Selective Hydrogenation of Biomass-derived Furanbased Compounds over Supported Ni-Pd Bimetallic Alloy Nanoparticle at Room-Temperature

M.Sc. Thesis

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Selective Hydrogenation of Biomass-derived Furanbased Compounds over Supported Ni-Pd Bimetallic Alloy Nanoparticle at Room-Temperature

A THESIS

Submitted in partial

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by

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INDIAN INSTITUTE OF TECHNOLOGY INDORE CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Selective Hydrogenation of Biomass-derived Furan-based Compounds over Supported Ni-Pd Bimetallic Alloy Nanoparticle at Room-Temperature** in the partial fulfillment of the requirements for the award of the degree of **Master of Science** and submitted in the **Discipline of Chemistry, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2016 to June 2018 under the supervision of Dr. Sanjay K. Singh, Associate Professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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Dedicated to my Parents.....

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ABSTRACT

The expanding consumption and reliance on fossil fuels have left no other choice but to search for some alternative sources. In search for some sustainable and renewable sources, biomass has drawn very much attention. Herein, we demonstrated a simple and productive methodology to hydrogenate the furan aldol adducts under mild and environmental friendly condition using cost-effective, highly active nanoparticles. We achieved selective hydrogenation of different furan aldol adducts at room temperature using H_2 balloon over supported bimetallic Ni_{0.9}Pd_{0.1} alloy nanoparticles to synthesize compounds like **1b**, **4a** which can be further functionalized to produce high-density fuel components. This method is very useful to synthesize long chain (C₈-C₁₆) fuel additives.

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ACRONYMS

GVL	γ-valerolactone
5-HMF	5-hydroxymethyl-2-furfural
5-MF	5-methyl-2-furfural
FA	2-furfuryl alcohol
PVP	polyvinylpyrrolidone
RHA	Rice-husk Ash
SEM	Scanning Electron Microscopy
HR-TEM	High-resolution Transmission Electron Microscopy
PXRD	Powder X-ray Diffractogram
EDS	Energy Dispersive X-ray Spectroscopy
SAED	Selected Area Diffraction
NMR	Nuclear Magnetic Resonance
HRMS	High-resolution Mass Spectroscopy
TMS	Tetramethylsilane
CDCl ₃	Chloroform-d

NOMENCLATURE

λ	Lambda
δ	Delta
nm	Nanometer
°C	Degree Celsius
mmol	Millimole
Å	Angstrom
MPa	Mega-Pascal
h	Hour
θ	Theta
0	Degree
mL	Milliliter
MHz	Mega-hertz
ррт	Parts per million
K	Kelvin
rpm	Resolution per minute
V	Volt

CHAPTER ONE

1. INTRODUCTION

1.1 General Introduction

The total energy sources of the world may be classified into three primary categories. These are fossil fuels, renewable sources and nuclear sources. The expanding consumption and reliance on fossil fuels have left no other choice but to search for some alternative sources. As indicated by a survey, the segments of the petroleum derivatives like coal, natural gas and oil shall keep going for another 114, 52 and 50 years respectively [1]. So, it is high time to look forward for some sustainable and renewable sources of transportable liquid fuels. In this regard, biomass has drawn tremendous attention. Biomass refers to living issues on earth but most often it alludes to the plant-derived materials [2,3].

Lignocellulosic biomass (e.g. bagasse, sugar cane, straw, wood waste etc.), amorphous sugar (e.g. glucose, starch etc.) and triglycerides (e.g. vegetable oil etc.) can be considered as the three main groups of biomass feedstock. Lignocellulosic biomass is one of the low-cost, quick developing, carbon rich and most abundant forms of the terrestrial biomass. The lignocellulosic biomass is fabricated with cellulose (long linear chain of glucopyranose units having an average molecular weight of around 100,000), hemicellulose (polysaccharide like glucose, fructose, mannose) and lignin (highly branched and substituted organic polymer) [4,5]. Among these three, cellulose possesses the highest percentage.

