Development of Metal Catalysts for the Transformation of Biomass-derived Furans to Value-added Chemicals

Ph.D. Thesis

by

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DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE

March 2018

Development of Metal Catalysts for the Transformation of Biomass-derived Furans to Value-added Chemicals

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree

of DOCTOR OF PHILOSOPHY

by

KAVITA GUPTA



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE March 2018



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "**Development of Metal Catalysts for the Transformation of Biomass-derived Furans to Value-added Chemicals**" in the partial fulfillment of the requirements for the award of the degree of **DOCTOR OF PHILOSOPHY** 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 2013** to **March 2018** under the supervision of **Dr. SANJAY KUMAR SINGH**, Associate professor, Discipline of Chemistry, Indian Institute of Technology Indore, 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.

Signature of the student with date (KAVITA GUPTA)

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

Signature of Thesis Supervisor with date

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Date:

Acknowledgements

It is my pleasure to acknowledge innumerable individuals who were with me for completion of my Ph.D. research.

First of all, I would like to express my sincere gratitude to my Ph.D. thesis supervisor Dr. Sanjay Kumar Singh for his continuous encouragement, enthusiasm and support during my Ph.D. study and research. Because of his motivation and faith, I could achieve best in all my ups and downs which has inspired me to thrive for excellence and nothing less.

I would like to thank Dr. Shaikh M. Mobin for single crystal X-ray support and his valuable guidance. My deeply thank to my PSPC members Dr. Biswarup Pathak and Dr. Preeti A. Bhobe for their guidance and valuable suggestions during my Ph.D. research.

With my heartfelt respect, I am grateful to thank Prof. Pradeep Mathur (Director, Indian Institute of Technology Indore) for his endless motivations and providing all the facilities at Indian Institute of Technology Indore.

I sincerely thank to Dr. Amrendra Kumar Singh (Head, Discipline of Chemistry, Indian Institute of Technology Indore) for his suggestions and guidance for various activities. I am also grateful to Dr. Suman Mukhopadhyay, Dr. Rajneesh Misra, Dr. Tridib K. Sarma, Dr. Satya S. Bulusu, Dr. Sampak Samanta, Dr. Tushar Kanti Mukherjee, Dr. Apurba Das, Dr. Chelvam Venkatesh and Dr. Anjan Chakraborty for their help and guidance in different aspects.

I am grateful to acknowledge all my teachers who have taught me in some or the other way since my childhood. I could never achieve anything without their guidance, blessing and support.

I extend my profound thanks to my group members; Dr. Rohit K. Rai, Dr. Deepika Tyagi, Mr. Ambikesh D. Dwivedi, Ms. Chinky Binnani, Mr. Debashis Panda, Mr. Dharmendra Panchariya, Mr. Mahendra Awasthi Mr. Soumyadip Patra, Mr. Vinod Kumar Sahu and Mr. SK Nazmul Hasan MD Dostagir for their constant co-operation and help. It has been inspiring and delightful to work with labmates and many friends together in my Ph.D. duration. I am grateful to record my thanks to Ms. Indrani Choudhuri, Ms. Roopali Prajapati, Ms. Linia Anie Sunny, Ms. Ankita Goswami, Dr. Thaksen Jadhav, Dr. Tamalika, Dr. Shivendra, Dr. Rajendra, Dr. Bhagwati, Dr. Bhausaheb, Dr. Manideepa, Dr. Archana, Dr. Anvita, Dr. Veenu, Dr. Anupam, Dr. Sonam, Dr. Debashish, Dr. Maruthi, Dr. Biju, Ms. Rekha, Mr. Arpan, Mr. Sagnik, Mr. Ramesh, Ms. Poulami, Mr. Akbar, Mr. Ajeet, Mr. Anup, Dr. Arup, Mr. Kuber, Ms. Jamuna, Ms Neha, Ms. Daisy, Ms. Anupama, Mr. Ashish, Ms. Isha and Ms. Vishakha. I am also thankful to all my friends who directly or indirectly helped me during my Ph. D.

Sophisticated Instrumentation Center (SIC), IIT Indore, FIST supported TEM facility to the Department of Chemistry, IISER Bhopal and SAIF, IIT Bombay are acknowledged for instrumental facilities.

I am glad to thank all technical staff of Sophisticated Instrumentation Center (SIC, IIT Indore); Ms. Sarita Batra, Mr. Kinny Pandey, Mr. Ghanshyam Bhavsar, Mr. Nitin Upadhyay and staff from Discipline of Chemistry; Mr. Manish Kushwaha, Ms. Vinita Kothari and Mr. Rameshwar Dauhare for their consistent support without which it was not possible to complete my work. I would also like to thank Ms. Anjali Bandiwadekar, Mr. Rajesh Kumar, library staff and other technical and non-technical staff for their constant help whenever required.

