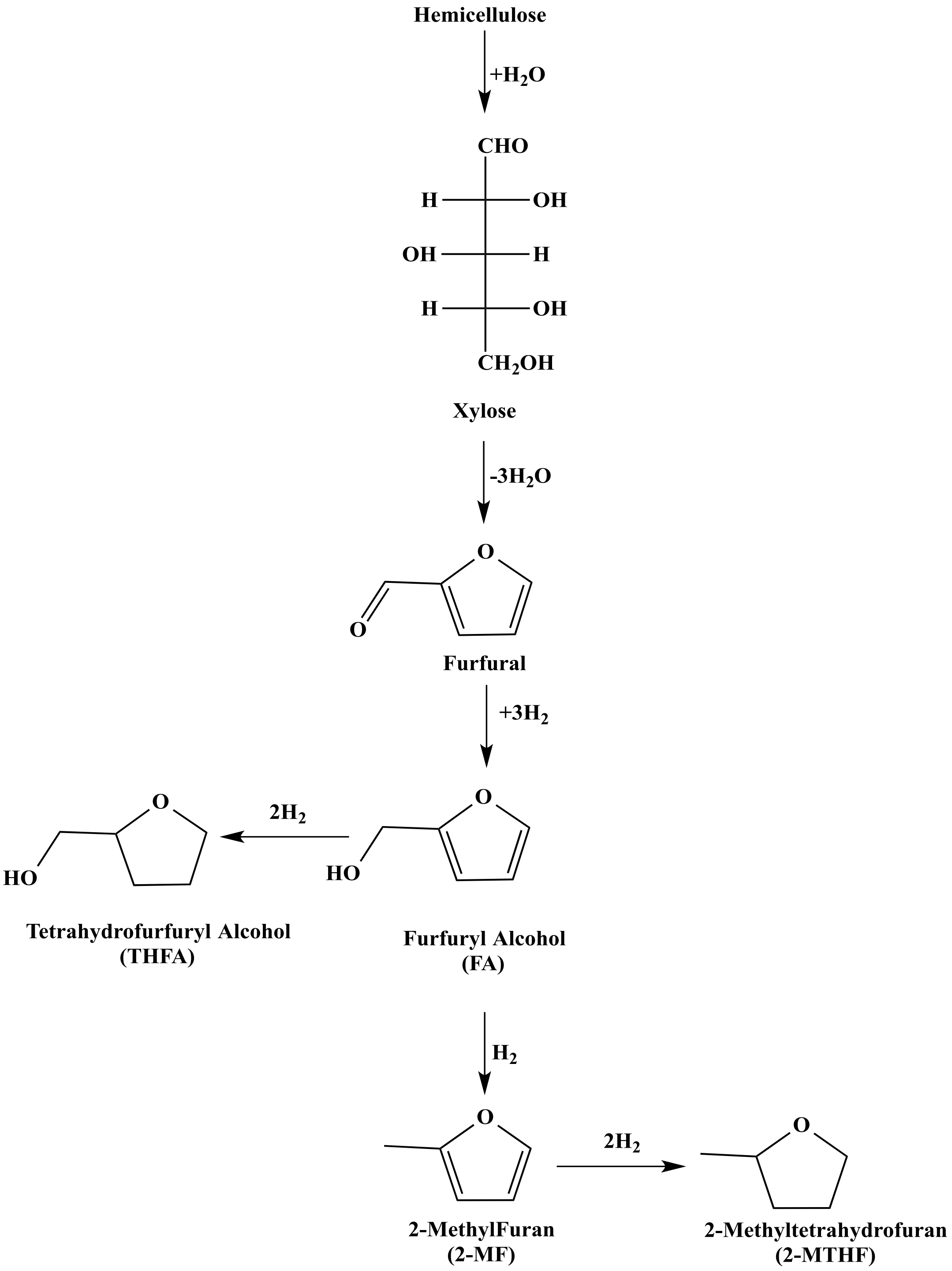
Hydrogenation of
Furfuryl alcohol and Furfural

Chapter 4

4.1 First Section: Furfuryl Alcohol hydrogenolysis and hydrogenation:

4.1.1 Introduction:

Recently, biomass has become one of the most important resources of renewable energy and it seems to have a promising future. The development of efficient technologies that can utilise biomass or biomass-derived chemicals represents a major challenge.[1-4] Most of the current research is based on the utilisation of chemical intermediates like furfural, furfuryl alcohol and attractive biofuels like 2-methylfuran, and 2-methyltetrahydrofuran.[1,5,6] Furan derivatives are considered to be important intermediates because of their rich chemistry and carbohydrates being their most dominant source. Recently, furan derivatives (furfural and furfuryl alcohol) have been prepared via the conversion of carbohydrates.[7-10] One of the methods used to obtain fuels from renewable feedstock resource is by pre-treatment through hydrolysis of the cellulosic and hemicellulosic components to produce sugar alcohols, such as sorbitol, xylitol, mannitol, lactitol or maltitol[11-15] which are subsequently converted into fuel components via chemical reactions.[16-18] Furfuryl alcohol is prepared through the hydrogenation of furfural using catalysts such as copper chromite[19] and nickel-based catalysts.[20] Furfural is formed from xylan contained in lignocelluloses through dehydration and hydrolysis.[1] Commercially, furfural is considered to be a platform chemical and it has been applied to the upgrading of fuels, such as furfuryl alcohol through hydrogenation and acid/base catalysed reactions.[1,21,22] Furfuryl alcohol has a variety of applications in the chemical industry. It is mainly used in the manufacturing of resins: as a starting material for the synthesis of tetrahydrofurfuryl alcohol, and as a chemical intermediate for the formation of perfumes, vitamin C, and lysine.[23-28] There are some studies which have reported on conversion of furfuryl alcohol into various fuel derivatives like 1,5-pentanediol,[19] tetrahydrofurfuryl alcohol,[20] and methylfuran[4]. All these derivatives are important in terms of their application, but their synthesis under green conditions is a challenge. 2-methylfuran is obtained from hydrogenation of furfuryl alcohol and furfural. It is mainly used for the synthesis of crysanthemate pesticides, perfume intermediates, and chloroquine lateral chains in medical applications.[29,30] Almost all the reported work on furfuryl alcohol hydrogenation is performed under harsh reaction conditions. In this chapter of the current study, an application of Pd-supported catalyst synthesised through a wet impregnation method is reported for the hydrogenation of derivatives of furfuryl alcohol under different reaction conditions such as pressure, solvent and amount of catalyst at room temperature. The unique catalytic activity and preferable selectivity to hydrogenated deoxygenation of C=O instead of a reduction of C=C in these furan substrates have not been mentioned under green conditions. In addition, furfural has been demonstrated by earlier studies, in that catalytic hydrogenation of furfural with copper catalysts at 200-300°C can produce 2-methylfuran.[31] Hydrogenation of furfural in liquid phase at a temperature of 180°C and pressure of 69–104 barg can be used to produce furfuryl alcohol and the process involves the utilisation of copper chromite ($CuCr_2O_4{\bullet}CuO$).[32] Hydrogenation of furfural in the gas phase with a zeolite (Cu/Fe) catalyst, results in its complete conversion and with increased selectivity to 2-methylfuran. The reaction is carried out at one bar and 252°C.[33] On the other hand, hydrogenation of furfural in a vapour phase under the same conditions with a copper-based catalyst also produces complete conversion of furfural.[29] The aim of this chapter is to explain how hydrogenolysis of furfuryl alcohol (first section) and furfural (second section) using heterogeneous catalysts takes place, and also how the variation of reaction conditions, solvent and supports affect the activity of the heterogeneous catalyst (Scheme 4.1). A range of metal catalysts have been prepared using different supports and their effects on the reaction have been studied.



Scheme 4.1: A pathway for the production of different compounds from hemicellouse.

4.1.2 Results and Discussion:

4.1.2.1 Blank reaction:

When using hydrogen it is important to confirm the absence of any possible background activity from species other than the reactants.[34] Blank tests were carried out in the absence of a catalyst; no conversion was observed at room temperature in the present study.

4.1.2.2 Study of Support Effect:

Noble metals (Au, Ag, Pd, Ru, Rh, Pt, Ir, and Os) are mainly used in supported form, unlike other base metals.[34] The role of the support is very important in heterogeneous catalysis and even under the same conditions diverse supports could lead to different activities.[35-38] A range of catalysts with different supports have been studied, namely $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, TiO_2, SiO_2, Al_2O_3, CeO_2 and graphite; Table 4.1 lists the supports along with their surface area used in this study. Hydrogenation of furfuryl alcohol has been investigated over HPA as support, but the results were not promising with respect to the desired product. This could be due to the decrease in surface area by loading metals (decrease from 131 to 25 with loading Au:Pd and to 31 when loading Pd) as shown in Table 4.1.

Table 4.1: Surface area of supports and catalysts by BET method:

Support materials	**Surface area (m^2/g)**
$Cs_{2.5}HPW_{12}O_{40}$	131
CeO_2	5
Graphite	11
TiO_2	55
Al_2O_3	155
SiO_2	245
Catalysts	**Surface area (m^2/g)**
5%AuPd/$Cs_{2.5}HPW_{12}O_{40}$	25
5%Pd/$Cs_{2.5}HPW_{12}O_{40}$	31
2.5%Au:2.5%Pd//CeO_2	58
2.5%Au:2.5%Pd//Graphite	9
2.5%Au:2.5%Pd//TiO_2	49
2.58%Pd//TiO_2	49
1.26%Pd//TiO_2	42
2.5%Au:2.5%Pd/Al_2O_3	57
2.5%Au:2.5%Pd/SiO_2	257

The reactions were performed at room temperature and hydrogen pressure was one bar at constant pressure (the reactor was charged at the desired pressure without refilling during the reaction). All catalysts with different support materials were calcined in static air at 400ºC for 3h. The reaction was found to be very selective to 2-methylfuran, with 5%AuPd/Al_2O_3 used, but with very low conversion. The conversion and selectivity kept increasing with different supports in the order TiO_2 > SiO_2 > CeO_2 > Graphite > Al_2O_3 and these were used as supports for Au:Pd catalysts; respectively under these conditions (at room temperature and one bar hydrogen constant pressure). This can be attributed to the catalytic properties of metals, which are often affected by the nature of the support material.[39] Au:Pd with TiO_2, SiO_2 and CeO_2 have a Au:Pd core-shell structure, as has been reported from previous literature.[40] It seems that the catalytic activity can be linked to the structure of the Au:Pd alloy changing in the catalyst, or it may be due to a synergistic effect.[40] Another reason may be the particle size and the distribution of metals on the surface of supports. Detailed studies on the particle size and distribution of Au:Pd on different supports synthesised through a similar method have been carried out by Edwards et.al. by using a STEM technique.[40] In the case of a metal supported catalyst, the area of metal (accessibility and dispersion) is one of the important factors in determining the catalytic effect. Generally, Table 4.1 shows that depositing Au and Pd metal onto the support slightly decreased the surface area. The lower surface area in metal supported catalysts may possibly be as a result of the blockage of the surface or pores of the support by the metal, or by another compound.[39] To study the influence of the support on furfuryl alcohol reduction, Au:Pd catalysts were synthesised on a range of support materials. In general, the supports CeO_2, TiO_2 and SiO_2 provided more active catalysts than Al_2O_3, and graphite for the hydrogenation of furfuryl alcohol, as shown in Table 4.2. However, the highest yield to 2-methylfuran was obtained over TiO_2, as a support while with Al_2O_3, there was low activity. The variation in catalytic activity can be linked to the chemical properties of supports and the structural interaction of Au:Pd nanoparticles.[41] Figure 4.1 shows the TEM image for a catalyst with Au:Pd/TiO_2. In the HRTEM image, large particles were observed in the bimetal Au:Pd catalyst support on TiO_2 with an average size 9.6 nm.

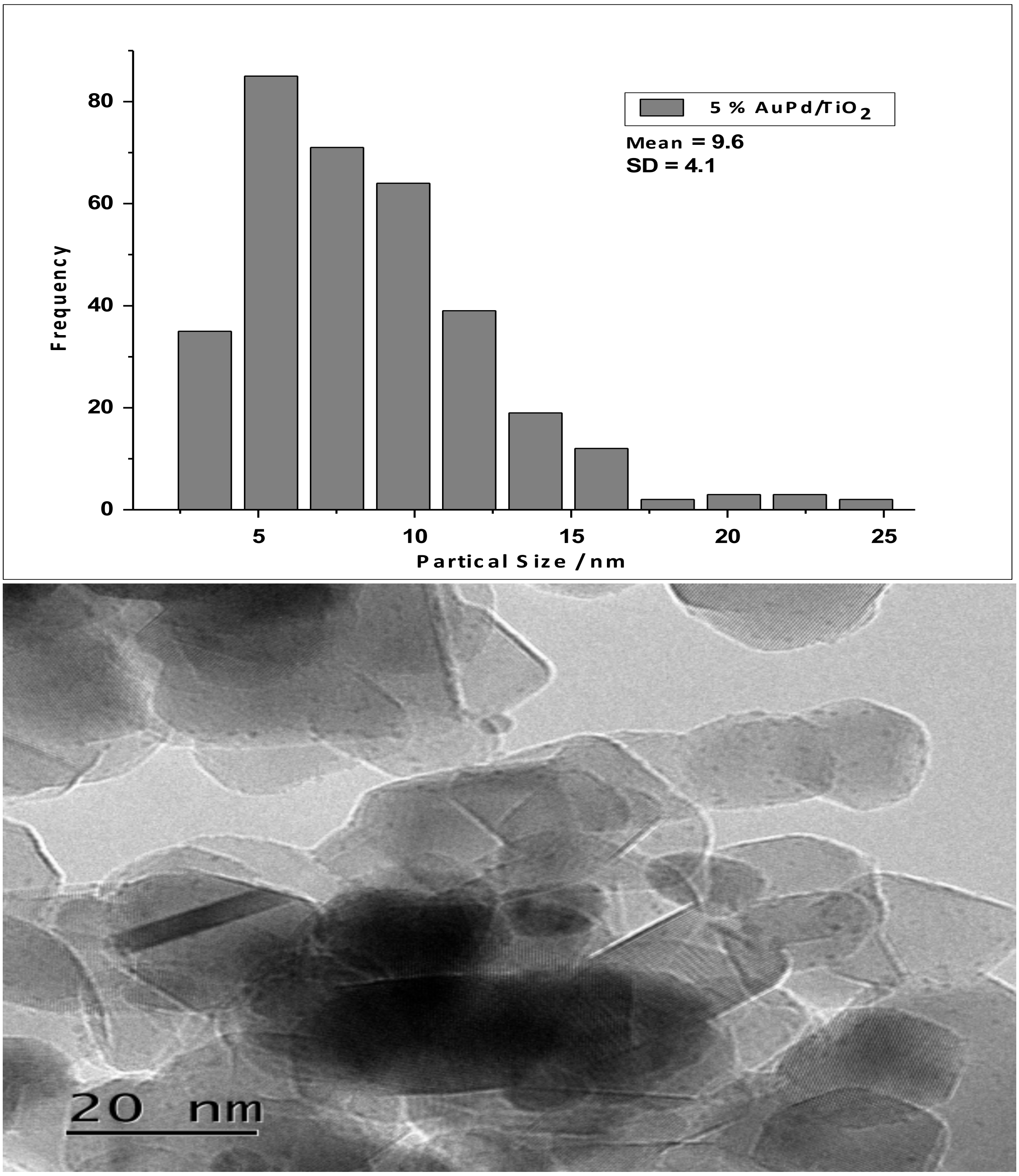


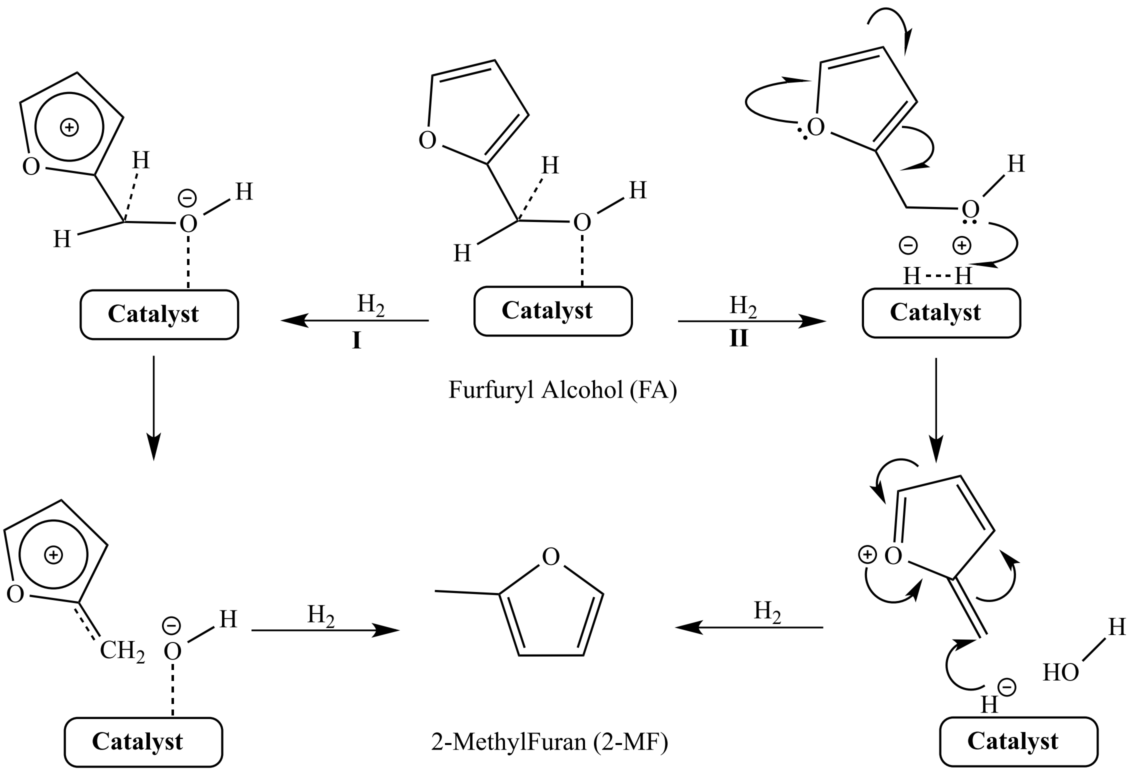
Figure 4.1: Particle size distribution data as determined from bright field TEM micrographs for 5%AuPd/TiO_2 prepared by the impregnation method.

Table 4.2: Effect of support on gold and palladium catalysts for furfuryl alcohol hydrogenation:

Catalyst	Conversion (%)	Selectivity (%)		
		2-methyltetra-hydrofuran	2 Methylfuran	Tetrahydro-furfuryl Alcohol
2.5%Au:2.5%Pd/Al_2O_3	1.7	0	100	0
2.5%Au:2.5%Pd/Graphite	4.8	0	33.6	66.4
2.5%Au:2.5%Pd/CeO_2	26.6	3.6	55.9	40.5
2.5%Au:2.5%Pd/TiO_2	65.5	0.9	88.2	10.9
2.5%Au:2.5%Pd/SiO_2	60.7	1.2	89.4	9.3

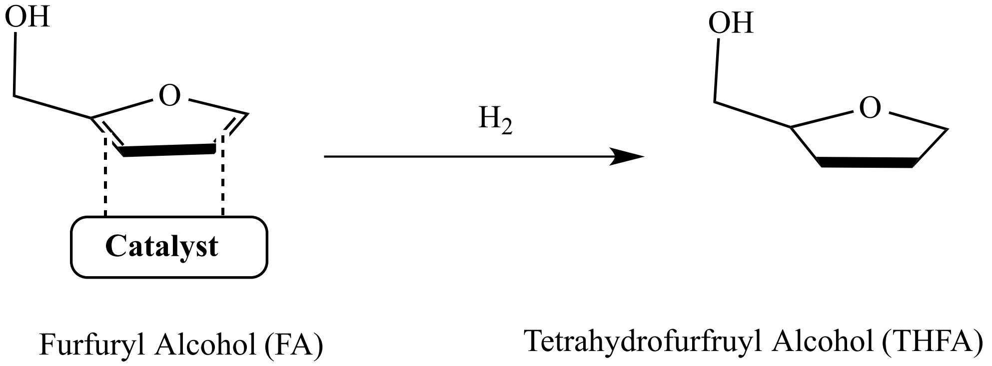
Reaction conditions:- 1000 mg of substrate, 100mg of catalyst, 20ml $C_2H_4Cl_2$, autoclave reactor, 25ºC, 1000 rpm, 3h, 1bar H_2 constant pressure.