Diesel fuel (C₁₀-C₁₉ range hydrocarbons) contains aliphatic hydrocarbons (64%), olefinic hydrocarbons (1-2%) and aromatic hydrocarbons (35%). The lignocellulosic biomass has limited direct usage as transportation fuel due to the structural complexity of it's units. Therefore, this can be converted into some furan-based platform molecules (Figure 1) for the production of fuel and other valuable chemicals. Fuel components like 2-

methylfuran, γ -valerolactone (GVL), 2,5-dimethylfuran produced from biomass derived furan-based platform molecules like 2-furfuraldehyde (furfural), 5-hydroxymethyl-2-furfural (5-HMF), 5-methyl-2-furfural (5-MF), 2-furfuryl alcohol (FA) and aldol adducts of the platform molecules show a high quality and efficiency [6-11]. But, compounds having short carbon chain are not appropriate for the direct usage as fuel due to insufficient energy density and low boiling points. Moreover, in order to increase the carbon chain length, aldol condensation with furans are one of the best applicable methods.



Figure 1: Biomass derived furan-based platform chemicals.



Figure 2: Long chain alkane from biomass derived furans.

The hydrogenated products have many applications other than the use as high density fuel additives. The hydrogenated products such as 1,5-bis(tetrahydrofuran-2-yl)pentan-3-one (**1b**), 4-(tetrahydrofuran-2-yl)butan-2-ol (**3b**) and others have enormous application not only in the production of fuel components having long carbon chain (C₈-C₁₈) but also in the synthesis of 1-octanol, ethyloctylether (important chemicals in perfume industry) [12-14]. Furthermore, tetrahydrofuran derivatives can also be

used in the production of oxocanes (important chemicals in natural product synthesis) through ring expansion [15]. The intermediate hydrogenated products are also very important for providing opportunity for further functionalization. Compound **1b** produced from compound **1** can further undergo aldol condensation followed by hydrodeoxygenation to produce a branched chain alkane which can be used as high-quality lubricant [16].

1.2 Review of Past Work and Problem Formulation

Different Ru, Ir, Pt, Pd and Ni based catalysts have been widely investigated for the hydrogenation of furan compounds [17-21]. Among these Pd based catalysts have been effectively investigated for the hydrogenation of furan derivatives. But, most of the reported studies use high temperature and high H_2 pressure. Toward this way, a Ni-Pd/Silica catalyst having the ratio of Ni/Pd = 7 was utilized by Nakagawa *et al.* (2010) to achieve the total hydrogenation of furan derivatives using 8 MPa of H_2 at 313 K in the presence of acetic acid [17]. But the recyclability of the catalyst was poor due to the significant leaching of Ni. The hydrogenation of the furan ring and olefinic double bond of the furan/acetone aldol adduct was achieved over Pd/CN@MgO employed by Li *et al.* (2014) [18]. Hydrogenation of furan/acetone aldol adducts was accomplished over Pd/Al₂O₃ utilizing high H_2 pressure (55 bar) at 393 K in methanol [19].

Pt-based catalysts examined for hydrogenation as well as hydrodeoxygenation of furan-acetone aldol adducts likewise required high H_2 pressure and high temperature (5.5 MPa, 220 °C) [20]. Similarly, high H_2 pressure and high temperature (20 bar, 373 K) were required for the hydrogenation of C=O and C=C bonds in furfural-acetone aldol adduct using a Fe-Ru catalyst (Fe-Ru@SILP) [21].

The above literature survey revealed that the vast majority of the catalysts used for the effective hydrogenation of the furan aldol adducts require high temperature and high H_2 pressure. So, it is important to look for highly

effective catalyst for the selective hydrogenation of furan aldol adducts at low temperature and low H₂ pressure.

1.3 The Aim and Strategy of Our Work

The aim of our work is to synthesize a highly effective catalyst to selectively hydrogenate different furan aldol adducts at room temperature using very low H₂ pressure in aqueous medium.

The strategy of our work is to synthesize the furan aldol adduct using furfural and acetone (Scheme 1) followed by the catalytic hydrogenation of the adduct to produce intermediate hydrogenated products selectively (Scheme 2).