I would like to thank IIT Indore for infrastructure and Council of Scientific & Industrial Research (CSIR), New Delhi for my Fellowship.

I am beholden to all my friends; Ms. Shalini Pathak, Dr. Nishant Verma, Mr. Manoj Kumar Ghosalya, Mr. Tarun Saxena, Ms. Sonika Singh, Ms. Nidhi Mittal and Ms. Yashu Varshney for their constant love and support.

Finally, I am pleased to acknowledge the people who mean the world to me; my parents (Shri Bhuvnesh K. Gupta and late Smt. Sudha), brother (Mr. Lovneet Kumar), sisters (Mrs. Ragini and Mrs. Monika) and all family members without their love and blessings I do not imagine my life. Thank you all for being a part of my life.

> Kavita Gupta IIT Indore



Abstract

Production of fuel and different value-added chemicals from widely distributed renewable biomass provides a facile path to reduce global dependence on the fossil resources. Different platform compounds isolated or produced from biomass such as sugars and furans are getting outstanding considerations for the synthesis of different industrially applicable chemicals and fuel components. As biomass-derived furans such as 2-furfuraldehyde (furfural), 5-hydroxymethyl-2-furfural (5-HMF) and others have highly reactive -CHO and/or -CH₂OH side chains with furan ring, these can be explored for the production of several valuable chemicals. In recent years, catalysts (homogeneous and heterogeneous catalysts) have provided efficient upgradation of biomass-derived furans through diverse catalytic reactions. This thesis comprises seven chapters. The first chapter narrates brief introduction about catalysis and biomass-derived compounds along with biomass-derived furans. This chapter includes thorough literature survey for the catalytic upgradation of biomass-derived furans and the importance of different transformed compounds in diverse fields. Successive chapters elucidate the detail studies on the syntheses and characterizations of homogeneous metal complexes (Ru-based complexes) and heterogeneous metal nanoparticles (Ni, Cu, Co and Pd) based catalysts for the catalytic upgradation of biomass-derived furans.

The main objectives of the present study are,

- To develop simple, water soluble and highly active metal complexes for catalytic transformation of biomass-derived furans to valuable ketoacid and diketones under environmental benign reaction conditions and study the mechanistic pathway of catalytic transformations.
- Design and synthesis of cost-effective high-performance supported and unsupported bimetallic M-Pd (M = Ni, Cu or Co) alloy nanoparticle catalysts (nano-catalyst) for oxidative and hydrogenating upgradation of biomass-derived furans and study the mechanistic aspects.

• To study the effect of synergistic interaction (between two metals of alloy bimetallic nano-catalyst) on the catalytic oxidation and hydrogenation of biomass-derived furans.

The contents of each chapter included in the thesis are, briefly, as follows:

Chapter 1. Introduction and Background

In this chapter, a brief introduction about catalysis and biomass-derived compounds along with biomass-derived furans is described. The chapter is summarized background of the catalytic upgradation of biomass-derived furans and the importance of different transformed compounds in the diverse fields.

Chapter 2. Materials and Instrumentation

In this chapter, materials and instruments employed in the different projects of the thesis are discussed.

Chapter 3. Catalytic transformation of biomass-derived furans to valuable ketoacid and diketones using water-soluble arene-ruthenium catalysts

In this work, we designed and developed water-soluble 8-aminoquinoline coordinated arene-ruthenium(II) complexes and explored their activity for the catalytic transformation of biomass-derived furans such as furfural, 5-HMF and 5-methyl-2-furfural (5-MF) to ketoacid (levulinic acid; LA) and diketones (1-hydroxyhexane-2,5-dione; 1-HHD, 3-hydroxyhexane-2,5-dione; 3-HHD and hexane-2,5-dione; HD) under moderate reaction conditions. Complete conversion of furfural to LA with >99% selectivity was attained with 1 mol% catalyst and 12 equivalents of formic acid at 80-100 °C. Different experimental observations and ¹H NMR studies have given more insights into the mechanistic pathway for the catalytic transformation of furans to open ring compounds. Furthermore, studies carried out with structural analogues of the active catalyst revealed a structure-activity relationship for the observed higher catalytic performance of arene-ruthenium(II) complex having 8-

aminoquinoline ligand. Results inferred that -NH moiety of 8-aminoquinoline ligand assisted the transfer hydrogenation where, probably, -NH moiety form hydrogen bonding with formyl group to bring the furfural in close vicinity of the ruthenium center and transfer H⁺ ion to formyl group to facilitate the formic acid driven transfer hydrogenation of furfural to furfuryl alcohol (a key intermediate). Moreover, high water-solubility of the studied catalyst resulted in high recyclability (up to 4 catalytic runs) without any remarkable loss in the catalytic activity. Molecular characterizations of the studied arene-ruthenium(II) complexes were also confirmed by different spectroscopic technique such as NMR, ESI-MS and single-crystal X-ray diffraction studies.