The reaction pathways proposed for furfuryl alcohol conversion are shown in scheme 4.2 and 4.3. 2-methylfuran[42] and tetrahydrofurfuryl alcohol[43,44] are the main products shown over catalysts.[4] It has been reported that product distribution can range significantly for Au and Pd. The hydrogenation of furfuryl alcohol selective to 2-methylfuran on metals surfaces has been investigated on different supports for these catalysts. Typically, group VIII metals tend to interact strongly with aromatic,[45] furanyl rings[46] and C=C double bonds.[47]



Scheme 4.2: Possible species on the surface during conversion of furfuryl alcohol. Redrawn (I).[4]

In particular, on Pd metal surfaces the terminal group and metal used to support interaction is so strong that the C-O bond in the terminal group weakens.[48] The Pd metal means an electron back donation into the hydroxyl group can occur, and this is thought to occur via a H attack on the C of the (C–O) alcohol in case of intermediates. This interaction weakens the C–O bond of alcohol, helping stabilisation and thus full hydrogenolysis can occur and contribute towards furfuryl alcohol hydrogenation over a Pd catalyst which leads to a significant extent of hydroxyl group leaving and achieving the 2-methylfuran, as suggested in scheme 4.2. On the other hand, based on the above discussion on the strong interaction between group VIII metals and C=C double bonds, the selectivity to tetrahydrofurfuryl alcohol could possibly have occurred on the metal surfaces. The C=C double bonds/metal interaction is so strong that π(C=C) in the ring of furfuryl alcohol breaks and leads to tetrahydrofurfuryl alcohol (Scheme 4.3).



Scheme 4.3: Possible species on the surface during conversion of furfuryl alcohol (FA) to tetrahydrofurfuryl alcohol (THFA).[24]

Generally, the mechanism of the heterogeneous catalytic hydrogenation of double bonds is not completely understood because it is a very difficult reaction to study.[49] In heterogeneous kinetic reactions achieving the data is easy through the measurement of decreasing hydrogen pressure, but the data is difficult to interpret.[49] In this section, the influence of supports has been observed on the activity of catalysts. The TiO_2 support shows the best result in this current work practically, thus the next section will study the influence of the ratio of Au:Pd loading on the TiO_2 support.

4.1.2.3 Study of gold and palladium ratio effect:

An attempt has been made in the current study to investigate the effect of gold and palladium ratios on the hydrogenation of furfuryl alcohol. The Au:Pd/TiO_2 catalysts were prepared using the impregnation method mentioned in the experimental chapter.

The results show that the gold and palladium ratio can influence the conversion and selectivity of the hydrogenation products from furfuryl alcohol. The reaction with 5%Au/TiO_2 showed no conversion under these conditions. However, the addition of palladium along with gold showed a significant increase in the conversion and selectivity as shown in Figures 4.2 and 4.3. The highest conversion and selectivity was observed with both 5%Au:Pd/TiO_2 and 2.58%Pd/TiO_2 and the selectivity was not much different for the gold and palladium ratio, which suggests that the hydrogenation of furfuryl alcohol is not significantly influenced by the ratio of gold and palladium. Using a catalyst with a high concentration of gold, the chosen pathway for furfuryl alcohol was redox with low activity, but after the addition of palladium metal, the conversion and selectivity to 2-methylfuran increased.[50]

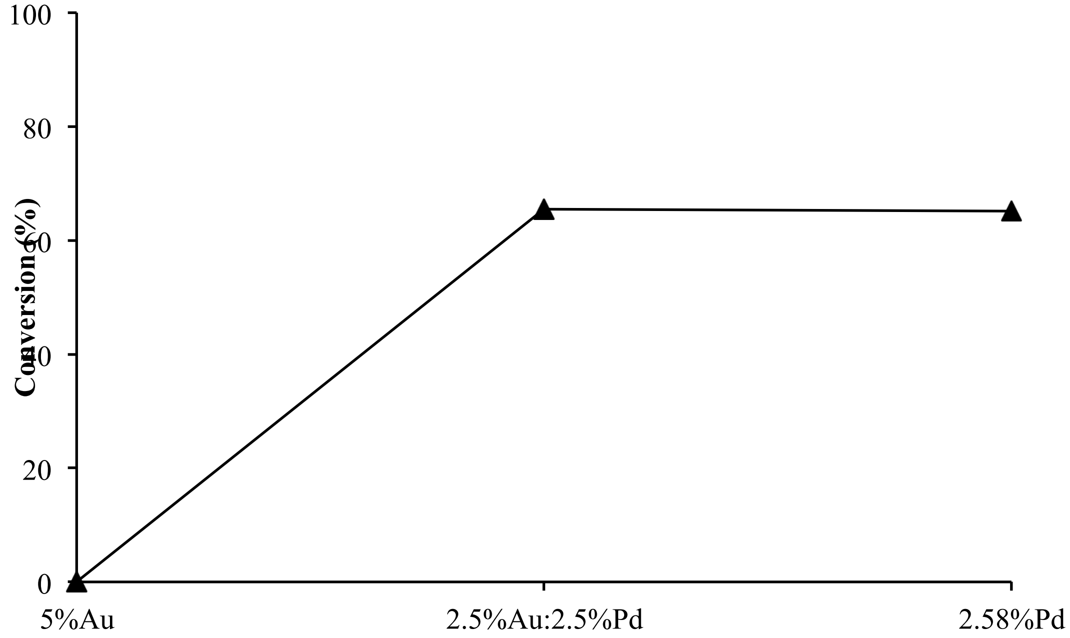


Figure 4.2 Gold and palladium ratio effect for the conversion of furfuryl alcohol**.** Reaction conditions:- 1000 mg of substrate, 100mg of catalyst, 20ml $C_2H_4Cl_2$, autoclave reactor, 25ºC, 1000rpm, 3h, 1bar H_2 constant pressure.

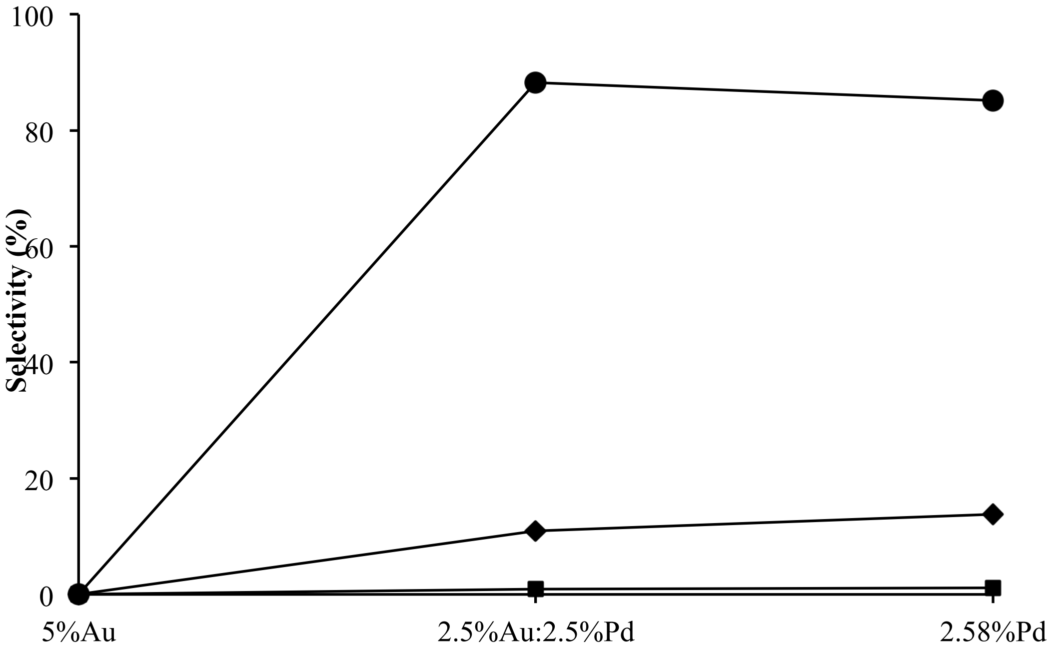


Figure 4.3 Gold and palladium ratio effect on selectivity**.** Reaction conditions:- 1000mg of substrate, 100mg of catalyst, 20ml $C_2H_4Cl_2$, autoclave reactor, 25°C, 1000rpm, 3h, 1bar H_2 constant pressure. (●) 2-methylfuran, (♦) tetrahydrofurfuryl alcohol, (■) 2-methytetrahydrolfuran.

Figures 4.4 and 4.5 show the XRD pattern of the supported Au:Pd catalysts with different ratios prepared by impregnation. The XRD pattern of the sample indicates the presence of a characteristic peak of Au or Au:Pd alloy at $2\theta=38.3^{o}$, 44.4^{o} and 64.4^{o}. No peak can be assigned to the diffraction of crystalline Pd particles due to small crystallite size, which is lower than the detectability limit of XRD[40] or due to the high metal dispersion on the TiO_2 support.[51] The TiO_2 used in the present work is a mixture of anatase and rutile, which remains stable during the preparation process. It indicates very small particles of Pd compounds (metallic Pd or PdO) are formed during catalyst preparation. XRD diffraction patterns for Au:Pd bimetallic catalysts clearly indicate the presence of Au or Au:Pd alloy peaks as shown in Figure 4.4 and Figure 4.5, whereas the Pd species were not detected probably due to the reason mentioned above. In addition,

Figure 4.26 was shown electron analysis (EDX) for Au:Pd metals and TiO_2 support. On the other hand, in recent years the price of gold has been rising significantly, and this has encouraged the study of Pd metal supports.

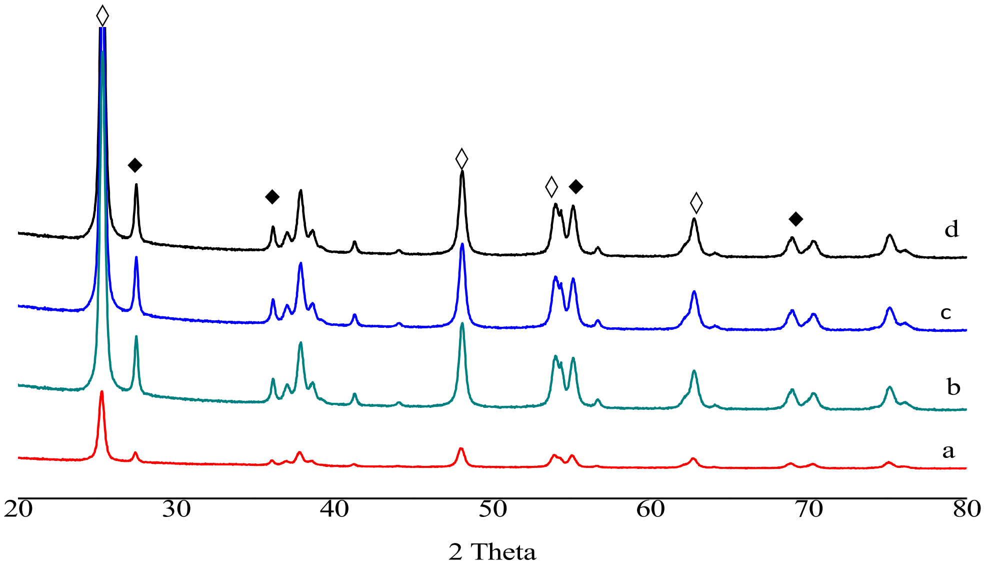


Figure 4.4: X-ray diffraction patterns of mono catalyst calcined in air 400°C. Key: (a) TiO_2, (b) 0.5wt%Pd/TiO_2, (c) 1.26wt%Pd/TiO_2 (d) 2.58wt%Pd/TiO_2. Symbol: (♦) TiO_2 anatase phase and (◊) TiO_2 rutile phase.

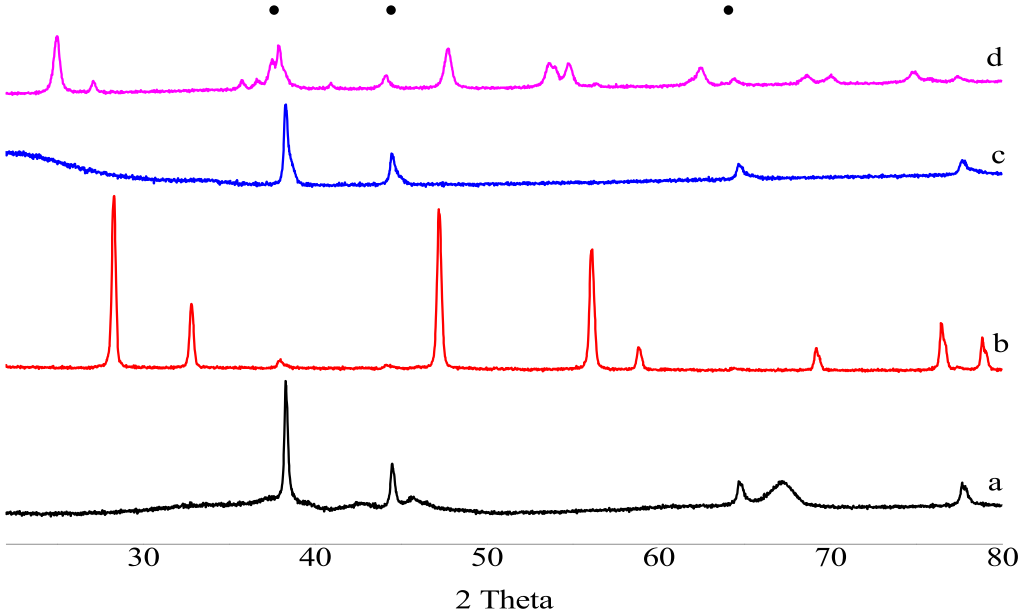


Figure 4.5: X-ray diffraction patterns of bimetallic 5%wtAu:Pd with different supports: (a) Al_2O_3, (b) CeO_2, (c) SiO_2, (d) TiO_2. (●) Au or Au:Pd alloy.

4.1.2.4 Study of palladium loading effect:

Different amounts of Pd metal supported on TiO_2 have been used to study the effect of Pd loading on the catalytic activity of conversion and selectivity، as shown in Table 4.3. It was found when Pd loading was increased from 0.5% to 2.58% that it increases catalytic activity and selectivity to 2-methylfuran. One bar constant pressure (pressure was built only once by filling the reactor and there was no refuelling during the reaction) was used to carry out the reaction at room temperature. The by-product formed in this reaction was tetrahydrofurfuryl alcohol. The substrate was not converted when a blank reaction was performed. Figure 4.4 shows the XRD pattern of different amounts of Pd when loaded. No significant change was noted for 0.5%, 1.26% and 2.58%Pd loading and no peak could be assigned to the diffraction of the crystalline particles of the catalyst. TiO_2 is a mixture of rutile and anatase and it was used to maintain stability during the reaction and this might be because the particles size for those catalysts are small. The TEM images of catalysts 0.5%, 1.26% and 2.58%Pd/TiO_2 are shown in Figure 4.6. It does not show any large size particles, which is in agreement with the XRD data. In the HRTEM images for three samples, very small particles in huge quantities were detected. The particles cannot be detected through the XRD because of their small average particle size, which is less than 2nm. These combinations with the XRD indicate that very small nanoparticles are produced by the impregnation method. The particles are very small in size, which would explain the increased catalytic activity; small particles detected in localised TEM images were studied.[52-54] Analysis of particle size distribution was performed for 0.5%, 1.26% and 2.58%Pd/TiO_2 catalysts. It is obvious that the particle size does not change with an increase in loading as shown in Figure 4.6. All catalysts revealed mean particle size of 1nm. The particle size distribution was the same for all catalysts. The increase in catalytic activity can be related to the increase in active metal concentration and more sites being available for catalytic activity.

Table 4.3: Effect of palladium loading on catalysts for hydrogenation of furfuryl alcohol:

Catalyst	Conversion (%)	Selectivity (%)		
		2-methyltetra-hydrofuran	2-Methylfuran	Tetrahydro-furfuryl Alcohol
0.5%Pd/TiO_2	21.4	0	49	51
1.26%Pd/TiO_2	46.2	0	92.5	7.5
2.58%Pd/TiO_2	65.1	1.1	85.2	13.8

Reaction conditions:- 1000mg of substrate, 100mg of catalyst, 20ml $C_2H_4Cl_2$, autoclave reactor, 25ºC, 3h, 1000rpm, 1bar H_2 constant pressure.

Deconvoluted XPS data for different amounts of Pd catalysts supported on TiO_2 is shown in Figure 4.7 the catalyst samples contained two types of Pd (*i.e.* Pd^{2+} and Pd^0). Moreover, the binding energy of Pd^{2+} was 337.6eV and Pd^0 was 335.8eV. Pd^{2+} was found to be the majority in all catalyst, while the Pd^0 was simply traces. The Pd^{2+}/Pd^0 ratio for the three samples was maintained in the range of 12-15. the abundance of Pd^{2+} shows that the active sites of the catalyst comprise Pd^{2+} instead of metallic Pd. Pd^{2+} might have a similar function as co-ordinated metal centres for the reduction of carbonyl group and H_2 activation[55] and it provides a reason for preferring a reduction of C=O rather than C=C bonds while the metallic Pd preferred a reduction of C=C bonds. The XPS, HRTEM and XRD data confirms that the catalyst samples were similar in their chemical nature even if the amount of Pd loaded differs. This means that the variation in catalytic activity was linked to the active sites. In addition, the catalyst samples were analysed through the MP-AES to examine the stability of the catalyst metal during the reaction and the results are presented in Table 4.4. Leaching was not observed significantly in all catalysts within experimental error and (Quantity error for MP-AES is ± 0.02 wt.%). However, the MP-AES analysis does show minor differences between the amount of Pd in fresh and the used catalysts. These differences could be contributed to estimate the amount of Pd leaching from the catalysts which is clearly a factor in deactivation. As mentioned in section 4.1.2.2, tetrahydrofurfuryl alcohol was obtained from the interaction between double bonds π(C=C) in the ring of furfuryl alcohol and metal. This interaction weakens the bond and this product is not preferred for high Pd loading as explained previously in section 4.1.2.3. Sitthisa et al.[46] has reported a very close observation of the generation of this species upon adsorption of aldehydes on Pd, Pt, Rh and Ru metal surfaces. Also Shekhar, et al. have reported the same.[56] In general, the hydrogenation of the double bond mechanism by the heterogeneous catalytic is not fully clarified. The mechanism is a very difficult reaction to study. The kinetics of the heterogeneous reaction and achieving the data, is easy by measuring decreasing hydrogenation pressure but it is difficult to understand.[49]

Table 4.4: MP-AES data of fresh and used catalysts:

Theoretical Pd loading (wt.%)	Fresh Catalysts Pd (wt.%)	Used Catalysts Pd (wt.%)
1	0.50	0.51
2.5	1.26	1.36
5	2.58	2.50

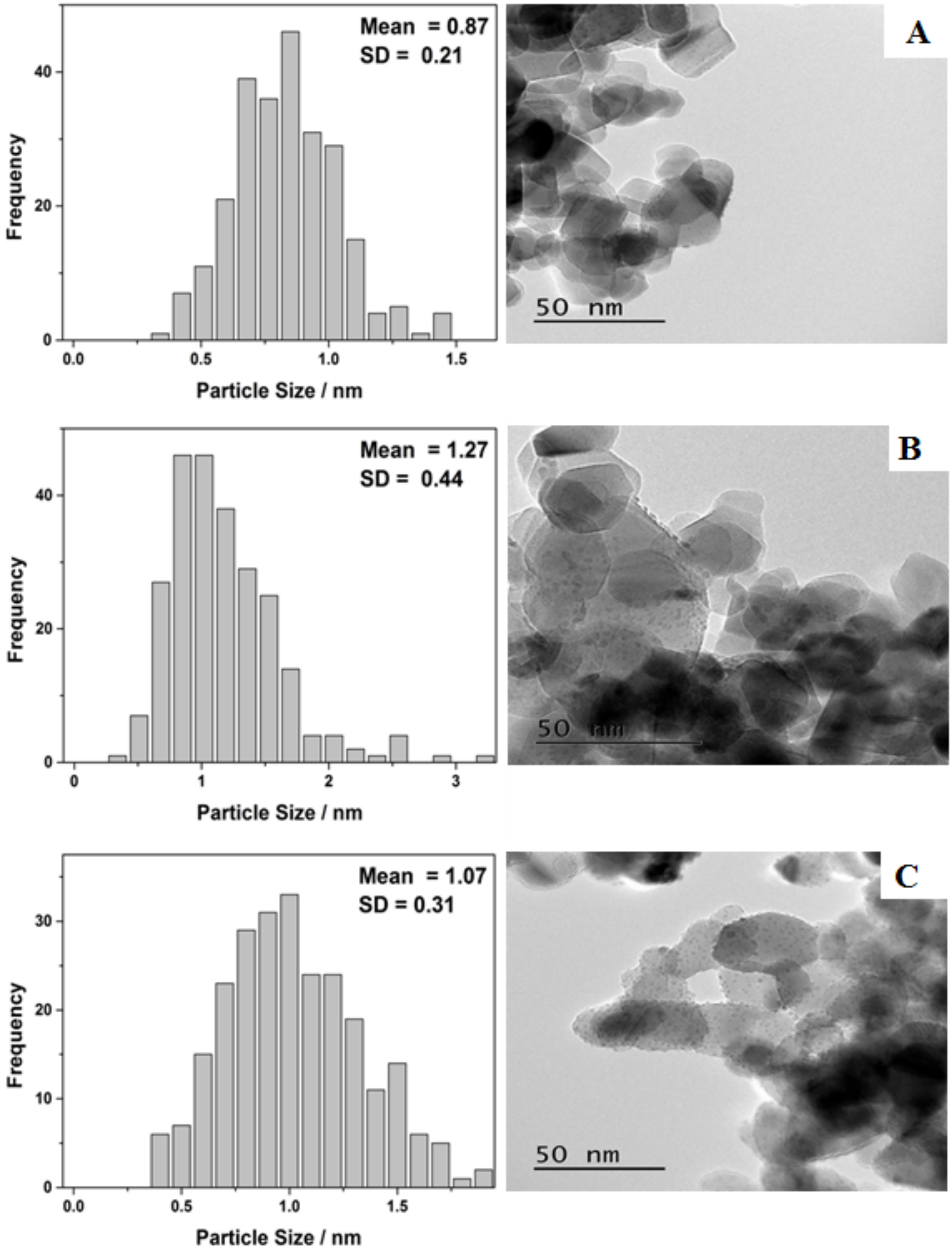


Figure 4.6: Particle size distribution data as determined from bright field TEM micrographs for (a) 0.5%Pd/TiO_2, (b) 1.26%Pd/TiO_2, (c) 2.58%Pd/TiO_2 prepared by the impregnation method.