Scheme 1: Aldol condensation of furfural with acetone



Scheme 2: Hydrogenation/hydrodeoxygenation of furan/acetone aldol adduct

CHAPTER TWO

2. EXPERIMENTAL SECTION

2.1 Materials and Instrumentation

All metal salts and chemicals were purchased from Sigma-Aldrich, Alfa Aesar and Merck, and used without further purification. Scanning electron microscopic (SEM) images, elemental mapping, energy dispersive X-ray spectroscopy (EDS) analyses and elemental mapping were carry out with a Supra55 Zeiss (operating voltage 5 kV) equipped with an Oxford instrument EDS X-ray spectrometer. Powder X-ray diffraction (PXRD) measurements were performed on the dried particles using a Rigaku SmartLab, Automated Multipurpose X-ray diffractometer at 40 kV and 30 mA using Cu Ka radiation ($\lambda = 1.5418$ Å). ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) were recorded in CDCl₃ on a Bruker Avance 400 spectrometer at 298 K using tetramethylsilane (TMS) as an external standard. Chemical shifts were reported in ppm relative to the center of the singlet at 7.26 ppm for CDCl3 in ¹H NMR and to the center of the triplet at 77.00 ppm for CDCl₃ in ¹³C NMR. High-resolution mass spectra (HRMS) were recorded on a micrOTOF-Q II mass spectrometer.

2.2 General Procedure for the Synthesis of Ni_{0.9}Pd_{0.1} Nanoparticle Supported on Silica, Rice-husk and Zeolite Respectively:

Bimetallic Ni_{0.9}Pd_{0.1} nanoparticle was synthesized following our earlier reported method which includes the polyvinylpyrrolidone (PVP) stabilized aqueous phase co-reduction of Ni^{II} and Pb^{II} salts using NaBH₄ [22,23]. In a typical procedure, at room temperature, an aqueous solution of NaBH₄ (0.0125g, in 5.0 mL of water) was added dropwise to a 5.0 mL homogeneous aqueous solution of Potassium tetrachloropalladate (II) (0.0016 g, 0.005 mmol), nickel (II) chloride hexahydrate (0.0107 g, 0.045 mmol) and PVP (0.0250 g). The content of the flask was sonicated for 10

minutes which results a black suspension of Ni_{0.9}Pd_{0.1} nanoparticle. The nanoparticles were collected by centrifugation at 5000 rpm x 2 for 5 minutes. An adequate amount of support (50 mg) was added in a 10 mL solution of distilled water and ethanol (3:1 v/v) containing freshly synthesized bimetallic alloy nanoparticles. The mixture was stirred for 4 h under argon atmosphere. The supported nanoparticles were centrifuged at 5000 rpm x 2 for 5 minutes. The obtained supported nanoparticles were washed with distilled water.

2.3 Synthesis of compound 1

For the synthesis of compound 1, in a 50 mL round-bottomed flask, furfural (10.0 mmol), acetone (5.0 mmol) and K₂CO₃ (10.0 mmol) were added in ethanol (10 mL). The mixture was stirred at 50 °C for 36 h. Afterwards, all volatiles were removed under reduced pressure. Distilled water (10 mL) was added to the residue followed by the addition of ethyl acetate (5 x 10.0 mL) to extract the organic compound. Anhydrous Na₂SO₄ was used to dry the organic layer. The organic part was filtered off and all of the volatiles were removed under reduced pressure. Purification of the obtained compound was done with column chromatography using a mixture of ethyl acetate and dichloromethane (2:8 v/v). Compound 1 was characterized by ¹H NMR, ¹³C NMR and HRMS. ¹H NMR (400 MHz, CDCl₃): δ = 7.52 (m, 2 H), 7.48 (d, 2 H, *J* = 12), 6.92 (d, 2 H, *J* = 16), 6.70 (d, 2 H, *J* = 4), 6.51 (dd, 2 H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 188.06, 151.47, 144.89, 129.18, 123.13, 115.86, 112.59 ppm; HRMS (ESI): observed m/z for C₁₃H₁₀O₃ [M+Na]⁺ = 237.0539, calculated m/z = 237.0522.