Chapter 4. Catalytic aerial oxidation of biomass-derived furans to furan carboxylic acids in water over bimetallic Ni-Pd alloy nanoparticles

In this chapter, we designed and synthesized bimetallic Ni_{1-x}Pd_x (0.10 \leq x \leq 0.75) alloy nano-catalysts and explored their activity for the catalytic aerial oxidation of different biomass-derived furans such as furfural, 2-furfuryl alcohol, 5-HMF, 5-MF and 5-methyl-2-furfuryl alcohol to corresponding furan carboxylic acids (2-furoic acid, furan-2,5-dicarboxylic acid (FDCA), 5-methyl-2-furoic acid (MFCA)) at 80 °C under aqueous reaction conditions. Among all, Ni_{0.90}Pd_{0.10} nano-catalyst (having very low Pd content) resulted in superior catalytic activity to attain high yields of corresponding furan carboxylic acid. Furthermore, results revealed that presence of Ni in the bimetallic $Ni_{1-x}Pd_x$ catalysts not only increased the catalytic performance for facile oxidation of biomass-derived furans (with high catalytic turnover) using aerial oxygen but also followed to high stability of Ni_{0.90}Pd_{0.10} nano-catalyst in the presence of air and water which led to high recyclability up to 10 catalytic runs. The highperformance of studied bimetallic Ni_{1-x}Pd_x catalysts was assigned to charge transfer from Ni (less ionization energy as compare to Pd) to Pd. Further, we also achieved a one-pot direct transformation of fructose to furan carboxylic acid products (such as FDCA) using Ni_{0.90}Pd_{0.10} nano-catalyst. The studied catalysts were characterized using different techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and powder X-ray diffraction (P-XRD).

Chapter 5. Catalytic aerial oxidation of 5-hydroxymethyl-2-furfural (5-HMF) to furan-2,5-dicarboxylic acid (FDCA) over Ni-Pd nanoparticles supported on Mg(OH)₂ nanoflakes for the synthesis of furan diesters

In this chapter, different bimetallic $M_{0.90}Pd_{0.10}$ (M = Ni, Co or Cu) alloy nanoparticles supported on in situ prepared Mg(OH)₂ nanoflakes were synthesized and explored for the catalytic aerial oxidation of biomass-derived 5-HMF to the industrially important FDCA without using any external base additive. Among different $M_{0.90}Pd_{0.10}/Mg(OH)_2$, $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ displayed higher catalytic activity. Furthermore, studies with Ni_{0.90}Pd_{0.10} supported on different supports such as SiO₂, Al₂O₃, ZnO and Mg(OH)₂ inferred that the basic nature of the $Mg(OH)_2$ facilitated the efficient oxidation of 5-HMF and avoids the usage of an external base additive. Moreover, reactions carried out with $Ni_{1-x}Pd_x/Mg(OH)_2$ (x = 0.10 to 1) and a physical mixture of Ni/Mg(OH)₂ and Pd/Mg(OH)₂ revealed that the remarkable synergistic interaction between Ni and Pd (attributed to electronic charge transfer) plays an important role in the achieved high catalytic performance of Ni_{0.90}Pd_{0.10}/Mg(OH)₂ towards the oxidation of 5-HMF to FDCA. Notably, Ni_{0.90}Pd_{0.10}/Mg(OH)₂ catalyst could be employed to the gram-scale oxidation of 5-HMF to FDCA. Thereafter, the prepared FDCA was explored for the synthesis of different furan diesters, to be utilized as precursors for the synthesis of bio-based polymers and plastics materials. Furthermore, structural and chemical characterization of Ni_{0.90}Pd_{0.10}/Mg(OH)₂ (highly active catalyst) was confirmed using P-XRD, TEM, EDS, SEM, elemental mapping, XPS and **ICP-AES** analysis.