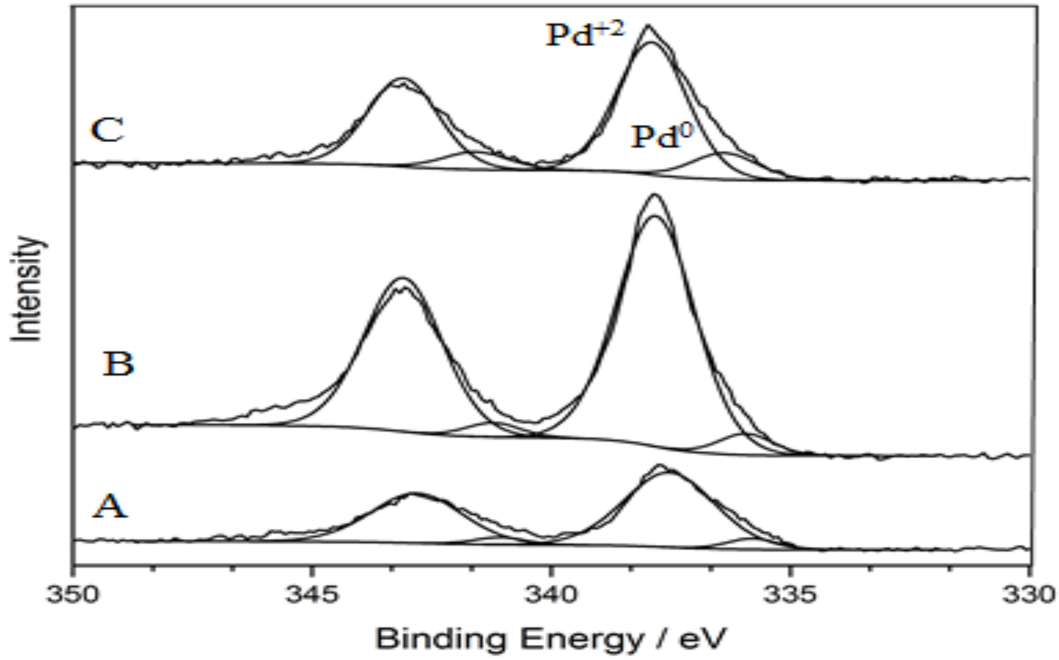


Figure 4.7. XPS profiles of TiO_2 supported Pd with different Pd loading (a) 0.5%Pd/TiO_2, (b) 1.26%Pd/TiO_2, (c) 2.58%Pd/TiO_2.

4.1.2.5 Study of pressure effect:

To study the effect of pressure on the hydrogenation of furfuryl alcohol, 2.58% Pd/TiO_2 was studied at room temperature using different pressures of hydrogen, from 1 to 3barg. The reaction was preformed for 30 min. The reactions were carried out in two ways constant pressure (pressure was built only once by filling the reactor and with no refuelling during the reaction), and continuously controlled pressure (pressure was kept constant by refilling during the reaction). Lower conversion was achieved with constant pressure compared to conversion with continuously controlled pressure (Table 4.5). This could be due to the increased amount of H_2 present in reactions with continuously controlled pressure. Furthermore, the increase in pressure caused an increase in catalytic activity with continuously controlled pressure, and the substrate was completely converted into products at 3barg pressure with high selectivity to 2-methylfuran. Tetrahydrofurfuryl alcohol was formed in the reaction as a by-product. It can be concluded that the pressure or amount of hydrogen are importing factors in obtaining selectivity.

Table 4.5: Effect of pressure for hydrogenation of furfuryl alcohol:

Pressure (bar)		**Conversion (%)**	**Selectivity (%)**		
			2-Methyltetra-hydrofurane	2-Methylfuran	Tetrahydro-furfuryl Alcohol
Constant pressure	1	28.5	0	97.7	2.3
	2	50.3	0	97.7	2.3
	3	73.1	0.6	96.6	2.8
Continuously controlled pressure	1	54.9	0	98.2	1.8
	2	53.1	0	96.8	3.2
	3	93.7	0.8	93.6	5.7

Reaction conditions:- 1000mg of substrate, 100mg of 2.58%Pd/TiO_2, 20ml $C_2H_4Cl_2$, autoclave reactor, 25ºC, 30min, 1000rpm.

4.1.2.6 Study of catalyst mass effect:

The effect of the catalyst's mass on activity has been studied. The amount of catalyst was varied: 25, 50, 100, 125 and 150 mg of 2.58%Pd/TiO_2. As shown in Figures 4.8 and 4.9, an increase in the amount of catalyst increased catalytic activity. Moreover, increased selectivity to 2-methylfuran was achieved when 100 and 125mg was used from the catalyst (2.58wt% Pd/TiO_2). With a further increase in amount of catalyst up to 150mg, the conversion continued increasing, however, there was a small decreased in the selectivity. The decrease in selectivity can be attributed to side reactions due to the excess amount of catalyst. It confirms the increased selectivity of the catalyst used for reducing C=O bonds to generate hydrocarbons and a reduction of C=C bond is almost absent even with a large amount of catalyst. It shows a different reaction pathway if the reaction occurs on the surface of the catalyst compared with the gas phase reduction of aldehydes or unsaturated hydrocarbons with Pd catalysts.[57]

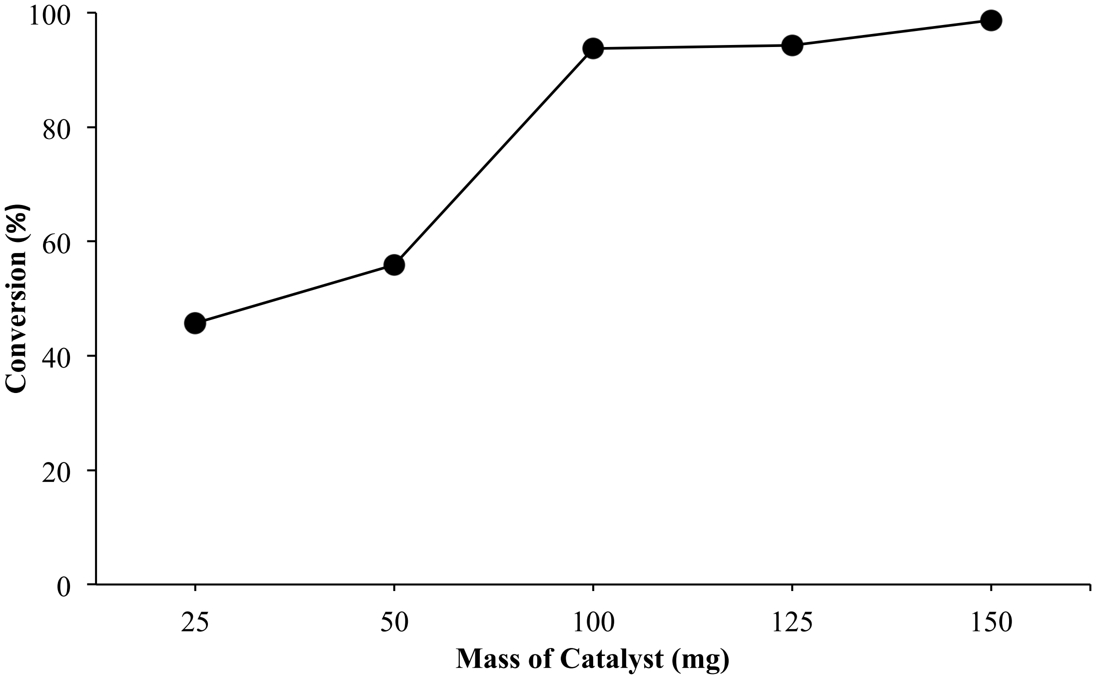


Figure 4.8: Catalyst mass effect for the conversion of furfuryl alcohol**.** Reaction conditions:- 1000mg of substrate, 2.58%Pd/TiO_2, 20ml $C_2H_4Cl_2$, autoclave reactor, 25°C, 30min. 1000rpm, 3bar, continuously controlled pressure.

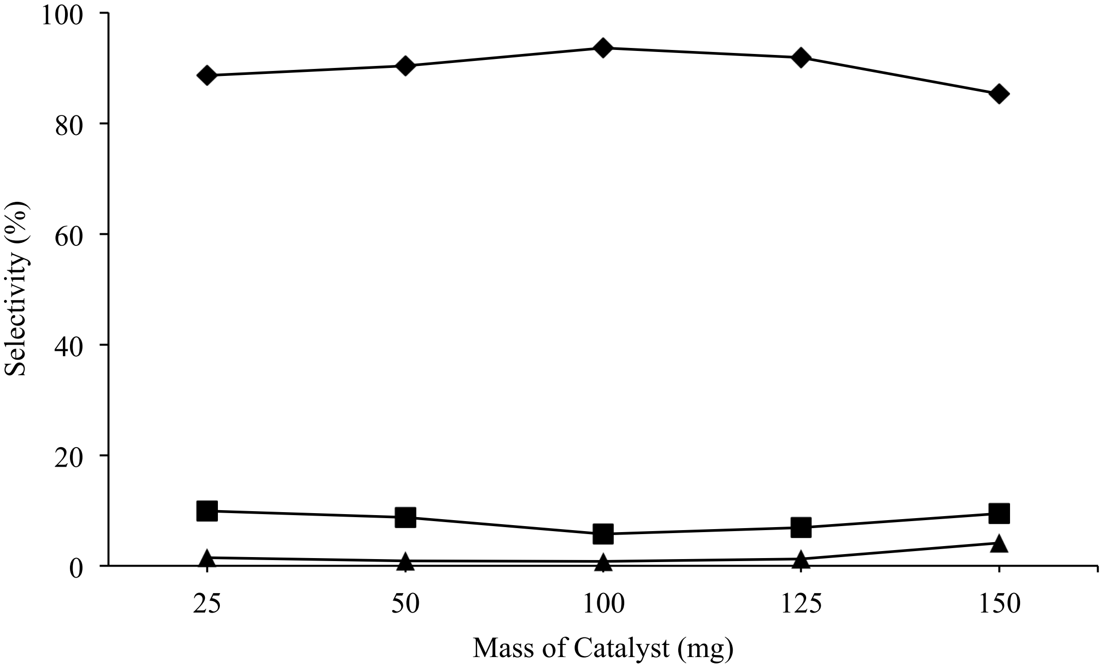


Figure 4.9: Catalyst mass effect for the selectivity during the hydrogenation of furfuryl alcohol. Reaction conditions:- 1000mg of substrate, 2.58%Pd/TiO_2, 20ml $C_2H_4Cl_2$, autoclave reactor, 25°C, 30min, 1000rpm, 3bar continuously controlled pressure. (▲) 2-methytetrahydrolfuran, (♦) 2-methylfuran, (■) tetrahydrofurfuryl alcohol.

4.1.2.7 Study of time on line effect:

The effect of reaction time for furfuryl alcohol using 2.58%Pd/TiO_2 at the optimal condition (25ºC, 3barge continuously controlled pressure H_2 pressure) for hydrogenation of furfuryl alcohol in 1,2-dichloroethane is shown in Figures 4.10 and 4.11. Under optimal conditions, it can be observed that there was a steady increase in the conversion with reaction time. The effect on conversion was remarkable and the selectivity to 2-methylfuran was stable during the reaction time. Furfuryl alcohol was fully converted after 30 minutes when using 1,2-dichloroethane as a solvent. The main product of furfuryl alcohol hydrogenation was 2-methylfuran and a very small amount of tetrahydrofurfuryl alcohol.

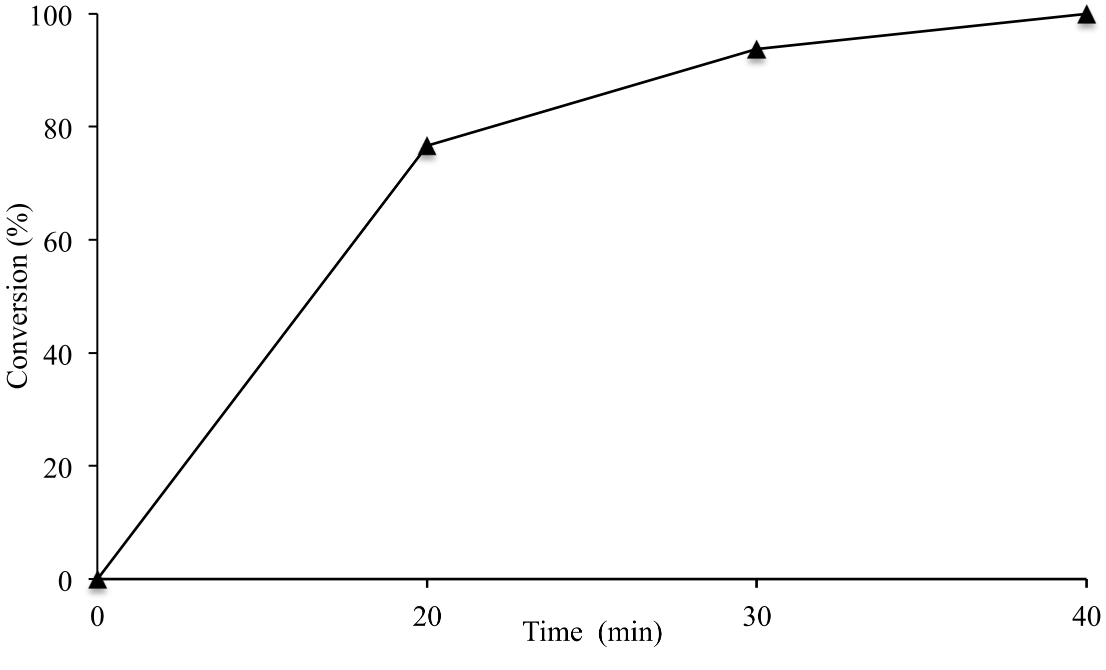


Figure 4.10: Effect of reaction time for the conversion of furfuryl alcohol. Reaction conditions: 1000mg of substrate, 100mg of 2.58%Pd/TiO_2, 20ml $C_2H_4Cl_2$, autoclave reactor, 25ºC, 1000rpm, 3bar H_2 continuously controlled pressure.

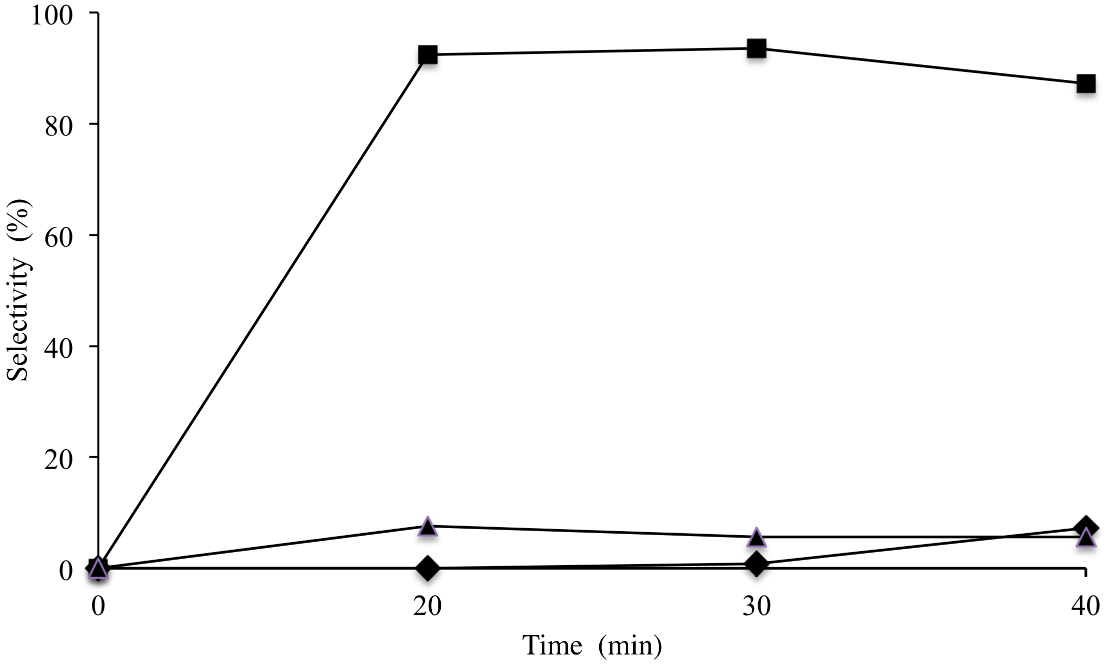


Figure 4.11: Effect of reaction time for the selectivity of furfuryl alcohol. Reaction conditions: 1000 mg of substrate, 100mg of 2.58%Pd/TiO_2, 20ml $C_2H_4Cl_2$, autoclave reactor, 25ºC, 1000rpm, 3bar H_2 continuously controlled pressure. (♦) 2-Methyltetrahydrofuran, (■) 2-Methylfuran, (▲) tetrahydrofurfuryl alcohol.

4.1.2.8 Study of Pd oxidation state through XPS:

The oxidation state of palladium on the catalyst surface plays a very significant role in the activity of the catalyst as shown in Table 4.6. As mentioned above Figure 4.7 clearly confirms, there are two types of Pd found on the surface of the catalyst (Pd^{2+} and Pd^0). The catalyst with a lower amount of Pd^{2+} on the surface showed less activity, however, the selectivity to 2-methylfuran kept increasing by increasing the Pd^{2+} species on the catalyst surface. Moreover, the pre-treatments of the catalyst had an effect on the conversion and selectivity of the catalyst. A higher amount of Pd^{2+} on the catalyst surface was observed after calcination of the catalyst in static air at 400°C for 3h. Oxidation of the catalyst showed a lower amount of Pd^{2+} species on the surface as is shown in Table 4.7. Edwards, et al[58] have reported that the surface ratio of Pd^0/Pd^{2+} is an important factor in controlling the hydrogenation of hydrogen peroxide, and a series of controlled reduction and re-oxidation of a sample shows how the Pd^0/Pd^{2+} surface ratio can influence the relative rates of hydrogen peroxide synthesis and hydrogenation.[58] The main presence of Pd^{2+} suggests active sites, which might have a similar function to co-ordinated metal centres for H_2 activation and reduction of the carbonyl group.[55] It also may explain why Pd^{2+} is preferably reduced for the terminal group while metallic Pd is preferably active for double bond reduction inside the furan ring.[59]

Table 4.6: study surface Pd^{2+} & Pd^0 effect on furfuryl alcohol hydrogenation:

Catalyst	**Conversion (%)**	**Selectivity (%)**			
		2-Methyltetra-hydrofurane	2-Methylfurane	Tetrahydro-furfuryl Alcohol	Others
2.58%Pd/TiO_2 [a]	93.7	0.8	93.6	5.7	0
2.58%Pd/TiO_2 [b]	100	1.3	64.7	11.1	23
2.58%Pd/TiO_2 [c]	99.3	1.7	73.2	11.3	13.9

Reaction conditions:- 1g of substrate, 0.1g of catalyst, 20ml $C_2H_4Cl_2$ as a solvent, autoclave reactor, 25ºC, 30min, 1000rpm, 3bar H_2 continuously controlled pressure.

a) Calcined under static air at 400°Cfor 3h.

b) Reduced in H_2/Ar at 200°C for 3h at a ramp rate of 5°C/min.

c) Oxidised in O_2 at 200°C for 3h at a ramp rate of 5°C/min.

Table 4.7: XPS analysis for percentages of Pd^{2+} and Pd^0 species:

Catalyst		Pd^{2+} (%)	Pd^0 (%)
2.58%Pd/TiO_2	Calcined [a]	86.75	13.25
	1st Reuse	0	100
	Reduced [b]	62.46	37.54
	Oxidised [c]	74.91	25.09

a) Calcined under static air at 400°C for 3h at a ramp rate of 20°C/min.
b) Reduced in H_2/Ar at 200°C for 3h at a ramp rate of 5°C/min.
c) Oxidised in O_2 at 200°C for 3h at a ramp rate of 5°C/min.