2.4 Synthesis of compound 2

To synthesize compound 1, in a 50 mL round-bottomed flask, 5methylfurfural (10.0 mmol), acetone (5.0 mmol) and K_2CO_3 (10.0 mmol) were added in ethanol (10.0 mL). The mixture was stirred at 50 °C for 36 h. Afterwards, all volatiles were removed under reduced pressure. Distilled water (10.0 mL) was added to the residue followed by the addition of ethyl acetate (5 x 10.0 mL) to extract the organic compound. Anhydrous Na₂SO₄ was used to dry the organic layer. The organic part was filtered off and all of the volatiles were removed under reduced pressure. Purification of the obtained compound was done with column chromatography using a mixture of ethyl acetate and dichloromethane (2:8 v/v). Compound 2 was confirmed by ¹H NMR, ¹³C NMR and HRMS. ¹H NMR (400 MHz, CDCl₃): δ = 7.50 (dd, 2 H), 6.96 (dd, 2 H), 6.69 (d, 2 H, *J* = 8), 6.21 (m, 2 H), 2.47 (s, 6 H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 188.14, 155.67, 150.19, 128.97, 121.76, 117.56, 109.21, 13.90 ppm; HRMS (ESI): observed m/z for C₁₄H₁₅O₃ [M+Na]⁺ = 265.0838, calculated m/z = 265.0835.

2.5 Synthesis of compound 3

Compound 3 was synthesized using furfural (10.0 mmol) and K₂CO₃ (10.0 mmol) in a 10.0 mL solution of acetone and ethanol (2:3 v/v). The mixture was allowed to be stirred for 1 h at 50 °C. Afterwards, all volatiles were removed under reduced pressure. Distilled water (10.0 mL) was added to the residue followed by the addition of ethyl acetate (5 x 10.0 mL) to extract the organic compound. Anhydrous Na₂SO₄ was used to dry the organic layer. The organic part was filtered off and all of the volatiles were removed under reduced pressure. Purification of the obtained compound was done with column chromatography using a mixture of ethyl acetate and dichloromethane (2:8 v/v). Compound 3 was analyzed and confirmed by ¹H NMR, ¹³C NMR and HRMS. ¹H NMR (400 MHz, CDCl₃): δ = 7.50 (m, 1 H), 7.28 (d, 1 H, *J* = 16), 6.67 (d, 1 H, *J* = 4), 6.62 (d, 1 H, *J* = 16), 6.49 (m, 1 H), 2.33 (s, 3 H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 197.80, 150.80, 144.95, 129.37, 124.20, 115.59, 112.47, 27.75 ppm; HRMS (ESI): observed m/z for C₈H₈O₂ [M+Na]⁺ = 159.0363, calculated m/z = 159.0417.

2.6 Synthesis of compound 4

Furfural (2.0 mmol) was dissolved in dichloromethane (3.0 mL). Acetyl acetone (2.5 mmol), piperidine (0.10 mmol) and acetic acid (0.10 mmol) were added one by one at 0 °C. The reaction mixture was allowed to be stirred over night at room temperature. Brine solution (10.0 mL) was added to the mixture. Extraction was done with dichloromethane (3 x 10.0 mL). The organic layer was dried over Na₂SO₄ and the volatiles were evaporated under reduced pressure. The product was purified with column chromatography using hexane and ethyl acetate (9:1 v/v). Compound 4 was analyzed and confirmed by ¹H NMR, ¹³C NMR and HRMS. ¹H NMR (400 MHz, CDCl₃): δ = 7.54 (s, 1 H), 7.15 (m, 1 H), 6.76 (d, 1 H, *J*= 4), 6.51 (dd, 1 H), 2.43 (s, 3 H), 2.36 (s, 3 H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 204.40, 195.82, 148.81, 146.52, 138.31, 124.93, 118.29, 112.94, 31.46, 26.12 ppm; HRMS (ESI): observed m/z for C₁₀H₁₀O₃ [M+Na]⁺ = 201.0526, calculated m/z 201.0522