4.1.2.9 Study of solvent effect:

Catalytic hydrogenation is usually carried out in a solvent for different reasons, such as to dissolve solid products and reactants; to absorb the heat of the reaction, and to keep the surface of the catalyst free from impurities and carbonaceous deposits. The nature of the solvent has a considerable effect on the conversion and/or the selectivity.[60] Following the initial experiments, hydrogenation of furfuryl alcohol was investigated using a range of different solvents. The reactions were performed using an autoclave and continuously controlled hydrogen pressure at 3barg, over a 2.58%Pd/TiO_2 catalyst at room temperature. The effect of different solvents on the reaction was studied and the results are shown in Table 4.8. The best activity of the catalyst with very high selectivity to 2-methylfuran and very low formation of tetrahydrofurfuryl alcohol, was when 1,2-dichloroethane was used as the solvent. On the other hand, a high conversion and good selective to 2-methylfuran when octane was used as solvent. Some longer chain alcohols and some dimers were formed. In contrast, very low reduction was seen when toluene and acetonitrile were used as solvents. It seems that the type of solvent influences the stability of the hydrogen species adsorbed on the surface. The activity of the H species can be changed through the interaction between H_2 and H, thus, influencing different reaction pathways.[61]

Table 4.8: Effect of Solvent on furfuryl Alcohol Hydrogenation:

Solvents	Conversion (%)	Selectivity (%)			
		2-Methyltetra-hydrofurane	2-Methylfurane	Tetrahydro-furfuryl Alcohol	Others
Acetonitrile	14.9	0	100	0	0
Toluene	3.4	0	100	0	0
1,2-dichloroethane	93.7	0.8	93.6	5.7	0
Octane	88.4	0	58.0	2.2	39.8

Reaction conditions:- 1000 mg of substrate, 100mg of 2.58%Pd/TiO_2, 20ml solvent, autoclave reactor, 25ºC, 30min, 1000rpm, 3bar H_2 continuously controlled pressure.

4.1.2.10 Reusability of Pd/TiO_2:

One of the main advantages of heterogeneous catalysts is the ease of their recovery and reusability. This successful recovery and re-use thereafter is a crucial feature. The reusability of a 2.58%Pd/TiO_2 catalyst was investigated and the results are shown in Table 4.9. After the reaction of furfuryl alcohol, the catalyst was recovered by centrifugation. The centrifuged catalyst was washed with 10ml acetone. This procedure was repeated three times before the catalyst was dried in the oven at 110°C overnight.

In the reusability experiment, larger amounts of the catalyst were used in the initial experiments so that the correct catalyst mass (100 mg) could be used in the following reactions. It is believed that washing the used catalyst with acetone removes all products that might block the active sites in the catalyst when the reaction is performed, thus the activity sites can be recovered. Table 4.9 shows the conversion of furfuryl alcohol and selectivity to 2-methylfuran and tetrahydrofurfuryl alcohol over 2.58%Pd/TiO_2 (calcined in static air at 400°C). It can be seen from Table 4.9 that the hydrogenation activity of the fresh catalyst was high for 2-methylfuran, while the activity of the used catalysts was significantly decreased. There are potential reasons for this, such as:

(a) loss of the active Pd^{2+} species through reduction. The XPS analysis has shown a clear loss of the active Pd^{2+} species through reduction when pretreated with H_2 and the disappearance of Pd^{2+} after the first reaction as shown in Table 4.7.

(b) Pd particle sintering, and

(c) the active Pd site being covered by coke or adsorbed reactants/products.[39,62]

Table 4.9: study of reusability on furfuryl alcohol hydrogenation:

Catalyst	Conversion (%)	Selectivity (%)		
		2-Methyltetra-hydrofurane	2-Methylfurane	Tetrahydro-furfuryl Alcohol
2.58%Pd/TiO_2	93.7	0.8	93.6	5.7
1st re-use	60	0.8	93.6	5.7

Reaction conditions:- 1000mg of substrate, 100mg of catalyst, 20ml $C_2H_4Cl_2$ as a solvent, autoclave reactor, 25°C, 30min, 3bar H_2 continuously controlled pressure.

4.2 Second Section: Furfural hydrogenolysis and hydrogenation:

4.2.1 Results and Discussion:

4.2.1.1 Blank reaction:

It is very important to confirm that no background activity is taking place, apart from the reactants, while using hydrogen.[34] For this purpose, a blank reaction is carried out without a catalyst during which time none of the substrate went through conversion at room temperature. The reactions were performed with octane, 1,2-dichloroethane, methanol, and toluene, as solvents. The hydrogen pressure of 3barg was continuously controlled for 120 mins.

4.2.1.2 Study of solvent effect:

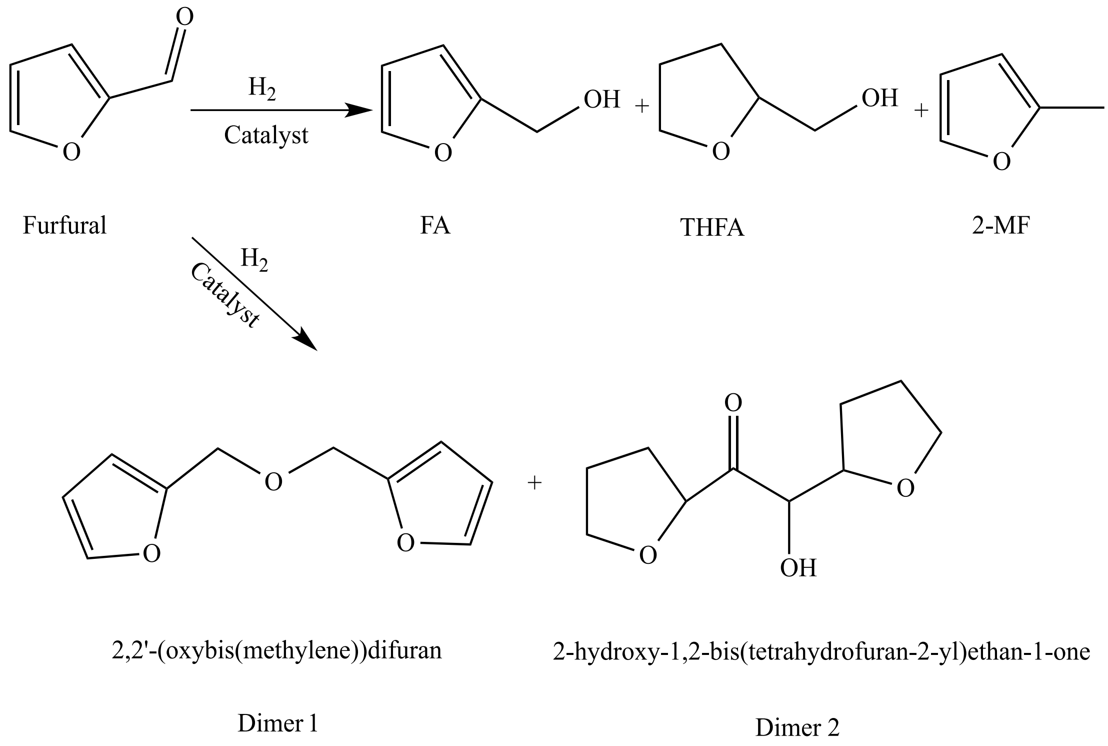
As mentioned in the first section, various solvents have been studied and a variation in the activity of catalyst was observed with respect to conversion and selectivity. A monometallic catalyst of 2.58%Pd metal was observed to have the highest catalytic activity for the hydrogenation of furfuryl alcohol and selectivity to 2-methyl-furan. The reactions were performed in the presence of 1,2-dichloroethane at room temperature and under a hydrogen pressure of 3barg (continuously controlled pressure). In the current work, furfuryl alcohol hydrogenation has been used as it is similar to that of the hydrogenation of furfural.[59] The reaction options proposed for furfural conversion are displayed in scheme 4.1. 2-methylfuran[4,42] and furfuryl alcohol[4,43] are the main products shown over Pd/TiO_2. The influence of solvents on products distribution has been studied in the hydrogenation of furfural, at 3barg continuously controlled pressure (pressure was kept constant by refilling during the reaction) and at room temperature. Table 4.10 shows different conversions of furfural with different solvents. However, the reaction products have been observed to be different and show high selectivity to 2-methylfuran with 1,2-dichloroethane as the solvent. The hydrogenation of furfuryl alcohol (first section) is similar to that of furfural. Using 1,2-dichloroethane as the reaction medium, a very high conversion (79%) of furfural and maximum selectivity to 2-methylfuran (65.8%) was obtained at 30 mins. Furfuryl alcohol was formed as an intermediate product after 30 mins. Also, dimers were formed as by-products.

Table 4.10: Effect of Solvent on furfural Hydrogenation:

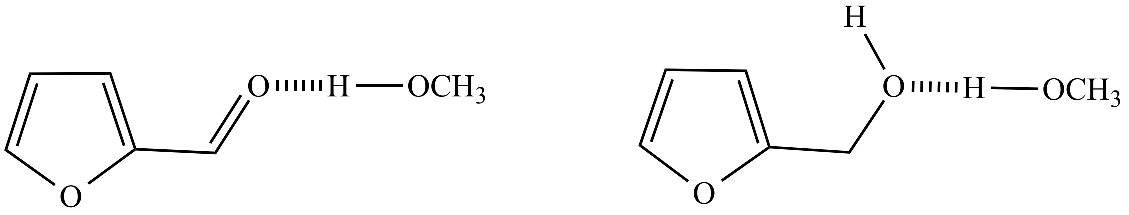
Solvents	**Conversion (%)**	**Selectivity (%)**						
		2-Methylfuran	2-Methyltetra-hydrofuran	Furfuryl Alcohol	Tetrahydro-furfuryl Alcohol	Dimer 1	Dimer 2	Others
1,2-dichloroethane	100	2.5	3.7	0	9	5.8	45.5	33.4
Toluene	98	42.8	0.6	4.1	10.3	0	42.3	0
Methanol	92.2	0	4.8	0	26.9	0	8	62.2
Octane	65.4	36.2	0	28.6	4.8	12.5	18	0

Reaction conditions:- 1g of substrate, 0.1g of 2.58%Pd/TiO_2, 15ml of solvent, autoclave reactor, 25ºC, 120min, 1000rpm, 3bar H_2 continuously controlled pressure.

On the other hand, there was a very high conversion and significant selectivity to 2-methylfuran when octane was used as the solvent. However, there was fully conversion and good selectivity to 2-methylfuran when toluene was used as solvents but dimer 2 is also a large part of product. In the present of methanol as solvent, the conversion was very high but not significant selectivity to 2-methylfuran. Also some dimers and some longer chain alcohols were formed. Moreover, in the presence of methanol, no hydrogenation of C=O was observed. This could be due to the methoxy group preventing adsorption onto the catalyst surface at the carbonyl group of furfural and at the hydroxyl group of furfuryl alcohol which formed as an intermediate product as shown in scheme 4.5. Generally, the solvent is provided to raise the concentration of dissolved hydrogen, thus causing an increase in the rate of the reaction. In some cases, the solubility of the hydrogen in the solvent can be directly related to the rate of the reaction.[63] It appears that the kind of solvent influences the stability of hydrogen species adsorbed onto the surface of the catalyst. The activity of H species can be manipulated by the interaction between H_2 and H, thus influencing different reaction pathways.[61] In the following sections, an attempted has been made to optimise the reaction conditions such as varying Pd ratios, using different metals catalysts (Au, Ru, Au:Pd and Ru:Pd), Pd loading effect, mass of catalyst effect, pressure effect and time on-line.



Scheme 4.4: Principal pathways for the hydrogenation of furfural.



Scheme 4.5: Possible methoxyl group preventing the adsorption onto the catalyst surface at the carbonyl group in the presence of methanol as the solvent.

4.2.1.3 Study of gold, ruthenium and palladium ratio effect:

In the current study numerous attempts have been made to investigate the effect of Au:Pd and Ru:Pd ratios on the hydrogenation of furfural, as shown Table 4.11. All catalysts comprised of a 5%wt. of total metal with changing Au, Ru and Pd ratios and they were prepared using the impregnation method. The reactions were performed at room temperature and under a hydrogen pressure of 3barg continuously controlled pressure with octane as the solvent. All catalysts were calcined in static air at a temperature of 400ºC for 3h. No conversion was observed when using Au/TiO_2 and Au:Pd/TiO_2 under these conditions. The highest conversion was obtained over Pd/TiO_2. The variation in catalytic activity can be related to a synergistic effect.[40] It has been observed that the monometallic Au or Ru catalyst sites are much less active for hydrogenation than palladium sites, as happened in the study of furfuryl alcohol (as per the first section). In both cases, the addition of Pd to Au or Ru decreased the activity of the catalyst for furfural hydrogenation as shown in Table 4.11. As mentioned in the first section[59], Pd is a good catalyst for hydrogenation reactions[64,65] which is possibly because of the Pd rich-H surface of the catalyst.[66] The activity of Pd/TiO_2 and the selectivity was also clearly affected by the Au or Ru with Pd ratio, which suggests that the hydrogenation of furfural is dependent on the ratio of Au or Ru and Pd. Hydrogenolysis may possibly be inhibited on the bimetallic catalysts, which could explain the stability of the surface species.[4,46] This behavior is similar to what has been confirmed by Sitthisa, et al. when they discussed the influence of Ni and Ni:Fe catalysts on the hydrogenation of furfural to methylfuran, particularly at low temperature.[4] From the results, it is clear that these catalysts can break the C-O bond more favorably than the C-C bond. In this case, the addition of hydrogen to the C=C bonds of the furan ring is sterically hindered.[67] Therefore, hydrogenation of furfural was considered to be a favourable reaction for achieving to 2-methylfuran and furfuryl alcohol as the main products. The product of furfuryl alcohol can be further converted to 2-methylfuran[42,59] and tetrahydrofurfuryl alcohol[4,44] as was mentioned in first section.[59] In general, the products show that hydrogenation is preferred over a Pd catalyst, particularly at room temperatures.[46,68] Moreover, Bradley et al. have described the strong adsorption of furfural on metals of group VIII because of the interaction between π orbitals with the metal *d* orbitals.[69] The selectivity to 2-methylfuran was observed and the C=O hydrogenolysis occurs mainly after achieving the hydrogenation of furfural to furfuryl alcohol, a mechanism proposed in Scheme 4.6. The hydrogenation of furfural using Pd/TiO_2 resulted in the formation of 2-methylfuran, furfuryl alcohol, tetrahydrofurfuryl alcohol and dimer 1 as proposed in Scheme 4.7, and dimer 2 as proposed in Scheme 4.8. However, the suggested mechanism of the dimers formations can be summarised as follows: over Pd, furfural may first be hydrogenated to produce furfuryl alcohol. This is followed by the addition of H_2 to the carbonyl group (C=O) bond; then it subsequently undergoes cleavage of hydrated furfural which may produce two molecules which could then convert to dimers. As a minor pathway, the catalyst may facilitate the dimerisation of the hydrogenation product furfural to dimers, which occurs under catalysis.[70] Recently the price of Au has increased significantly and this has caused the search for alternative metals to Au. Ru is attractive as at current its price is compared with the price of gold. Furthermore, the potential addition of Ru to Pd to be of potential interest as Ru forms alloys.[71] On the other hand, since the Ru is well-known as an active catalyst for hydrogenation reactions, it may show some activity for furfural hydrogenation, as does Pd.[72] Ruthenium seems to show activity for the hydrogenation reaction that is between gold and palladium when supported on TiO_2. This is similar to what has been reported by Graham and co-workers when they discuss the synthesis of H_2O_2 using Ru, Au and Pd supported on titania.[20,24,72] Besides the background, the influence of monometallic Ru and adding Ru to Pd supported on TiO_2 has been investigated. The result shows catalytic activity, for Ru and Ru:Pd ratios for hydrogenation of furfural as well. Low conversion was obtained using a monometallic Ru/TiO_2 catalyst with high selectivity to furfuryl alcohol. However, the conversion was increased when Pd metal was loaded to Ru to support TiO_2, catalytic activity as well as selectivity to 2-methylfuran as shown in Table 4.11.

Table 4.11: Effect of support on Ru and Pd catalysts for furfural hydrogenation:

Catalyst	Conversion (%)	Selectivity (%)					
		2-Methylfuran	Furfuryl Alcohol	Tetrahydro-furfuryl Alcohol	Dimer 1	Dimer 2	Others
5%Ru/TiO_2	8.2	0	100	0	0	0	0
4%Ru:1%Pd/TiO_2	5.0	9.2	83.8	0	6.8	0	0
3%Ru:2%Pd/TiO_2	21.5	15.1	67.9	0	1.6	0	15.5
2.5%Ru:2.5%Pd/TiO_2	33.8	14	58	0.4	0	27.6	0
2%Ru:3%Pd/TiO_2	30	8.7	65.8	0	5.3	0	18.5
1%Ru:4%Pd/TiO_2	39.3	51.5	45.3	1.1	2.1	0	0
0.5%Ru:4.5%Pd/TiO_2	39.2	50.8	39.8	1.8	0	7.6	0
2.58%Pd/TiO_2	65.4	36.2	28.6	4.8	12.5	18	0

Reaction conditions:- 1000mg of substrate, 100mg of catalyst, 15ml of octane as a solvent, autoclave reactor, 25°C, 120min, 1000rpm, 3bar H_2 continuously controlled pressure.

The variation in catalytic activity can be related to the variation in active Ru:Pd ratios and more sites being available for catalytic activity. The variation in activity could be affected by a synergistic effect of Ru:Pd ratios. Figure 4.12 shows the XRD pattern of different amounts of Ru:Pd ratio. Significance did not change for all catalysts and TiO_2 is a mixture of rutile and anatase. Deconvoluted XPS data was obtained for different ratios of Ru:Pd catalysts supported on TiO_2. Figure 4.13 indicates 3d doublet peak for Pd/PdO with component deconvolution. Ru peak analysis is tricky in this case due to strong overlapping with the adventitious Carbon binding energy at 284.5eV.

A binding energy of 336.2eV and 341.5eV for $3d_{5/2}$ and $3d_{3/2}$ respectively which is in close agreement with values reported by Kim et al[72] for PdO, while the binding energy of 334.6eV and 339.9eV attributed to the $3d_{5/2}$ and $3d_{3/2}$ double peak respectively for Pd metal. These peak binding energies confirms with the reported values for Pd by Jenks et al[73] The peaks in Figure 4.13 show no peak linked to Pd on 5%Ru/TiO_2 catalyst. However, it indicates Pd in varying oxidation state for PdO spectra detecting a high valence of Pd^{2+}, Pd-Pd indicates a low valence of Pd^0. At variation Ru:Pd catalyst, increasing loading of Pd influences the display of Pd on the surface as observed for 1%Pd:4%Ru and 4%Pd:1%Ru catalyst, with 1%Pd:4%Ru/TiO_2 catalyst exhibiting the highest selectivity to 2-methylfuran but with very low conversion. However, 4%Pd:1%Ru/TiO_2 catalyst displays the highest conversion and significant selectivity to 2-methylfuran. This is evident by domination of the $3d_{5/2}$ peak intensity attributed to PdO at 336.2eV, as well as increases the concentration and FWHM from 1.9-2.0 for 1%Pd:4%Ru/TiO_2 and 4%Pd:1%Ru/TiO_2 catalyst respectively. In addition, the Ru:RO_2 ratios of (3:2) and (1:1) for 1%Pd:4%Ru/TiO_2 and 4%Pd:1%Ru/TiO_2 catalyst respectively which could be effected on catalyst activity. An abundance of Ru^{4+} and Pd^{2+} shows the active sites of catalyst and it could have favoured a reduction in C=O. The XPS, and XRD data confirms that the catalyst samples were similar in chemical nature even if the amount of Ru:Pd ratios were different. This means the difference in catalytic activity was related with the active sites. In this current study, the initial results, show the effect of the addition of Ru in bimetallic catalysts but is less effective than Pd under those conditions. However, it may be desirable to carry out further studies and more characterisations of the Ru and Ru:Pd ratios and it may provide encouraging results in the future. This will form the basis of an independent and subsequent study.

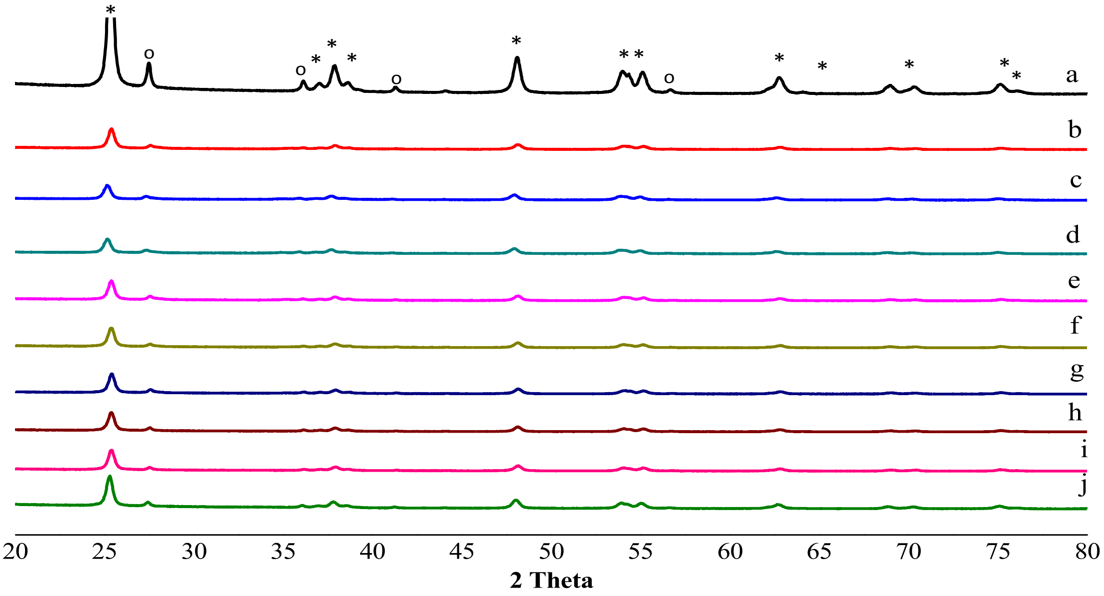


Figure 4.12: X-ray diffraction patterns of mono catalyst calcined in air 400ºC. Key: (a) TiO_2, (b) 5%Ru/TiO_2, (c) 4.5%Ru:0.5Pd/TiO_2, (d) 4%Ru:1%Pd/TiO_2, (e) 3%Ru:2%Pd/TiO_2, (f) 2.5%Ru:2.5%Pd/TiO_2, (g) 2%Ru:3%Pd/TiO_2, (h) 1% Ru:4%Pd/TiO_2, (i) 0.5%Ru:4.5%Pd/TiO_2, (j) 5%Pd/TiO_2. Symbol: (*) TiO_2 anatase phase and (○) TiO_2 rutile phase.

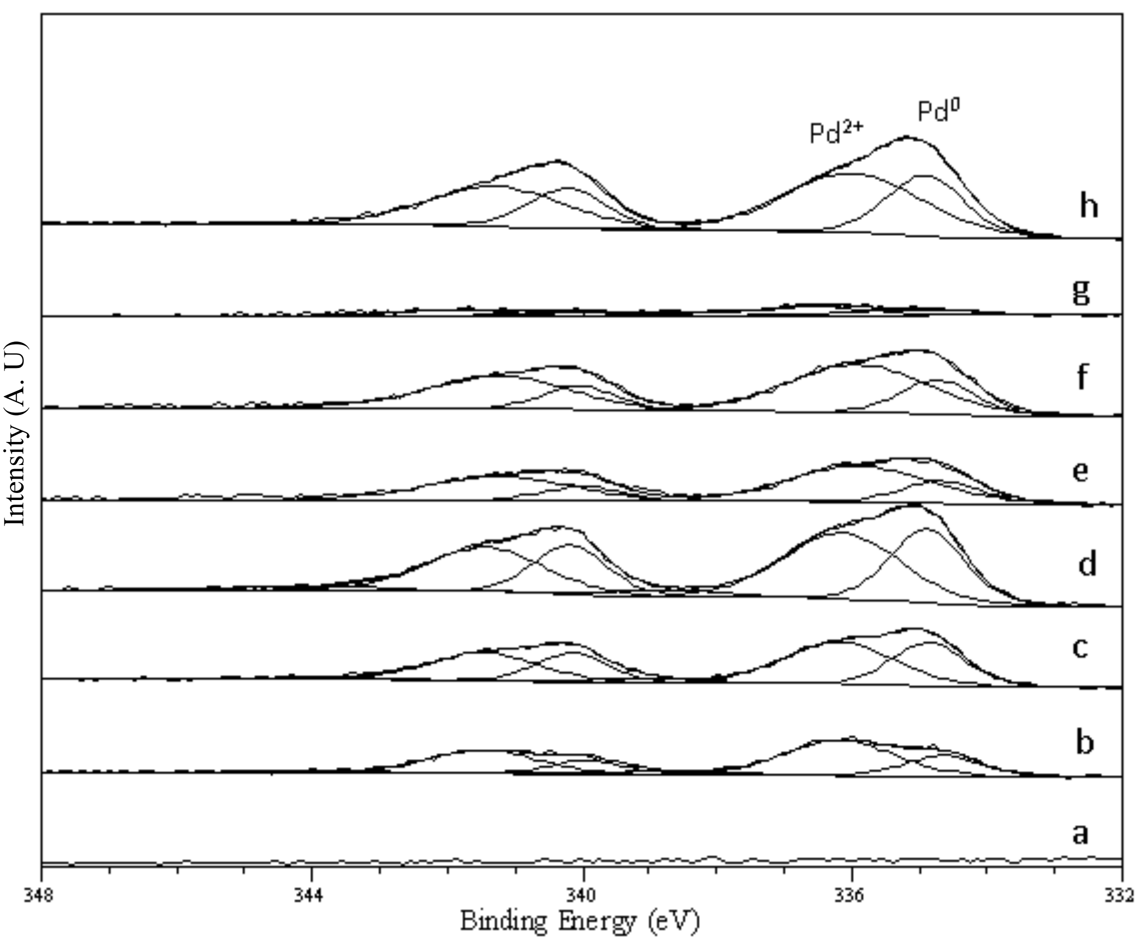
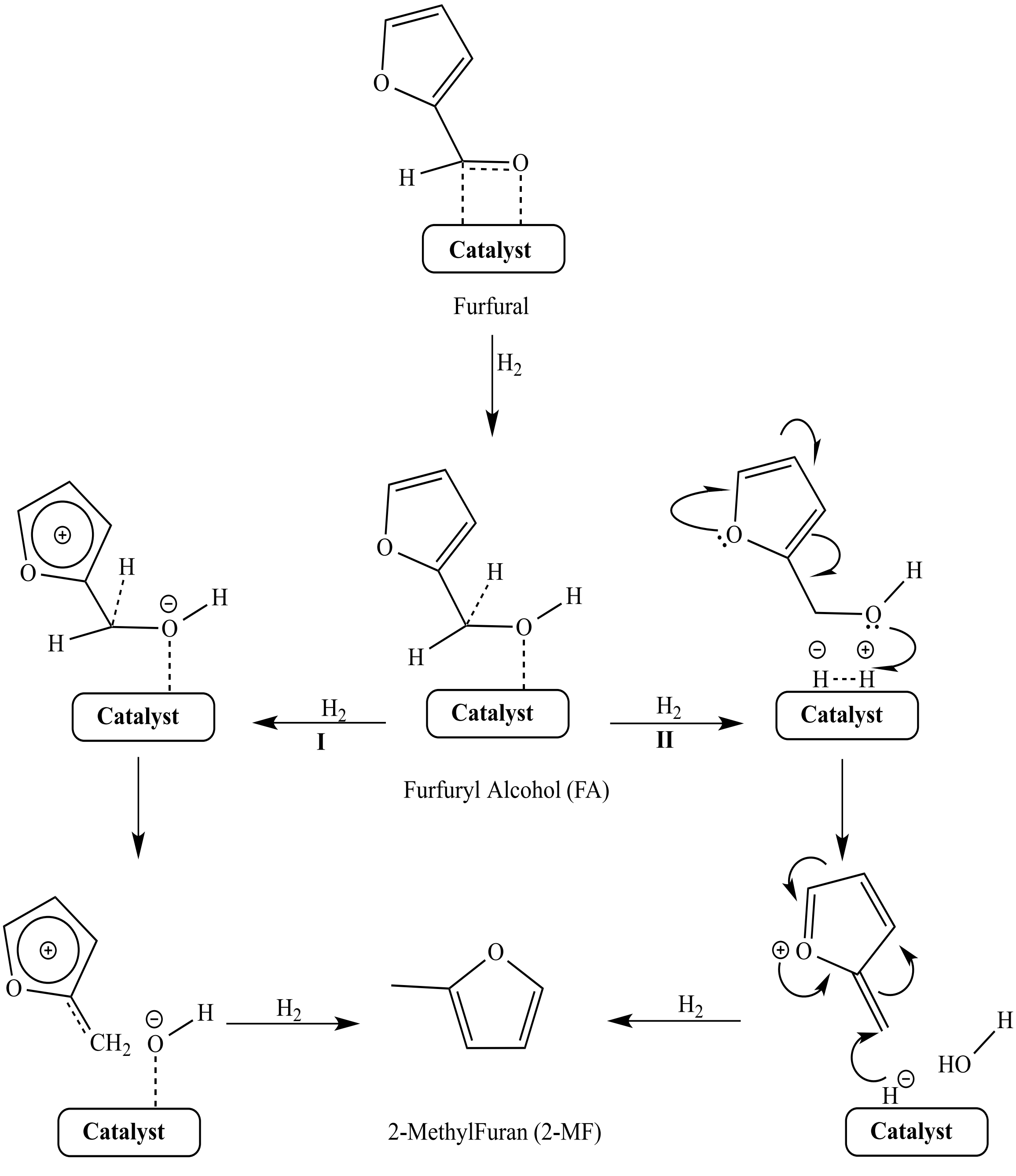
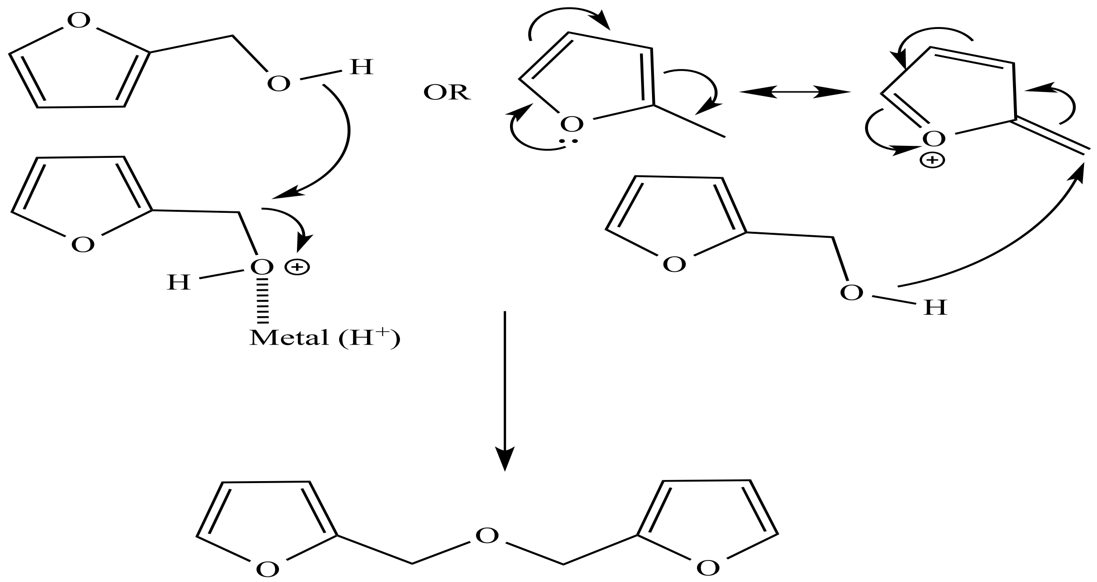


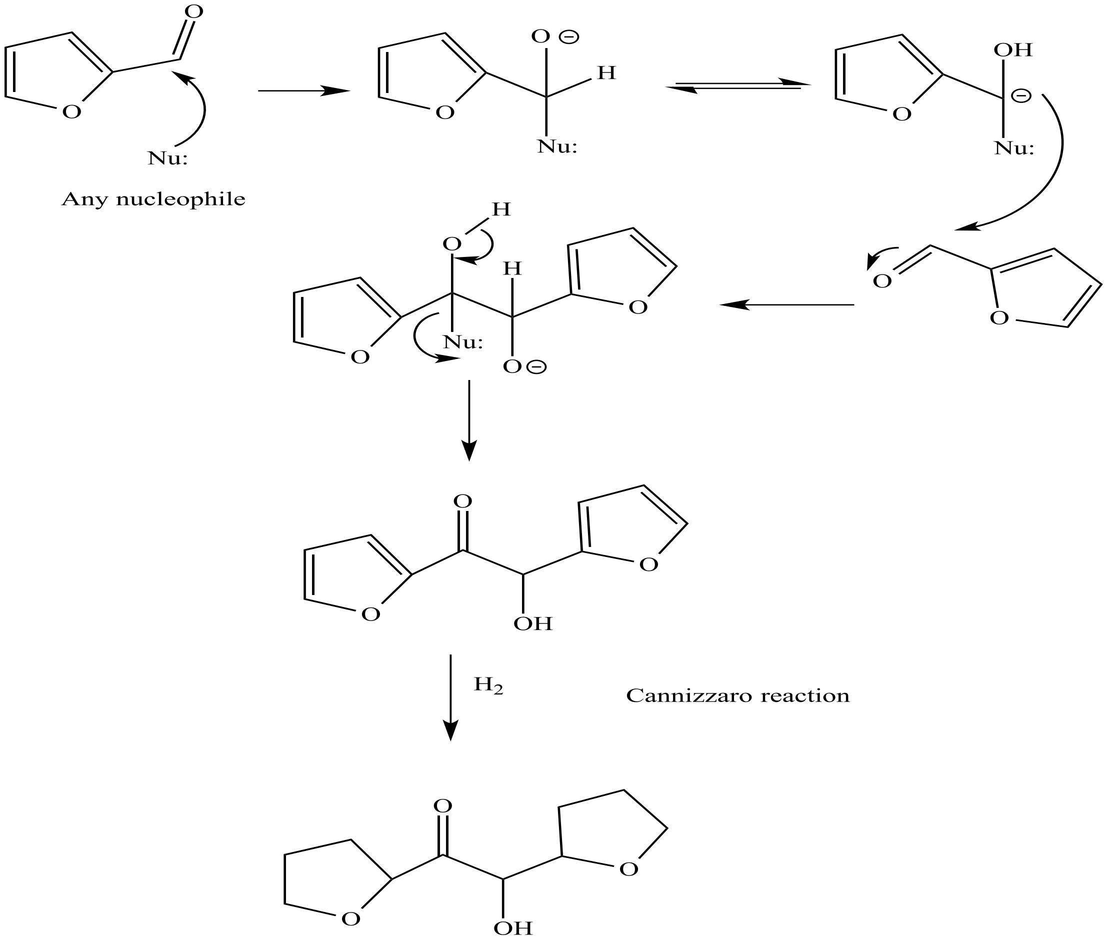
Figure 4.13: XPS profiles of TiO_2 supported Pd with different Pd:Ru ratios. a) 5%Ru/TiO_2, b) 2.5%Ru:2.5%Pd/TiO_2, c) 1%Pd:4%Ru/TiO_2, d) 4%Pd:1%Ru/TiO_2 e) 3%Ru:2%Pd/TiO_2, f) 2%Ru:3%Pd/TiO_2, g) 0.5%Ru : 4.5%Pd/TiO_2, h) 4.5%Ru:0.5%Pd/TiO_2.



Scheme 4.6: The reaction mechanism proposed for the hydrogenation of furfural.[74]



Scheme 4.7: The reaction mechanism proposed for the hydrogenation of furfural to form dimer 1.



Scheme 4.8: The reaction mechanism proposed for the hydrogenation of furfural to form dimer 2.

4.2.1.4 Study of palladium loading effect:

Various loadings of Pd supported on TiO_2 have been studied and a variation in the activity of catalysts has been observed with respect to both conversion and selectivity. The results from all catalytic activity have been presented in Table 4.12. However, it has been found that when Pd loading was increased from 0.5% to 2.58%, catalytic activity as well as selectivity to 2-methylfuran, increased. A continuously controlled pressure of 3barg was used to perform the reactions at room temperature. In addition, the increase in the concentration of the Pd catalyst increases selectivity to 2-methylfuran since an increase in the quantity of the catalyst makes more active sites available to the substrate.[4,70] Figure 4.4, as illustrated in first section, characterises the XRD pattern of the Pd catalyst with various loadings. There are no peaks in the diffractogram, which indicates a variation in crystalline particles in the case of varying Pd loading. This research makes use of the TiO_2 mixture of rutile and anatase, which demonstrates stability during the course of the manufacturing process. No large size particles of the Pd or Pd containing compounds were synthesised during the preparation of the catalyst. This is because the particle size of the metal particles is considered to be a crucial factor which influences the activity of the supported catalysts. The TEM images of catalysts with 0.5%, 1.26 and 2.58%Pd/TiO_2 are shown in Figure 4.6 in the first section. During this research and as discussed in the hydrogenation of furfuryl alcohol section, huge Pd particles could not be examined through microscopic images. However, the HRTEM images contained a large number of minute particles for all catalysts. Since the average particle size of supported Pd catalysts was less than 2nm, they were not detected in the XRD pattern. The findings from the HRTEM and XRD analysis show that extremely small nanoparticles were produced by the impregnation method. This research involves an attempt to obtain data related to the particle size which is revealed by the localised TEM images. It is highly anticipated that minute particles will demonstrate increased catalytic activity.[75] Various loadings of Pd catalysts of different sizes were tested during this study. It is evident from Figure 4.6 that the difference between the sizes of particles is very small and all particles demonstrated a size of about 1nm. All catalysts had the same particle size distribution. For that reason, it can be stated that the improvement in catalytic activity was due to the higher concentration of active metal which a made higher number of sites available for the catalytic activity. Deconvoluted XPS data from TiO_2-supported Pd catalysts containing varying loadings of Pd is shown in Figure 4.7 (discussed in first section). The types of Pd (Pd^{2+} and Pd^0) having binding energies of 337.6eV (in case of Pd^{2+}) 335.8eV (in case of Pd^0) are found on the surface of catalysts. Moreover, in all catalysts, ratios of these forms of Pd are kept in the range of 12-15. Most of the catalysts are made up of Pd^{2+} while extremely small quantities of Pd^0 are found in Pd/TiO_2 catalysts. Existence of Pd^{2+} as the dominant constituent making up the active sites indicates that they might facilitate the reduction of H_2 and the carbonyl group by acting as coordinated metal centres[58]. This could explain the preferable reduction of the carbonyl group and the reduction of C=C bond by Pd^0 on a preferential basis. Data obtained from the XRD, HRTEM and XPS prove that quite a comparable chemical nature was demonstrated by all catalysts, which suggests that difference in catalytic activity could be due to the difference in the number of active sites available in the catalyst. Conversely, the difference may be due to a higher number of active sites after an increase in the loading of Pd which results in more hydrogenation.

Table 4.12: Effect of palladium loading on furfural hydrogenation:

Catalyst	**Conversion (%)**	**Selectivity (%)**				
		2-Methylfuran	Furfuryl Alcohol	Tetrahydro-furfuryl Alcohol	Dimer 1	Dimer 2
0.5%Pd/TiO_2	20.7	7	73.1	14.3	0	5.1
1.26%Pd/TiO_2	53.2	19.9	39.7	6.7	1.9	31.8
2.58%Pd/TiO_2	65.4	36.2	28.6	4.8	12.5	18

Reaction conditions:- 1000mg of substrate, 100mg of catalyst, 15ml of octane as a solvent, autoclave reactor, 25°C, 120min, 1000rpm, 3bar H_2 continuously controlled pressure.

4.2.1.5 Study of pressure effect:

2.58%Pd supported on TiO_2 was tested using different continuously controlled different pressures of H_2 (1 to 3barg). The reaction was performed at a continuously controlled pressure (the pressure was kept constant by refilling during the reaction), at room temperature for 120min, as is similar to that of the hydrogenation of furfuryl alcohol in the first section. The conversion and selectivity is presented in both Figures 4.14 and 4.15. A very slight change in conversion was observed for all continuously controlled pressures. In addition, the selectivity to 2-methylfuran was very small, increasing under these same conditions. However, furfuryl alcohol was formed in the reaction as an intermediate product and its selectivity was significantly decreased at

3barg of continuously controlled pressure. This may have been caused by an increase in the amount of H_2 in reactions with continuously controlled pressure. Furthermore, an increase in pressure caused an increase in catalytic activity. Furfuryl alcohol can be hydrogenated to 2-methylfuran and tetrahydrofurfuryl alcohol, as reported in the first section.[59] Tetrahydrofurfuryl alcohol and dimres were formed in the reaction as by-products, as was proposed previously. It can be concluded that the pressure or the amount of hydrogen is an important factor in obtaining selectivity.

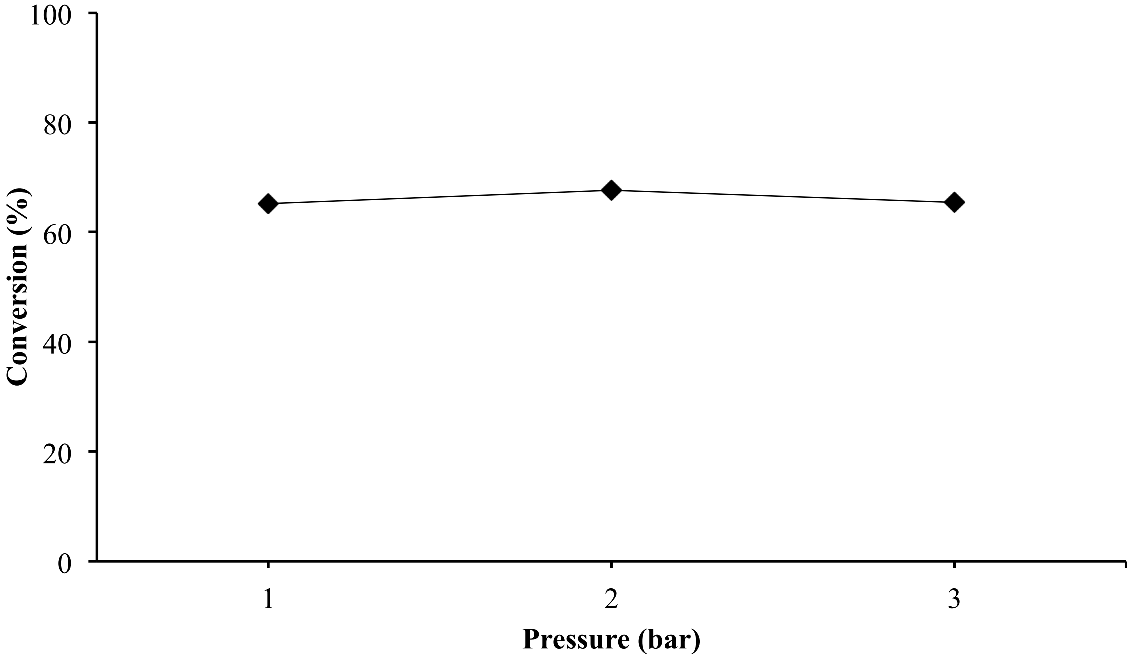


Figure 4.14 Study of the pressure effect for the conversion of furfural. **Reaction conditions:-** 1000mg of substrate, 100mg of 2.58%Pd/TiO_2, 15ml of octane as a solvent, autoclave reactor, 25ºC, 120min, 1000 rpm, H_2 continuously controlled pressure.