2.7 Synthesis of compound 5

2-Methylfuran (10 mmol) and *para*-toluene sulfonic acid (0.11 mmol) were taken in a 50 mL round-bottomed flask. Furfural (2 mmol) was added dropwise under stirring at room temperature. The mixture was stirred for 6 h at 50 °C. After extraction with dichloromethane, the organic phase was treated with NaHCO₃ and was dried over anhydrous Na₂SO₄. The excess 2-methylfuran was evaporated using a rotary evaporator to give the desired product. Compound 5 was characterized by ¹H NMR, ¹³C NMR and HRMS. ¹H NMR (400 MHz, CDCl₃): δ = 7.36 (m, 1 H), 6.33 (m, 1 H), 6.12 (dd, 1 H), 5.99 (d, 2 H, *J* = 4), 5.91 (dd, 2 H), 5.43 (s, 1 H), 2.27 (s, 6 H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 152.56, 151.53, 150.31, 141.83, 110.28, 107.89, 107.06, 106.22, 39.04, 13.58 ppm; HRMS (ESI): observed m/z for C₁₅H₁₄O₃ [M+Na]⁺ = 265.0841, calculated m/z = 265.0835.

2.8 Synthesis of compound 6

2-Methylfuran (10 mmol) and *para*-toluene sulfonic acid (0.11 mmol) were taken in a 50 mL round-bottomed flask. 5-methy-2-furfuraldehyde (2 mmol) was added dropwise under stirring at room temperature. The mixture was stirred for 6 h at 50 °C. After extraction with dichloromethane, the organic phase was treated with NaHCO₃ and was dried over anhydrous Na₂SO₄. The excess 2-methylfuran was evaporated using a rotary evaporator to give the desired product. Compound 6 was characterized by ¹H NMR, ¹³C NMR and HRMS. ¹H NMR (400 MHz, CDCl₃): δ = 5.98 (m, 3 H), 5.91 (m, 3 H), 5.38 (s, 1 H), 2.27 (s, 9 H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 151.40, 150.65, 107.75, 106.16, 39.10, 13.58 ppm; HRMS (ESI): observed m/z for C₁₆H₁₆O₃ [M+Na]⁺ = 265.1007, calculated m/z = 279.0092.

2.9 General Procedure for the Catalytic Room Temperature Hydrogenation of Furan Aldol Adducts.

Furan aldol adducts were catalytically hydrogenated in a 50.0 mL roundbottom reaction flask. Typically for the hydrogenation reaction, 1.0 mmol of furan aldol adduct was added to 10.0 mL of an aqueous suspension of 5.0 mol% Ni_{0.9}Pd_{0.1}/support nanoparticle catalyst, and reaction mixture was set to be stirred at 30 °C equipped with a H₂ balloon for the desired reaction time. The catalyst was recollected using centrifugation at 5000 rpm for 10 min and the obtained solution was extracted using ethyl acetate (5 x 10.0 mL). Anhydrous Na₂SO₄ was used to dry the organic layer. The organic part was filtered off and all of the volatiles were removed under reduced pressure. The isolated products were analyzed and confirmed by ¹H NMR and HRMS. Conversion and selectivity of the obtained products were confirmed by ¹H NMR.