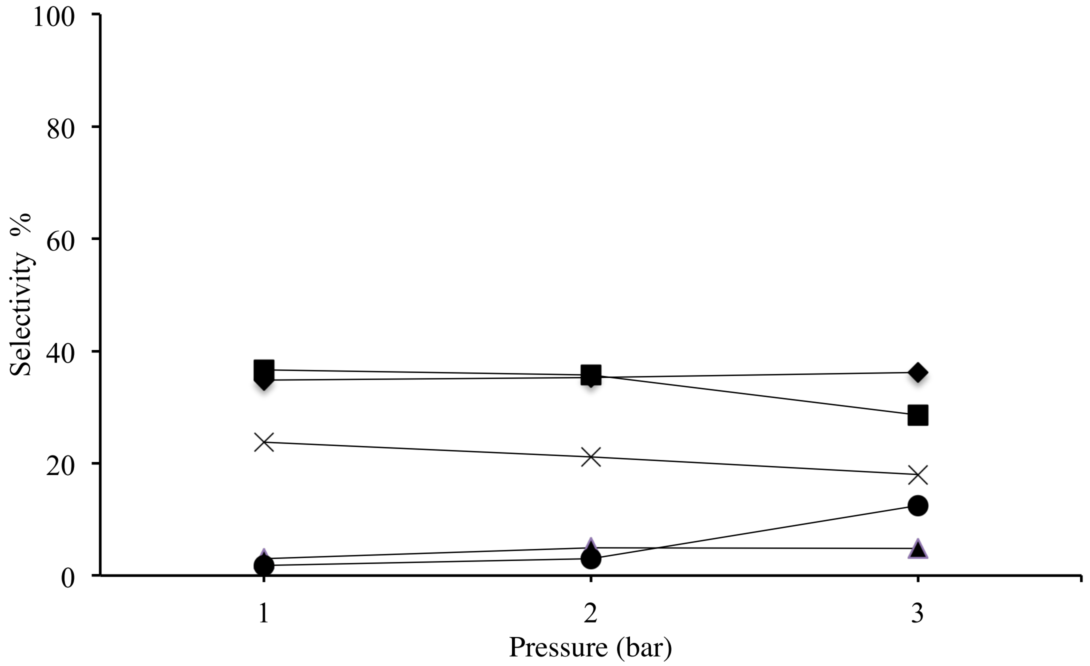


Figure 4.15: Study of the pressure effect for the selectivity of furfural. **Reaction conditions:-** 1g of substrate, 100mg of 2.58%Pd/TiO_2, 15ml of octane as a solvent, autoclave reactor, 25ºC, 120min, 1000rpm, H_2 continuously controlled pressure. (♦) 2-methylfuran, (■) furfuryl alcohol, (▲) tetrahydro-furfuryl alcohol, (●) Dimer1, (x) Dimer2.

4.2.1.6 Study of catalyst mass effect:

The influence of the amount of catalyst on activity was studied. The catalyst amount was varied from 25 to 200 mg of 2.58% Pd/TiO_2. As shown in Figures 4.16 and 4.17, an increase in the amount of catalyst enhanced the overall catalytic performance. The conversion of the reaction was stable when using 100 to 200 mg 2.58wt% Pd/TiO_2. However the selectivity to 2-methylfuran kept increasing when using 200 mg of catalyst and dimers were decresed significantly. This may be attributed to a further reduction in Pd cation. It confirms the very high selectivity observed using the Pd catalyst for the reduction of C=O to produce hydrocarbons, whereas the C=C reduction is inhibited even with the higher catalyst amounts. This proposes a different reaction pathway on the surface of the supported Pd catalysts, compared with the gas phase reduction of unsaturated hydrocarbons or aldehyde by using Pd catalysts.[59]

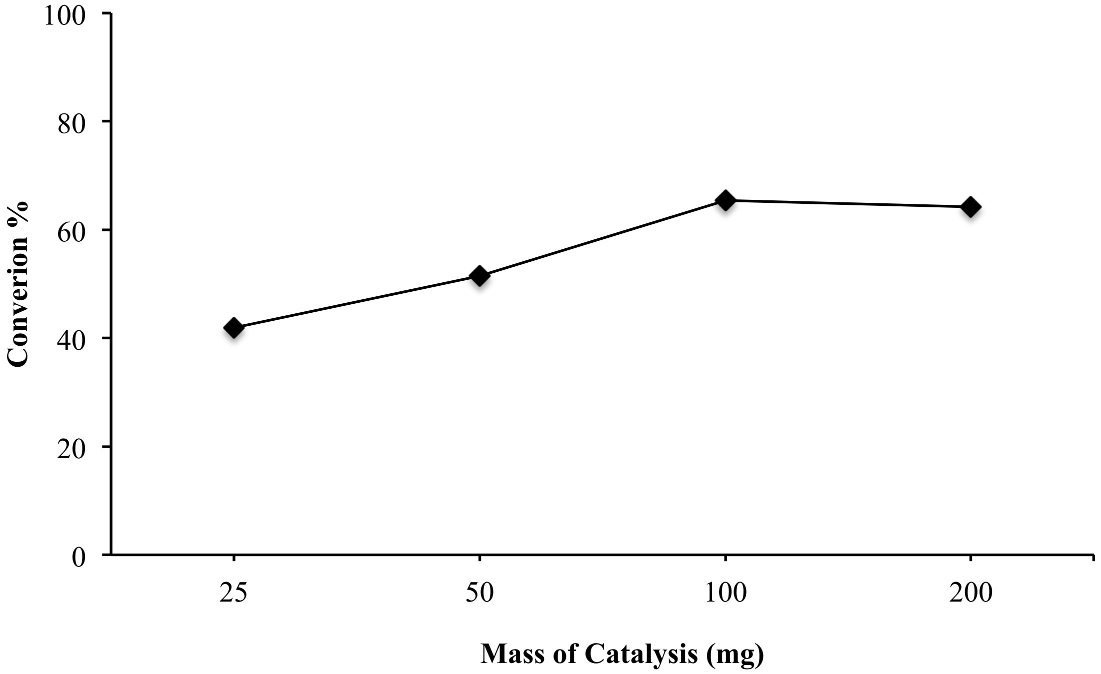


Figure 4.16: Catalyst mass effect for the conversion of furfural**.** Reaction conditions:- 1000mg of substrate, 2.58%Pd/TiO_2, 15ml octane, autoclave reactor, 25°C,120min, 1000rpm, 3bar, continuously controlled pressure.

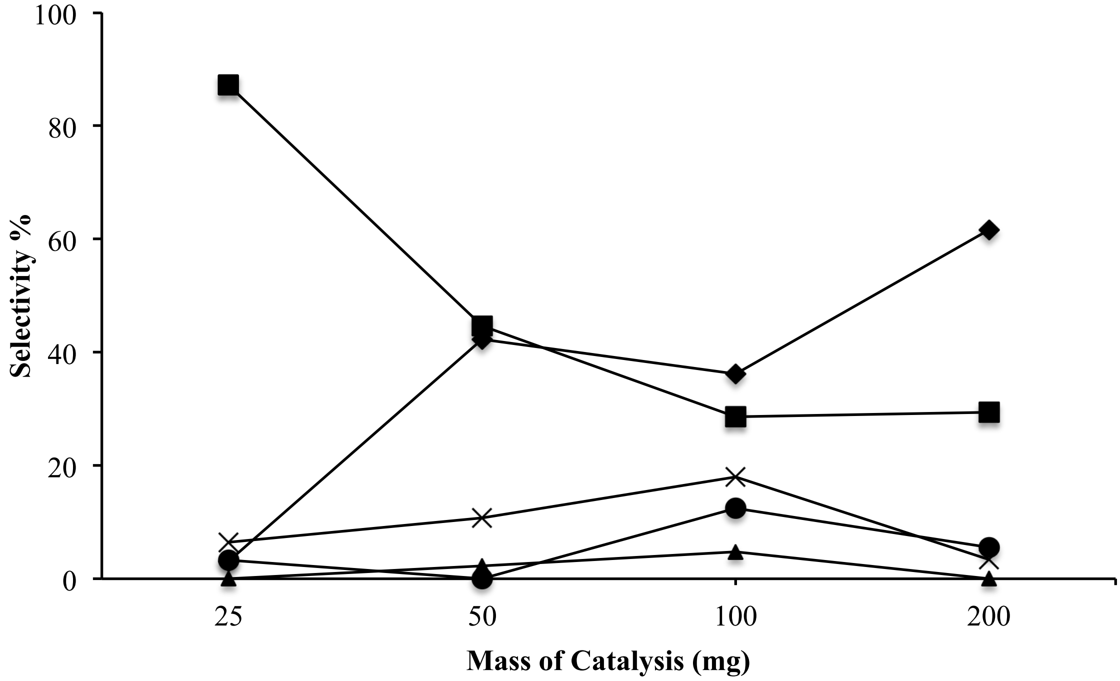


Figure 4.17: Catalyst mass effect for the selectivity during the hydrogenation of furfural. Reaction conditions:- 1000mg of substrate, 2.58%Pd/TiO_2, 15ml octane, autoclave reactor, 25ºC, 120min, 1000rpm, 3bar continuously controlled pressure. (♦) 2-methylfuran, (■) furfuryl alcohol, (▲) tetrahydrofurfuryl alcohol, (●) Dimer 1, (x) Dimer 2.

4.2.1.7 Study of stirring effect:

Mass transport plays a crucial role in catalysis, and hence continuous stirring of the reaction contents is recommended to reduce heat as well as the diffusion limitations between the catalyst particles and the bulk liquid phase. The effect of speed of stirring on the reaction has been tested at room temperature and the results are presented in Figure 4.18 and 4.19. It is obvious from the figures that with an increase in the speed of stirring, the conversion of furfural increases. However, at speeds of 1000 and 1500 rpm, the reaction became stable suggesting that it was proceeding under the influence of kinetic control. For that reason, the speed of 1000 rpm was chosen for stirring in the following experiments. In addition the selectivity for 2-methylfuran was increased significantly with increasing stirring speed.

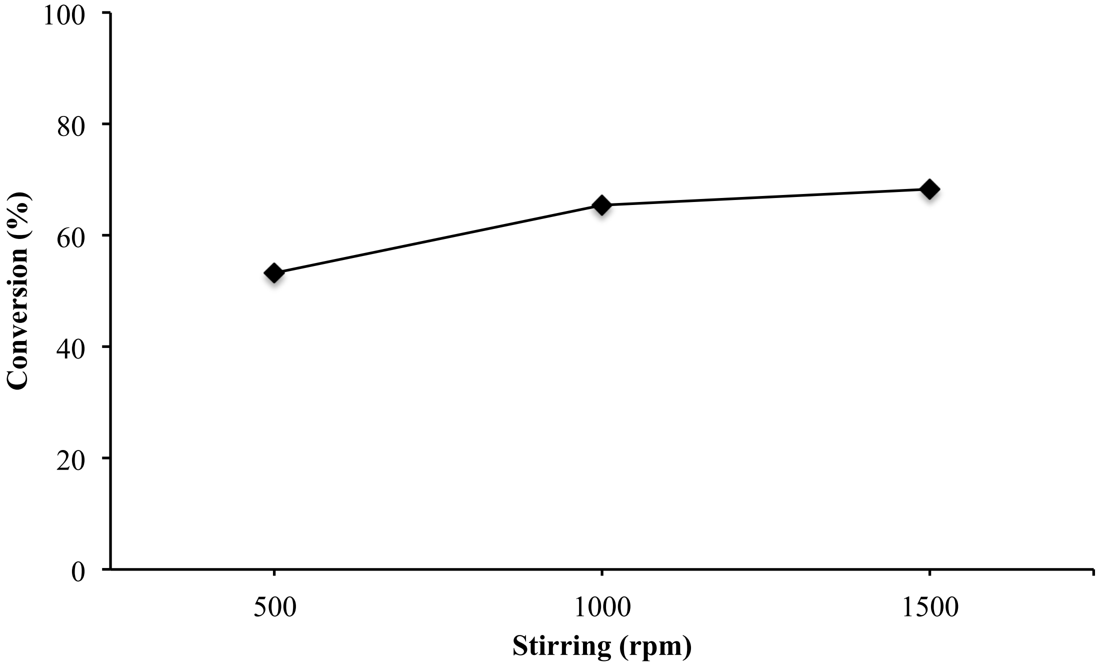


Figure 4.18: study of stirring speed effect for the conversion of furfural. Reaction conditions: 1000mg of substrate, 100mg of 2.58%Pd/TiO$_2$, 25ºC, 120min, 3bar H$_2$ continuously controlled pressure, 15ml of octane as a solvent, autoclave reactor.

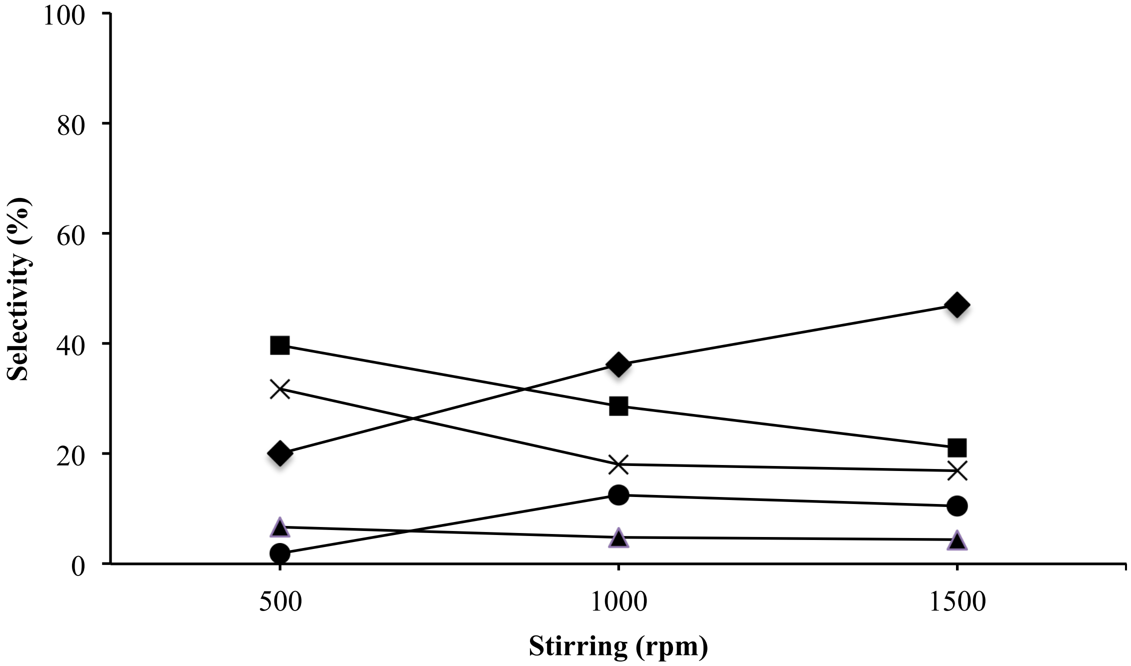


Figure 4.19: study of stirring speed effect for the selectivity of furfural. Reaction conditions: 1000mg of substrate, 100mg of 2.58%Pd/TiO$_2$, 25ºC, 120min, 3bar H$_2$ continuously controlled pressure, 15ml of octane as a solvent, autoclave reactor. (♦) 2-methylfuran, (■) furfuryl alcohol, (▲) tetrahydrofurfuryl alcohol, (●) Dimer 1, (x) Dimer 2.

4.2.1.8 Study of time on line effect:

The effect of the reaction time on the conversion and selectivity is shown in Figures 4.20 and 4.21. The reactions were performed over 2.58%Pd/TiO_2 at optimal conditions (25ºC, 1000rpm, 3barg continuously controlled H_2 pressure). All reactions were carried out in the presence of octane as the petroleum solvent. As the data shows conversion steadily increased, and the selectivity to 2-methylfuran did not change much after 3h of reaction. However, this increase in conversion with time was not linear, indicating that the catalysts deactivated slightly as the reaction time increased. Generally, deactivation of the catalyst can occur due to many reasons such as the loss of the active Pd^{2+} type by reduction, the sintering of Pd particles and the blockage of the active sites by by-products. Moreover, furfuryl alcohol was formed in the reaction as an intermediate product and its selectivity steadily decreased with time.

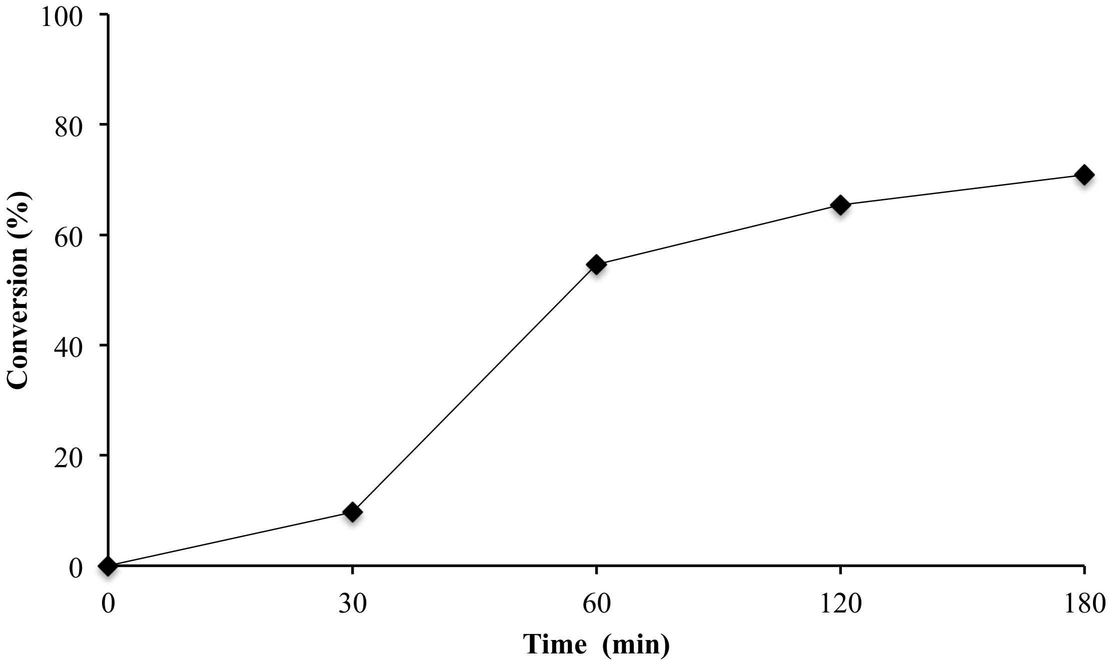


Figure 4.20: Effect of reaction time on the conversion of furfural. Reaction conditions: 1000mg of furfural, 100mg of catalyst, 15ml of octane as a solvent, autoclave reactor, 25ºC, 1000rpm, 3bar H_2 continuously controlled pressure.

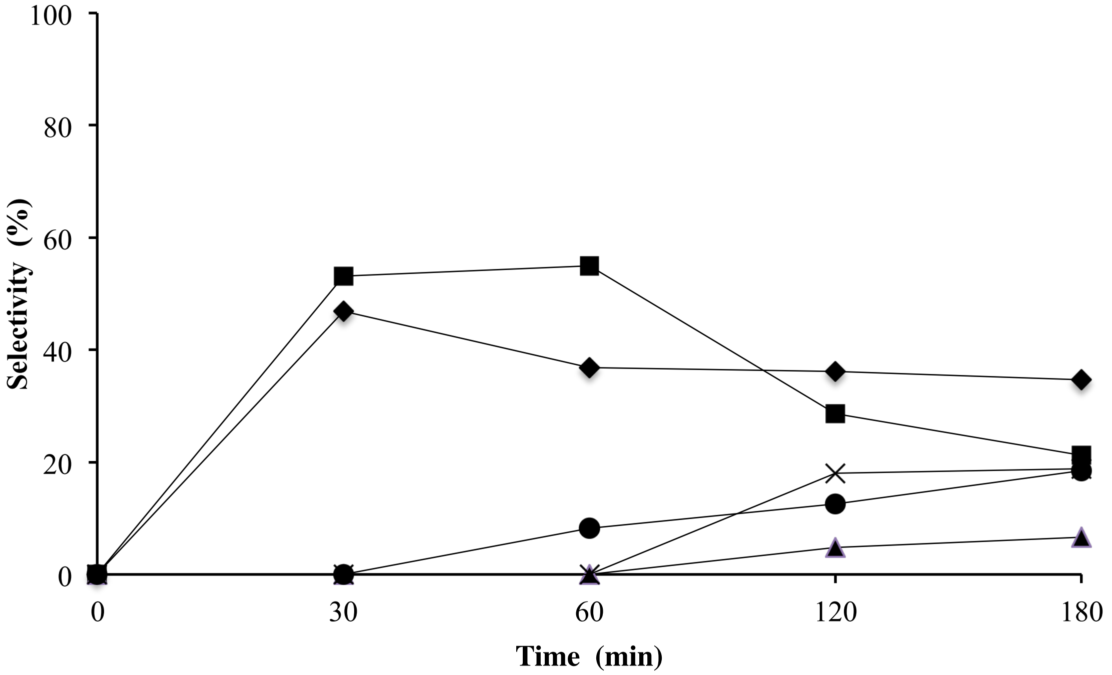


Figure 4.21: Effect of reaction time on the selectivity of furfural. Reaction conditions: 1000mg of furfural, 100mg of catalyst, 15ml of octane as a solvent, autoclave reactor, 25ºC, 1000rpm, 3bar H_2 continuously controlled pressure. (♦) 2-methylfuran, (■) Furfuryl alcohol, (▲) tetrahydofurfurylalcohol, (●) Dimer1, (×) Dimer 2.

4.2.1.9 Study of Pd oxidation state through XPS:

The palladium catalyst oxidation state has an effect on the catalytic activity of the catalyst, as shown in table 4.13. As observed in the first section (Figure 4.7), two species of Pd were detected on the surface of the catalyst (Pd^{2+} and Pd^0). The catalyst with the higher amount of the Pd^{2+} on the catalyst surface showed more activity. In addition, the increase in selectivity can be linked to the increase in the Pd^{2+} species on the catalyst surface and consequently the availability of active sites. Moreover, the pre-treatments may have caused an increase in the activity of the catalyst. The calcination of the catalyst under static air at 400°C for 3h resulted in a higher amount of Pd^{2+} being on the catalyst surface, as reported in first section (Table 4.7). Edwards, et al[57] suggest that the surface ratio of Pd^{2+} to Pd^0 may have contributed towards the increase in the ability to control the hydrogenation of H_2O_2, and a series of controlled reductions. Re-oxidation of a sample shows how the Pd^{2+}/Pd^0 surface ratio can affect H_2O_2 synthesis and hydrogenation.[58] The main presence of Pd^{2+} proposes active sites, which could have a function similar to co-ordinated metal centres for H_2 activation and reduction of C=O.[58] Also, it could suggest that Pd^{2+} preferably reduces C=O while metallic Pd is preferably active for C=C reduction.[55]

Table 4.13: Effect of surface palladium furfural Hydrogenation**:**

Catalyst	**Conversion (%)**	**Selectivity %**				
		2-Methylfuran	Furfuryl Alcohol	Tetrahydro-furfuryl Alcohol	Dimer 1	Dimer 2
2.58%Pd/TiO_2[a]	65.4	36.2	28.6	4.8	12.5	18
2.58%Pd/TiO_2[b]	57.3	25.1	30.4	5.1	1.5	37.5
2.58%Pd/TiO_2[c]	53.4	24.9	34	5.1	0	36

Reaction conditions:- 1000mg of substrate, 100mg of catalyst, 15ml of octane as a solvent, autoclave reactor, 25ºC, 120min, 3bar H_2 continuously controlled pressure, 1000 rpm.

a) Calcined under static air at 400 C for 3h.
b) Reduced in H_2/Ar at 200°C for 3h at a ramp rate of 5°C/min.
c) Oxidised in O_2 at 200°C for 3h at a ramp rate of 5°C/min.

4.2.1.10 Reusability of Pd/TiO_2:

Heterogeneous catalysts are easily recovered and reusable. The successful recovery and re-use thereafter is an essential feature of green chemistry. As mentioned before in the first section, the reusability was tested for the catalyst 2.58%Pd/TiO_2 and the result is shown in table 4.14. The catalyst was recovered by centrifugation after the reaction. The centrifuged catalyst was washed with 10ml acetone. This practice was repeated three times before the catalyst was dried in the oven at 110°C overnight. In the re-use experiment, larger amounts of the catalyst were used in the initial experiments so that the correct catalyst mass (100 mg) could be used in the following reactions. It is supposed that washing the used catalyst with acetone removes all products that might block the active sites of the catalyst when the reaction is carried out, thus the activity sites can be recovered. Table 4.14 shows the conversion of furfural and the selectivity of 2-methylfuran, furfuryl alcohol, tetrahydrofurfuryl alcohol and dimers over 2.58%Pd/TiO_2 (calcined in static air at 400°C). The fresh catalyst was high for 2-methylfuran, while the activity of the used catalysts decreased with regards to furfuryl alcohol in particular. There are several possible reasons, for example:

(a) Similar furfuryl alcohol may be from loss of the active Pd^{2+} species by reduction. The XPS analysis has shown a clear loss of the active Pd^{2+} species through reduction when pretreated with H_2 and the disappearance of Pd^{2+} after the first reaction.

(b) Pd particle sintering.

(c) Active Pd site coverage by coke or adsorbed reactants/products.

Table 4.14: study of reusability of furfural hydrogenation:

Catalyst	Conversion (%)	Selectivity %				
		2-Methylfuran	Furfuryl Alcohol	Tetrahydro-furfuryl Alcohol	Dimer 1	Dimer 2
2.58% Pd/TiO_2	62.4	36.2	28.6	4.8	12.5	18
1st re-use	53.4	25	34	5	0	36

Reaction conditions:- 1g of substrate, 0.1g of catalyst, 15ml of octane as a solvent, autoclave reactor, 25ºC, 120min, 3bar H_2 continuously controlled pressure.
Details recovery: 300mg of catalyst, 15ml of octane as a solvent, autoclave reactor, 25ºC, 120min, 3bar H_2 continuous pressure then the catalysis was washed and dried in an oven at 110°C for 16h.

4.3 Catalyst characterisation:

Various catalysts were prepared using the impregnation method and tested for the said reaction, according to the preparation procedure explained in Chapter Two. The particle size distributions of the catalysts with different loading were analysed. The Au:Pd/TiO_2 catalyst was prepared and this comprises of larger particles while there were no large palladium particles observed on the microscopic images. Catalysts were characterised through scanning electron microscopy (SEM), High-resolution transmission electron microscopy (HRTEM), X-ray Photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), temperature-programmed reduction (H_2-TPR), and surface area measurements (BET). The characterization results are presented in the following sections.

4.3.1 X-Ray Diffraction (XRD):

Powder X-ray diffraction (XRD) is a method used to determine crystaline materials of crystalline as it reveals useful information about the crystal structures of the material via diffraction patterns. Powder XRD was carried out using a PANalytical X'Pert Pro with a CuK α X-ray source run at 40 kV and 40 mA fitted with an X'Celerator detector. Each sample was scanned from $2\theta=10$ to 80 for 30 min. The catalysts were ground into fine powder form and loaded on a silicon wafer. The results obtained were compared with the information in the ICDD library for each catalyst. An XRD pattern of TiO_2 support and Pd-supported catalysts is shown in Figure 4.4. A comparison with pure TiO_2 support reveals that most of the reflections stem from the support. The diffraction pattern results for supported Pd catalysts with different loading show no significant difference was observed from 0.5wt% to 2.58wt% Pd loading due to the attribution smaller crystallite size which is lower than detectability limit of XRD[59] Figure 4.5 displays the XRD diffraction patterns of 5%AuPd supported on different materials (γ-Al_2O_3, SiO_2, TiO_2 and CeO_2). The Au:Pd and Ru:Pd bimetallic catalysts clearly indicates the presence of Au, Ru or Ru:Pd and Au:Pd alloy peaks. The XRD pattern of the sample indicated the presence of a characteristic peak of Au or Au:Pd alloy at $2\theta=38.3$, 44.4^o and 64.4^o. Unfortunately, the diffraction pattern of 2.58wt%Pd/TiO_2 did not show any clear peaks assigned to either metallic Pd or PdO. The diffraction lines corresponding to the TiO_2 (Degussa) support (P25) were clearly detected at 27.5^o, 36.2^o, 54.5^o and 69.2^o for the rutile phase, whereas diffraction peaks corresponding to anatase phase TiO_2 could be observed as characteristic peaks at $2\theta=25.3^o$, 48.0^o, 53.8^o, and 62.6^o. In addition, the XRD pattern of the sample indicates the presence of a characteristic peak of Ru or Ru:Pd alloy at 2θ =27.3°, 28.1°, 29.6°, 31.6°, 34.4°, 40.4° and 44.2°.

4.3.2 Temperature-programmed reduction (TPR):

TPR analysis has been used to investigate the reducibility of the 2.58%Pd/TiO_2 catalyst under different pretreatment conditions. TPR analysis shows that the catalyst calcined under static air was more reducible compared to the catalyst, which is oxidised by oxygen or reduced by hydrogen (Figure 4.22). The TPR profiles of 5%AuPd/TiO_2 and 2.58%Pd/TiO_2 catalysts are compared in Figure 4.22. 2.58%Pd/TiO_2 (calcined under static air) is much more easily reduced and the reduction of Pd/TiO_2 is complete below 100°C.[51] However, The TPR profiles of Ru and Ru:Pd catalysts are compared in Figure 4.23. All catalysts (calcined under static air) were reduced and the reduction of Ru:Pd is complete between 150 -200°C

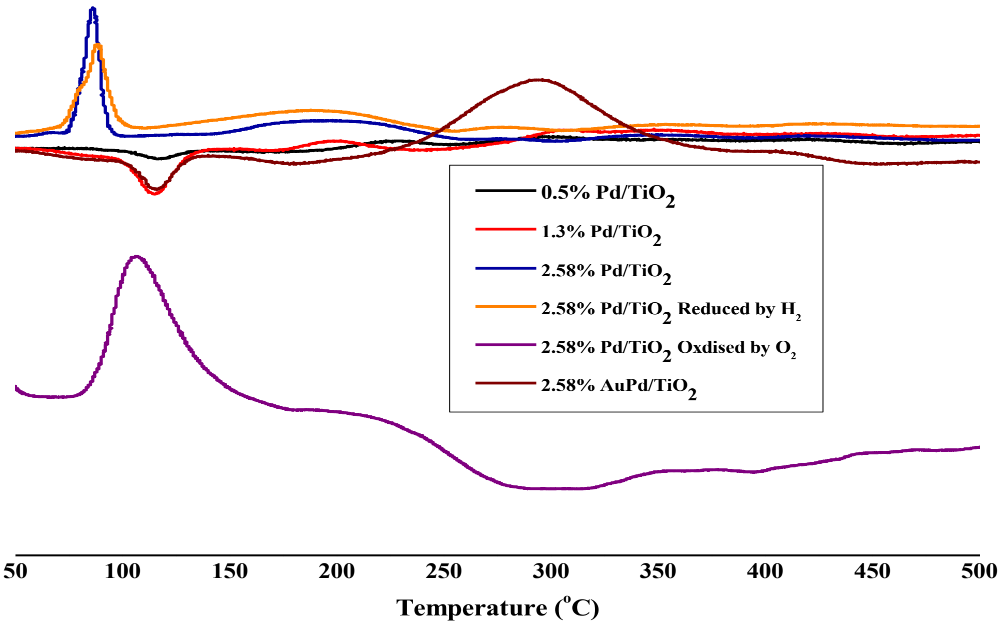


Figure 4.22 TPR measurements of the 5%AuPd, 0.5%Pd/TiO_2, 1.26%Pd/TiO_2, 2.58%Pd/TiO_2, **Calcined** under static air at 400 C for 3h, **Reduced** in H_2/Ar at 200°C for 3h at a ramp rate of 5°C/min, **Oxidised** in O_2 at 200°C for 3h at a ramp rate of 5°C/min.

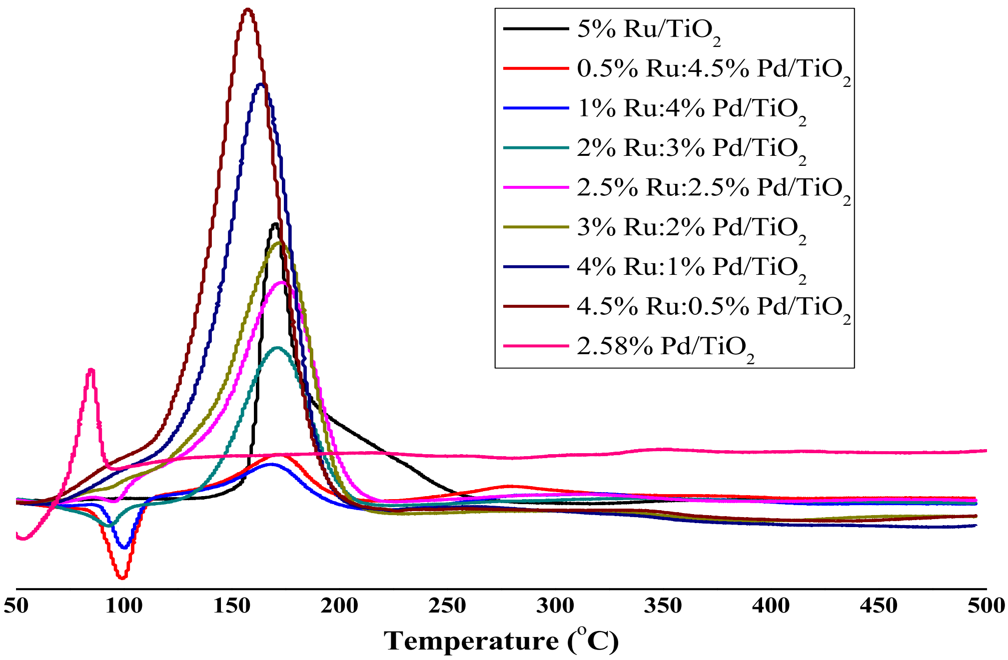


Figure 4.23: TPR measurements of the 5%Ru/TiO_2, 4.5%Ru:0.5%Pd/TiO_2, 4%Ru:1%Pd/TiO_2, 3%Ru:2%Pd/TiO_2, 2.5%Ru:2.5%Pd/TiO_2, 2%Ru:3%Pd/TiO_2, 1% Ru:4%Pd/TiO_2, 0.5%Ru:4.5%Pd/TiO_2, 5%Pd/TiO_2.

4.3.3 Surface area measurements (BET):

The total surface area often plays an important role in determining the performance of a catalyst.[46,68] In this study, the surface area of the synthesised catalysts was measured using the BET method. Depositing the Pd metal onto the TiO_2 support slightly decreased the surface area from 55 to 49 m^2/g. Supporting the 2.58%Pd/TiO_2 catalysts did not alter the BET surface area, indicating the stability of the TiO_2 support. However, in this study, the total BET surface area has not been considered as an important factor with respect to catalytic conversion and selectivity obtained for the hydrogenation of furfuryl alcohol.

4.3.4 Thermogravimetric analysis (TGA):

The catalyst was also characterised using thermogravimetric analysis in order to examine the behaviour of the catalyst under thermal conditions. Experiments were carried out between 25°C to 500°C with a ramp rate of 20°C/min in an air atmosphere. Figure 4.24 reveals that the fresh catalyst was thermally stable showing no effect from temperature,that is no weight loss was observed. However, the used catalyst exhibited ca. 4.5 wt.% loss starting at a temperature of ca. 250°C until 450°C. This weight loss could be due to the carbonaceous deposits on the catalyst surface leaving in the form of CO_2 in the air atmosphere.

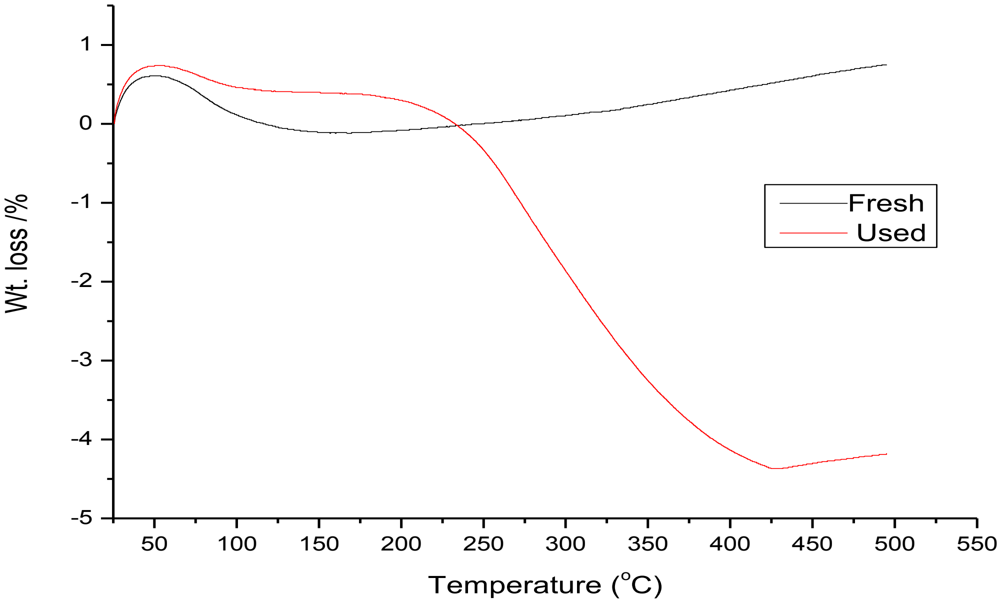


Figure 4.24: Thermogravimetric analysis (TGA) of catalyst 2.58%wtPd/TiO_2.

4.3.5 Microwave Plasma Atomic Emission Spectroscopy (MP-AES):

The actual metal loadings were performed using Agilent 4100 MP-AES (Microwave Plasma Atomic Emission Spectroscopy) for all catalysts. Catalysts of around 5mg were digested using 20% aqua regia, and all the particles in the solution were removed before the analysis.

4.3.6 Electron microscopy and High Resolution Transmission Electron Microscopy (HRTEM) and (SEM and TEM):

The SEM image of catalysts prepared by impregnation of the palladium metal shows small metal particles (Figure 4.25). The SEM images reveals that the surface morphologies of Pd/TiO_2, Au:Pd/TiO_2 and TiO_2. Moreover, the SEM images show the difference in morphology between the undoped TiO_2 and Pd/TiO_2 and Au:Pd/TiO_2 catalyst. After adding metals to it, these spheres agglomerated and lost their spherical morphology due to the stirring effect. EDX analysis of the catalysts prepared using impregnation of the 2.58%Pd/TiO_2 is shown in Figure 4.26. The EDX analysis reveals metal loading for the catalysts.

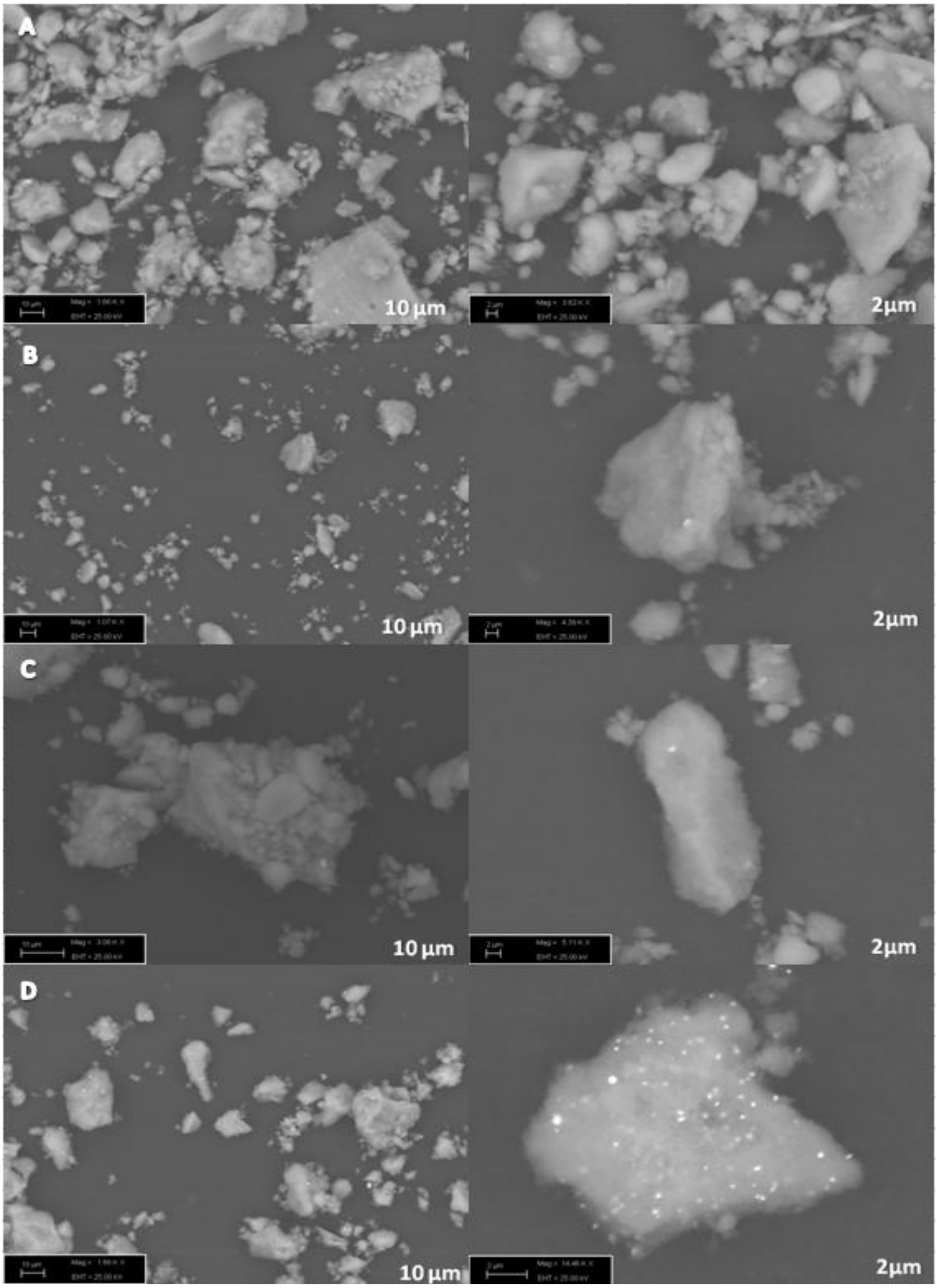


Figure 4.25: an SEM image of A) 0.5%Pd/TiO_2, B) 1.26%Pd/TiO_2, C) 2.58%Pd/TiO_2, and D) 5%AuPd/TiO_2 prepared by Impregnation method.