CHAPTER THREE

3. RESULTS AND DISCUSSION

3.1 Characterization of Bimetallic Supported Ni-Pd alloy nanoparticles

Bimetallic Ni-Pd alloy nanoparticles were synthesized and supported over silica, rice-husk and zeolite 4 Å following our earlier reported methods [22,23]. A 20 value of 40° in the powder X-ray diffractogram (PXRD) (Figure 5g) shows the presence of (111) lattice plane. PXRD analysis also suggest a face centered cubic (fcc) structure of the nanoparticles. The shifting of 20 value of the Ni_{0.9}Pd_{0.1} nanoparticles toward the higher value as compare to that of Pd (111) and lower value as compared to that of Ni (111) plane suggests the formation of Ni-Pd alloy nanoparticle cancelling out the chance of the segregation of Ni and Pd nanoparticles. The presence of fcc (111) lattice plane is also suggested by the selected area diffraction (SAED) pattern (Figure 3d). The sizes of the particles are in the range of 2-4 nm as suggested by the high-resolution transmission electron microscopic (HR-TEM) images (Figure 3a-b). Moreover, as indicated by the energy dispersive X-ray spectroscopic (EDS) analysis (Figure 3c) and elemental mapping (Figure 3f-g), Ni and Pd metals are uniformly distributed in the Ni-Pd alloy nanoparticles. Also, the 9:1 atomic ratio of Ni to Pd is suggested by EDS and TEM analysis.



Figure 3: (a) HR-TEM image of fresh Ni_{0.90}Pd_{0.10} nanoparticles. (b–c) HR-TEM image and corresponding EDS analysis. (d) SAED pattern. (e) FEG-TEM images and (f, g) the corresponding elemental mapping showing Pd (f) and Ni (g) for fresh Ni_{0.90}Pd_{0.10} nanoparticles. Reprinted with permission from (ACS Sustainable Chem. Eng., 2018, 6, 4793-4800). Copyright (2018) American Chemical Society.



Figure 4: (a-c) SEM images of RHA, silica and zeolite supported Ni-Pd nanoparticles respectively, (d-f) PXRD of RHA, silica and zeolite supported Ni-Pd nanoparticles respectively.



Figure 5: (a-c) EDX analysis of Ni-Pd/RHA, Ni-Pd/silica and Ni-Pd/zeolite respectively, (d-f) elemental mapping showing Ni (d), Pd (e) and Si (f) present in Ni-Pd/silica nanoparticles. (g) PXRD of unsupported Ni_{0.9}Pd_{0.1} nanoparticles.

The PXRD analysis of the supported nanoparticles (Figure 4d-f) shows the characteristic peaks for the supports and peaks for Ni_{0.9}Pd_{0.1} is hardly seen. This is due to the high amount of support (rice-husk, silica and zeolite 4 Å) used in the synthesis of the particles. The PXRD analysis also suggests that the nanoparticles are highly dispersed. The scanning electron microscopic (SEM) images (Figure 4a-c) show the presence of high amount of supports used. This is also supported by the energy dispersive X-ray spectroscopic (EDS) analysis (Figure 5a-c) where very high amount of Si and Al have been detected as compared to Ni and Pd. The EDS analysis of the nanoparticles also shows the atomic ratio of Ni to Pd to be 9:1 in the supported form. From elemental mapping(Figure 5d-f), uniform distribution of supported Ni-Pd nanoparticles is observed. This suggests no change of property of Ni-Pd alloy nanoparticles when the particles are supported.

3.2 Synthesis of compound 1-6

Compound 1 was synthesized following earlier reported methods [16, 24, 25].



Scheme 3: Synthesis of compound 1 and 2



Scheme 4: Synthesis of compound 3



Scheme 5: Synthesis of compound 4



Scheme 6: Synthesis of compound 5 and 6

3.3 Catalytic Hydrogenation Reaction

The catalytic hydrogenation of compound 1 was carried out over supported Ni-Pd alloy nanoparticles at room temperature. For the reaction, H₂ balloon was used. Performing the reaction for 24 h with rice-husk supported catalyst, 1,5-bis(tetrahydrofuran-2-yl)pentan-3-one (1b) was synthesized with high selectivity (70%) (Scheme 7), (Table 1, entry 2). The rest is the total hydrogenated product 1,5-bis(tetrahydrofuran-2-yl)pentan-3-ol (1a). Reduction of the reaction time to 16 h does not alter the result very much but increases the selectivity of 1b slightly (75%) (Table 1, entry 2). Further decrease in the reaction time to 8 h results the production of 1,5-di(furan-2yl)pentan-3-one (1c) with low selectivity (17%) (Table 1, entry 3). Similar series of experiments were performed with silica and zeolite supported Ni-Pd nanoparticles (Table 1, entry 4-9). 1,5-bis(tetrahydrofuran-2-yl)pentan-3-one (1b) was synthesized with high selectivity using both the silica and zeolite supported catalysts at 16 h (Table 1, entry 5,8). Performing the hydrogenation reaction for 16 h was found to be the best condition to produce 1b with high selectivity and yield (75%). In all the cases, the conversion was >99%.



Scheme 7: Catalytic hydrogenation of compound 1

Serial	Support	Amount	Temperature	Time	Conversion	Selectivity
number		of	(°C)	(h)	(%)	(%)
		support				(1a:1b:1c)
		(mg)				
1	RHA	50	30	24	>99	30:70:0
2	RHA	50	30	16	>99	25:75:0
3	RHA	50	30	8	>99	20:63:17
4	Silica	50	30	24	>99	20:80:0
5	Silica	50	30	16	>99	20:80:0
6	Silica	50	30	8	>99	18:68:14
7	Zeolite	50	30	24	>99	25:75:0
8	Zeolite	50	30	16	>99	25:75:0
9	Zeolite	50	30	8	>99	23:71:6

Table 1: Hydrogenation of compound 1: Reaction optimization^a

^aReaction Condition: substrate (1 mmol), catalyst (5 mol%), H₂ balloon, water (10 mL), 30 $^{\circ}\text{C}$



Figure 6: Time-dependent reaction profile for the hydrogenation of compound 1

To find out the active site of the catalyst used in the hydrogenation, we performed the reaction with 5 mol% Ni/RHA under analogous reaction

condition. The reaction came up with no conversion. But, performing the reaction with 5 mol% Pd/RHA resulted full conversion (>99%). This result shows that the Pd is the active site in the Ni-Pd catalyst. Again, performing the reaction with 0.5 mol% Pd/RHA (the amount of Pd present in the catalyst) resulted in a very low conversion (30%). But, the Ni_{0.9}Pd_{0.1}/RHA catalyst results in full conversion (Scheme 8). This result indicates the role of Ni in Ni_{0.9}Pd_{0.1} catalyst.



Scheme 8: Hydrogenation of compound 1 using RHA supported Ni and Pd monometallic nanoparticles

The role of Ni can be explained by the fact that Ni has standard reduction potential of -0.23 V which is lesser than that of Pd (+0.83 V). Thus, the transfer of electron density from Ni to Pd center becomes more feasible and Pd center becomes more negative which helps in the dissociation of H₂ in the hydrogenation reaction. The high ratio of Ni and Pd is very effective because Pd becomes surrounded by more number of Ni. This results in the accumulation of more negative charge on Pd.

Moreover, Pd is known to have high tendency to adsorb C=C double bond and electropositive character of Ni helps in the adsorption of C=O double bond. Thus, the planar furan aldol adducts are easily adsorbed over the Ni-Pd nanoparticles. This is supported by the fact that when the reaction was performed with compound **2**, no conversion was occurred (Scheme 9). This is due to the steric interaction generated by the methyl groups resulting a weak interaction between the compound and catalyst surface.



Scheme 9: hydrogenation of compound 2

Among the three supports used, silica shows slightly higher activity than rice-husk and zeolite. This is obvious because all the three supports have silica content in major amount. A comparative study of the effect of the supports is given in the figure 7. Using unsupported Ni-Pd nanoparticles, we can synthesize **1a** with >99% selectivity at 24 h *[24]*. Reduction of time results to 16 h in the production of compound **1b** with low selectivity (30%). Interestingly, introduction of support results in the production of **1b** with high selectivity.



Figure 7: Comparative study of the activity of supported and unsupported catalysts in the hydrogenation of compound 1

Based on the observations above, a possible hydrogenation pathway can be proposed (Figure 8).



Figure 8: Possible hydrogenation pathway of furans aldol adducts

According to the pathway, the olefinic double bond first gets hydrogenated followed by the hydrogenation of furan ring and carbonyl group respectively. During the total course of the mechanism, compound **1c** is produced first followed by the production of compound **1b** and **1a** respectively. The successive addition of hydrogen to the substrate decreases the adsorption ability of Pd towards the intermediate hydrogenated compounds resulting easy removal of the products. Therefore, hydrogenation of aldol adducts follows the order: exocyclic C=C double bond > furan ring > C=O double bond.