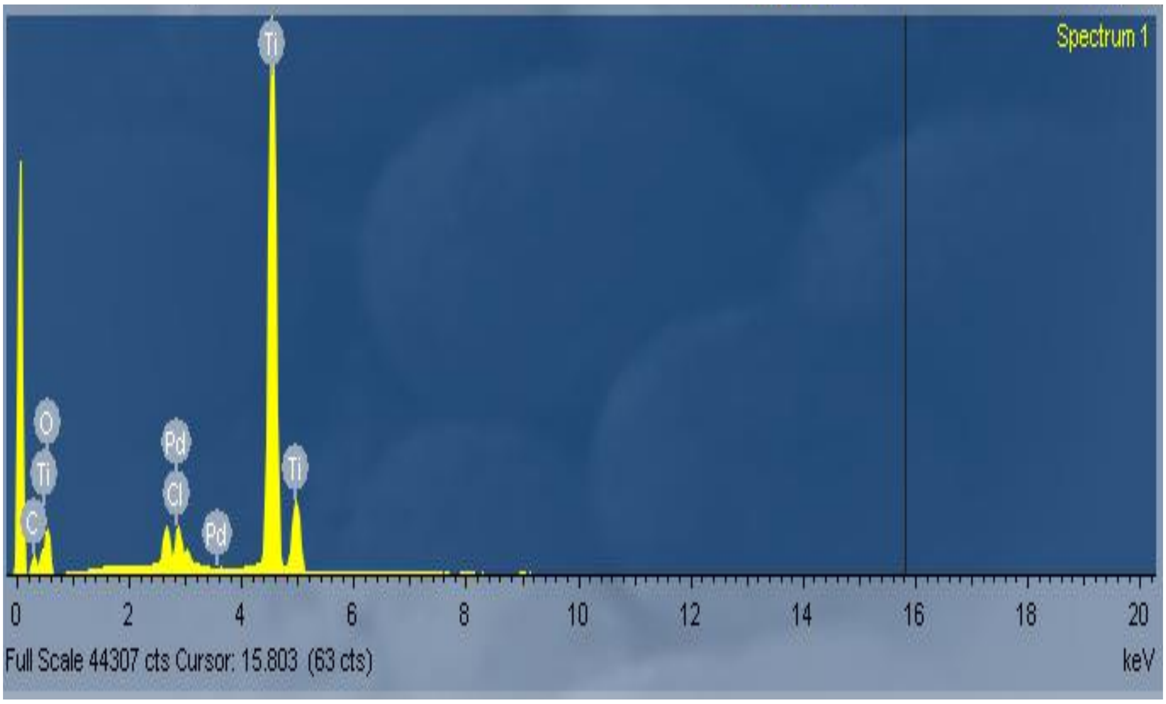


Figure 4.26: EDX analysis of a 2.58%Pd/TiO_2 catalyst prepared by impregnation.

Transmission electron microscopy (TEM) was performed on a Jeol 2100 microscope operated at 200kV and fitted with an Oxford Instruments EDX analyser. Samples were prepared by dispersion in methanol and dropped on to holey carbon film, 300 mesh copper grids. Particle size distributions (PSD) were determined by counting 150 particles using Image J software. TEM was used to study the effect of the loading of metal on the particle size distribution. Catalyst samples (*i.e.* 5%AuPd/TiO_2, 2.58%, 1.26% and 0.5%Pd/TiO_2) that have the same support morphology and phase were used. Representative micrographs of catalysts and their corresponding metals particle-size distributions are shown in Figure 4.27. In the current work TEM has been used to examine some of these catalysts, and it is an important parameter which can, be explain the activity of the catalyst, as shown previously in Figure 4.1 and 4.6. Analysis of particle size distribution was carried out for 0.5%, 1.26% and 2.58%Pd/TiO_2 catalysts. It is obvious that the particle size does not change with an increase in loading as shown in Figure 4.6. In other words, all catalysts showed a mean particle size of 1nm. The particle size distribution was the same for all catalysts.[76,77]

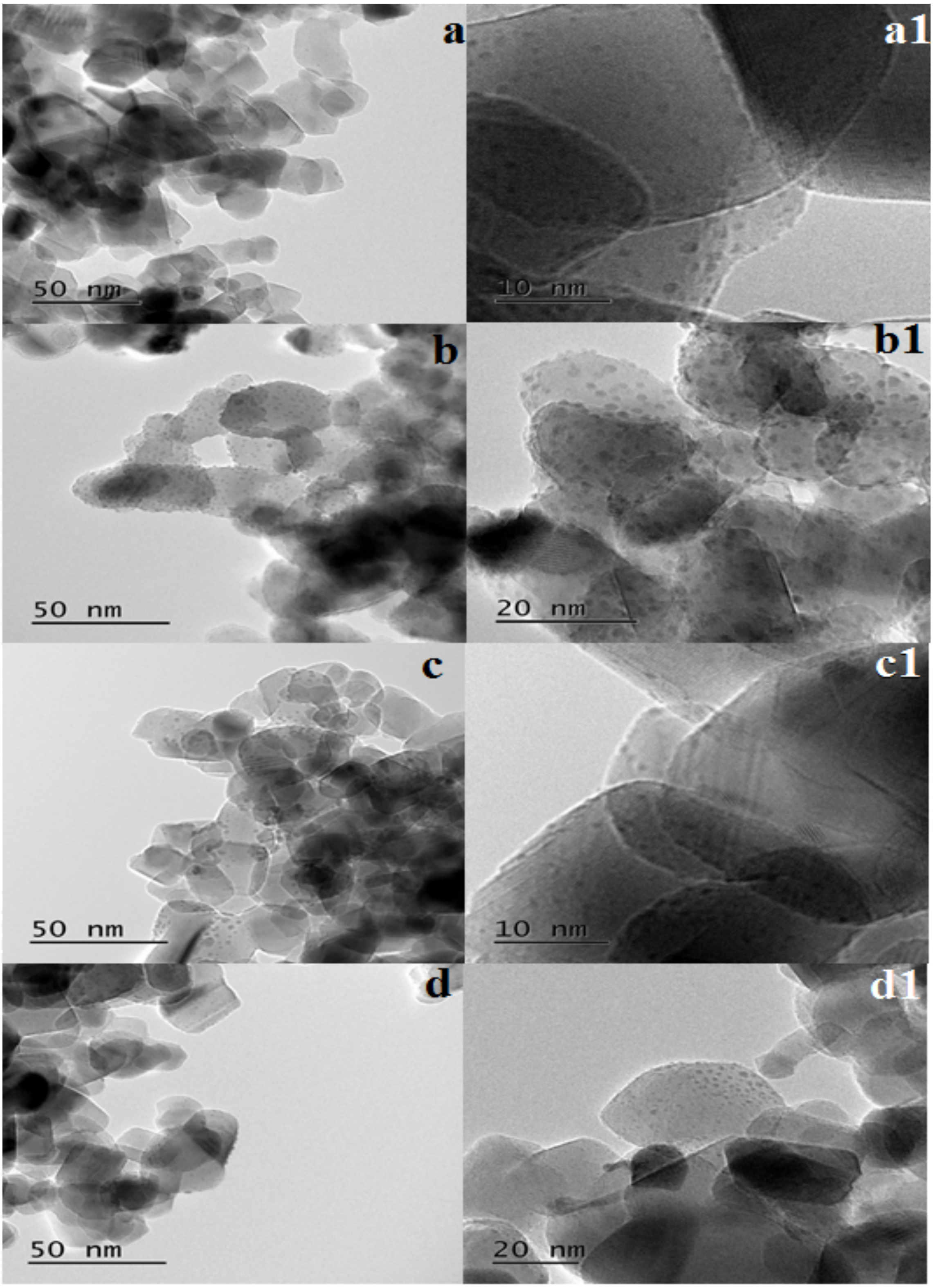


Figure 4.27: Bright field TEM micrographs of (a,a1) 5%AuPd/TiO_2, (b,b1) 2.58%Pd/TiO_2, (c,c1) 1.26%Pd/TiO_2, and (d,d1) 0.5%Pd/TiO_2 prepared by Impregnation method.

4.3.7 X-ray photoelectron spectroscopy (XPS):

The X-ray photoelectron survey spectra of the catalysts were studied to determine surface elemental content (atom %), and these are summarised in Table 4.7 Deconvoluted XPS profiles of TiO_2-supported Pd catalysts with different loadings of Pd are shown in Figure 4.7. The catalyst samples contained two types of Pd (*i.e.* Pd^{2+} and Pd^0). Moreover, binding energy of Pd^{2+} was 337.6eV and Pd^0 was 335.8eV. Pd^{2+} for the majority of catalysts, while the Pd^0 was in traces. In different samples, the ratio of Pd^{2+} to Pd^0 was maintained, ranging from 12 to 15. An abundance of Pd^{2+} shows the active sites of the catalyst comprise of Pd^{2+} instead of metallic Pd.

On the other hand, Deconvoluted XPS data of Ru:Pd/TiO_2 catalysts with different ratios shown in Figure 4.13. Palladium in varying oxidation state for PdO spectra showing a high oxidation state of Pd^{2+} and a low valence of Pd^0. Ruthenium contained two types oxidation state for RuO_2 spectra detecting a high oxidation state of Ru^{4+} and a low valence of Ru^0 with all samples. Furthermore, binding energy of Pd^{2+} and Pd^0 were 336.2eV and 334.6eV respectively. Ru peak analysis is awkward due to overlap with the Carbon binding energy at 284.5eV.

4.4 Conclusions:

- This study has shown that the furfuryl alcohol can be converted to 2-methylfuran with high selectivity, and the reaction can be carried out at room temperature with very low pressure, with supported Pd catalysts.
- The impregnation method was used to prepare a Pd catalyst and its particles were very small in size (less than 2nm). The Pd catalyst used only O-H hydrogenated deoxygenation in furfuryl alcohol and C=C was reduced very little under these reaction conditions.
- The only, by-product detected in the reaction mixture was tetrahydrofurfuryl alcohol (less than 6%).
- The current study has described a method that offers the possibility of synthesis of 2-methylfuran.
- In the second section, the highest selectivity for 2-methylfuran (62%) and high conversion (64%) were achieved from the hydrogenation of furfural in the presence of a petroleum solvent, octane, under green conditions with very low-pressure continuously controlled H_2 pressure for 120 mins and 200mg from 2.58%Pd/TiO_2.
- Moreover, under these conditions, full conversion and high selectivity to 2-methylfuran was observed in the presence of $C_2H_4Cl_2$ for 60 mins and 100mg from 2.58%Pd/TiO_2.
- The simpler preparation method and higher activity of the Pd catalysts suggests great possibilities for this very important area. Moreover, selective formation of 2-methylfuran is an attractive aspect of the method.

- Furthermore, selective formation of 2-methylfuran is an attractive way of the method being carried out.
- This study has explained a method, which offers the possibility of the synthesis of 2-methylfuran from furfural.
- 2-methylfuran is an essential petroleum derivative from reaction conditions which consume a minimum amount of energy in the form of heating or hydrogen; and the catalyst is also prepared using a simple method.

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Chapter 5

Conclusion and future work

Chapter 5

5. Conclusion and future work:

5.1 Conclusion:

The developments in conversion technology are many, and biomass resources have the potential to take a central position as feedstock for humanity, particularly as renewable carbon sources for transportation of fuel and bulk chemicals.[1] The most important current discussions in the chemical industry concern petroleum and the manufacture of carbon-based compounds. The rising budget and falling supply of oil has resulted in further motivation to look for possible alternative routes for producing solvents, fuels and bulk chemicals from biomass as an alternative. The hydrogenation of hydrocarbons (C_6 and C_5) to produce bio-renewable feedstock and organic compounds is very important for modern chemical processes. The hydrogenation of hydrocarbons, such as alcohols and aldehyde, using metal catalysts under green chemistry conditions, has been confirmed as providing an alternative and the most attractive feedstock, as it is the only widely available carbon source, apart from coal and oil.[2,3]

The aim of this thesis has been met and the outcomes are described as follows: Firstly, as explained in the third chapter, the major goal was to test whether catalysts that have been confirmed to be useful for the hydrogenation of cyclohexanol and cyclohexene can also be applied to the hydrogenation of the hydroxyl group of all the products identified. Furthermore, it has been shown that the catalysts are effective under mild conditions using low pressure H_2 as hydrogenate, which represents a significant improvement in the environmental impact of this reaction. Secondly, the goal was to examine whether the hydroxyl functional group and double bond can be reduced selectively to 2-methylfuran whilst avoiding opening of the furan ring; this is presented in the fourth chapter (first section). Finally, the fourth chapter (second section) is an extension of the previous chapter, but using aldehyde, with the same aim as set out in the first section.

In chapter three, the liquid phase hydrogenation of cyclohexanol over $Pd/Cs_{2.5}H_{0.5}PW_{12}O_{40}$ reveals results favourable to those obtained with other catalysts. In addition, high cyclohexanol conversions of up to 34% with over 60% cyclohexane selectivity were obtained at 150ºC and low H_2 pressure. A low Pd loading was found to be enough to obtain a high performance. Furthermore, Pd supported on the heteropolyacid was studied as a multifunctional catalyst for the conversion of cyclohexanol under mild conditions, and also the synergy of palladium metal and the Brønsted acid sites of the heteropolyacid support were required. A major rise in the cyclohexanol conversion was detected with the palladium-supported catalyst. Moreover, the results show that the palladium-supported catalyst was more active for the direct hydrogenation of cyclohexanol, which led to the best selectivity of cyclohexane and cyclohexene. On the other hand, in the presence of nitrogen gas, a high Pd loading at 150ºC provided the best conditions at a low pressure of 1 bar N_2 hence, with 2.58%Pd loading, the yield of cyclohexanol was 25-27% and selectivity was up to 63%.

However, when using H_2 reactions, a low Pd loading of 1wt% under optimum conditions at a low pressure of 1bar H_2 achieved a high cyclohexanol yield of approximately 34% and selectivity above 73% was reached.

Chapter Four (the first section) describes how in the liquid phase, hydrogenation of furfuryl alcohol was performed using different pressures of hydrogen from 1 to 3 barg. The reactions were performed in two ways, at a constant pressure (pressure was built only once by filling the reactor and there was no refuelling during the reaction) and under continuously controlled pressure (pressure was kept constant by refilling during the reaction). The products of the reactions of furfuryl alcohol using Au, Au:Pd and Pd catalysts under green conditions have been investigated in detail and were found to be effective under green conditions using hydrogen. Furfuryl alcohol was fully converted over 2.58%Pd/TiO_2 with high selectivity to 2-methylfuran after hydrogenation when the reaction was performed in an autoclave reactor. However, it was shown that the design of the catalysts and control of the reaction conditions could enable a certain degree of control over the reaction products. The influence of a bimetallic catalyst was also tested for furfuryl alcohol. Through the examination of various ratios of Au:Pd supported on TiO_2 it can be concluded that there was a synergistic effect between Au and Pd. The conversion of furfuryl alcohol depends on the ratio of Au and Pd. Monometallic Pd/TiO_2 was observed to have high activity, and the hydrogenation pathway was favoured with a significant increase in selectivity towards the desired products, as well as an increase in the conversion of furfuryl alcohol, depending on the loading of Pd/TiO_2. Moreover, the oxidation state of palladium on the catalyst surface has an effect on the activity of the catalyst. The catalyst with a lower concentration of Pd^{2+} on the catalyst surface revealed less activity. However, the activity of the catalyst increases by increasing the Pd^{2+} species present on the catalyst surface. On the other hand, the effects of supports were tested, hence the oxide supports were more active for the hydrogenation of furfuryl alcohol than graphite supports, particularly TiO_2 and the highest selectivity towards hydrogenation for the desired products was obtained over SiO_2 as the support. In addition, the effect of a solvent was investigated. The highest selectivity for 2-methylfuran was achieved in the presence of a 1,2-dichloroethane solvent, under green conditions.

In the second section, liquid phase hydrogenation of furfural was carried out under similar conditions (as used for furfuryl alcohol). The reaction was performed at a continuously controlled pressure and using different pressures of hydrogen from 1 to 3 barg. On the other hand, the effects of metals (Pd/TiO_2, Au/TiO_2, Ru/TiO_2, $Au:Pd/TiO_2$ and $Ru:Pd/TiO_2$) were studied of the activity of hydrogenation for the desired products. They were found to be efficient under green conditions using hydrogen. However, various ratios were investigated on TiO_2 and it was found that there is a bimetallic affect between Au, Ru and Pd. The conversion of furfural is affected by the ratio of Au, Ru and Pd. In addition, it was found that monometallic Au and Ru catalyst sites are much less active for hydrogenation than palladium sites. In both, the addition of Au or Ru to Pd decreased activity for the furfural hydrogenation yield. Monometallic Pd/TiO_2 was observed to have high activity, and the hydrogenation was significantly increased in terms of selectivity towards the desired products, and there was also an increase in the conversion of furfural, which may be dependent on the loading of Pd/TiO_2. Furfural was converted over 2.58%Pd/TiO_2 with high selectivity to 2-methylfuran after hydrogenation. In addition, the effect of a solvent was investigated, and hence, the highest selectivity to 2-methylfuran was achieved in the presence of a solvent, 1,2-dichloroethane; also, high selectivity to 2-methylfuran was achieved in the presence of a petroleum solvent, octane, under green conditions.

5.2 Future work:

Some of the areas in this thesis could be developed further. The utilisation of biorenewable feedstock using palladium or other metal catalysts on different supports could be studied in more depth. The following suggestions may support improving on this and gaining further understanding of the mechanism of hydrocarbon hydrogenation:

- It was discovered, as shown in Chapter Three, that cyclohexanol can be hydrogenated using 1bar hydrogen at 150°C. However, performing this reaction under high pressure and at a high temperature in an autoclave would improve the activity.
- One of the limitations of this thesis is the low activity of the reused Pd supported on the TiO_2 catalyst due to the adsorption of the product. Therefore, other methods are required to enhance the activity of the reused catalysts, such as a new preparation method.
- The new method could be useful for aldehyde and alcohol hydrogenation, particularly when ratios of metal composition are used. However, the Pd:rich composition catalysts are more suitable catalysts for hydrogenation reactions, and this possibility is something for future investigation.

- Pd^{2+} seems to be an important factor for the hydrogenation of furfuryl alcohol and furfural, therefore development of a catalyst containing just Pd^{2+} may possibly lead to an increase in activity.
- Alloying the catalyst with a second metal may lead to an improvement in catalytic activity. However, bimetallic systems such as Pd, Ni, Ru, Pt, Au and Rh may possibly lead to an improvement in activity or selectivity.
- It has been proven in this study that the solvents have a significant impact during a reaction, and hence, other solvents are required to investigate the activity of the catalysts.
- Promotion of catalyst activity and selectivity by using extra hydrogen resources such as formic acid in the hydrogenation of furfural, and performing the reaction in an autoclave, may lead to the enhancement of hydrogenation products.
- Optimisation of the hydrogenation of furfural and furfuryl alcohol performing the reaction in another reactor, such as the Radleys carousel glass stirred reactor may improve the activity of the reaction.
- Additional characterisation of catalysts is necessary to enhance understanding and to explain the difference in activity and selectivity achieved when using different metals and supports.

5.3 References:

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