3.4 Hydrogenation of other furan-based compounds

Inspired by the above results, the catalytic activity of the supported Ni-Pd alloy nanoparticles was further checked for the hydrogenation of other

furan-based compounds. Compound **3** was hydrogenated (Scheme 10) to produce 4-(tetrahydrofuran-2-yl)butan-2-ol (**3a**) and 4-(tetrahydrofuran-2-yl)butan-2-one (**3b**) with selectivity 40% and 60% respectively.



Scheme 10: hydrogenation of compound 3

The activity of supported Ni-Pd alloy nanoparticles was successfully employed in the hydrogenation of compound **4** (Scheme 11) to produce 3-((tetrahydrofuran-2-yl)methyl)pentane-2,4-dione (4a) exclusively with >99% selectivity (yield = 93%). This can be explained using the inability of supported Ni-Pd nanoparticle to hydrogenate the carbonyl groups due to the steric interaction generated by the α -methyl groups.



Scheme 11: hydrogenation of compound 4

The adsorption of substrates plays a crucial role in the hydrogenation reaction. This is supported by the fact that compound 6 and 7 does not give any reaction under the analogous reaction condition (Scheme 12). This is due to the tetrahedral nature of the central carbon atom and the presence of methyl groups in the compounds.



Scheme 12: Hydrogenation of compound 5, 6

CHAPTER FOUR

4. Conclusion

In conclusion, we have achieved a feasible and highly effective way to hydrogenate biomass-derived furan aldol adducts over supported Ni_{0.9}Pd_{0.1} nanoparticle at room temperature (30 °C) under environmental friendly condition. We achieved a way to produce tetrahydrofuran compounds which have long carbon chain (C_8 - C_{16}). We found the supported Ni_{0.9}Pd_{0.1} alloy nanoparticle catalysts to be active in hydrogenation of furan ring and olefinic C=C double bond to produce 1,5-bis(tetrahydrofuran-2-yl)pentan-3-one (1b) with high selectivity which has many applications as high density fuel additives and as lubricant. So, this catalyst and procedure can be of practical interest for selective hydrogenation of biomass-based furan compounds. Our findings have shown the use of H₂ balloon which replaces the high pressure of H₂ gas used in the literatures. Also, to be used in the industry, our catalyst is cost-effective having very low amount of costly Pd. Our present work will give deep understanding of other highly effective, low cost catalysts and catalytic methods to use mild and environmental friendly condition.

APPENDIX A.



¹H NMR, ¹³C NMR and HRMS spectrum of compounds.

Figure 9: ¹H NMR spectrum of compound 1



Figure 10: ¹³C NMR spectrum of compound 1



Figure 11: HRMS of compound 1



Figure 12: ¹H NMR spectrum of compound 2



Figure 13: ¹³C NMR spectrum of compound 2



Figure 14: HRMS of compound 2



Figure 15: ¹H NMR spectrum of compound 3



Figure 16: ¹³C NMR spectrum of compound 3



Figure 17: HRMS of compound 3



Figure 18: ¹H NMR spectrum of compound 4



Figure 19: ¹³C NMR spectrum of compound 4



Figure 20: HRMS of compound 4



Figure 21: ¹H NMR spectrum of compound 5



Figure 22: ¹³C NMR spectrum of compound 5



Figure 23: HRMS of compound 5



Figure 24: ¹H NMR spectrum of compound 6



Figure 25: ¹³C NMR spectrum compound 6



Figure 26: HRMS spectrum of compound 6



Figure 27: ¹H of compound 1a



Figure 28: HRMS of compound 1a



Figure 29: ¹H NMR spectrum of compound 1b



Figure 30: HRMS of compound 1b



Figure 31: ¹H NMR spectrum of 3a



Figure 32: HRMS of compound 3a



Figure 33: ¹H NMR spectrum of compound 4a



Figure 34: HRMS of compound 4a

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