Chapter 6. Bimetallic Ni-Pd alloy nanoparticles: An efficient catalyst for the room temperature hydrogenation of biomass-derived furans and furan/acetone aldol adducts

In this chapter, an efficient and environmental benign hydrogenation of biomass-derived furans and furan/acetone aldol adducts (having C5-C15 carbon) has been explored over simple, cost-effective and highly active bimetallic Ni-Pd alloy nanoparticles catalysts under aqueous reaction conditions at room temperature using H₂ gas at atmospheric pressure. For the optimization of reaction conditions, 2-furfuryl alcohol (furfuryl alcohol) was used as a model substrate. Among all studied bimetallic Ni_{1-x}Pd_x (x = 0.10 to 0.75) as well as monometallic nanoparticles catalysts, Ni_{0.90}Pd_{0.10} (having only 10% Pd in comparison to Ni) outperformed and displayed the highest TON for the hydrogenation of furfuryl alcohol to tetrahydro-2-furfuryl alcohol (THFAL). Time-scale analyses for the hydrogenation of aldol adducts revealed that Ni_{0.90}Pd_{0.10} catalysts show high efficiency towards the hydrogenation of C=C over C=O bond. Furthermore, studied Ni_{0.90}Pd_{0.10} catalyst displayed high stability under the employed reaction conditions and could be reused for five catalytic runs without any significant loss in the catalytic activity.

Chapter 7. Conclusions and future scopes

Conclusions

The conclusions of different projects included in this thesis are as follows:

- 1) We developed high-performing water-soluble arene-ruthenium(II) 8-aminoquinoline, 2,2'-bipyridine 8complexes (having or hydroxyquinoline ligand) catalysts for the catalytic transformation of different biomass-derived furans such as furfural, 5-HMF and 5-methyl-2furfural (5-MF) to value-added ketoacid and diketones under moderate reaction conditions. Our findings revealed that N-H moiety of 8aminoquinoline facilitated the enhanced catalytic activity of the Rucomplex where, probably, N-H moiety form hydrogen bonding with furfural and bring it in close vicinity of ruthenium centre. Furthermore, N-H moiety may also transfer a H⁺ ion to a formyl group and resulted to facile transfer hydrogenation of furfural to furfuryl alcohol in the presence of formic acid.
- 2) We also developed cost-effective high-performing bimetallic $Ni_{1-x}Pd_x$ (0.10 $\leq x \leq 0.75$) alloy nanocatalysts (heterogeneous catalyst) for the oxidation of biomass-derived furans. Results inferred that high synergistic

interaction between Ni and Pd, due to the electronic charge transfer from Ni to Pd, contributed significantly in the observed high catalytic performance with low leaching and high reusability of $Ni_{0.90}Pd_{0.10}$ catalyst.

- 3) Different bimetallic M-Pd (M = Ni, Cu or Co) alloy nanoparticles supported over *in situ* generated Mg(OH)₂ have also synthesized and explored for an efficient oxidation of 5-HMF to FDCA without addition of an external base. Results attained with Ni_{0.90}Pd_{0.10} supported on different supports such as SiO₂, Al₂O₃, ZnO and Mg(OH)₂ suggested that the basic nature of Mg(OH)₂ was favourable for efficient oxidation of 5-HMF and to avoid the usage of an external base additive.
- 4) Bimetallic Ni-Pd alloy nano-catalysts were also explored for the room temperature hydrogenation of biomass-derived furans and aldol adduct of furan, where we studied the effect of alloying of non-noble metal (Ni) with noble metals (Pd) on the catalytic hydrogenation of furans derivatives.

In conclusion, diverse homogeneous and heterogeneous catalytic systems were developed and extensively employed during various projects (catalytic upgradation of biomass-derived furans) included in this thesis. The studied catalysts represent a class of low-cost high-performance, stable (towards air, water and other reaction conditions), recyclable catalysts and hence can also be explored for several other catalytic reactions and approaches.

Future scope

The relevant future scope of the work included in this thesis has been discussed briefly.

Publications

- Gupta K., Rai R. K., Singh S. K. (2018) Metal catalysts for Efficient Transformation of Biomass-derived HMF and Furfural to Value Added Chemicals: Recent Progress, ChemCatChem, 10, 2326-2349 DOI: 10.1002/cctc.201701754. (IF 4.803)
- Gupta K., Tyagi D., Dwivedi A. D., Mobin S. M., Singh S. K. (2015) Catalytic transformation of bio-derived furans to valuable ketoacids and diketones by water-soluble ruthenium catalysts, Green Chem., 17, 4618-4627 (DOI: 10.1039/c5gc01376c). (IF 9.125)
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- Dwivedi A. D., Rai R. K., Gupta K., Singh S. K. (2017) Catalytic Hydrogenation of Arenes in Water Over In Situ Generated Ruthenium Nanoparticles Immobilized on Carbon ChemCatChem, 9, 1930-1938 (DOI : 10.1002/cctc.201700056). (IF 4.803)
- * Publications 1-5 are the part of this thesis.

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Acronyms

TON	Turnover numbers
TOF	Turnover frequency
UV-vis	UV-visible spectroscopy
PXRD	Powder X-ray diffraction
TEM	Transmission electron microscopy
HR-TEM	High resolution transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
SAED	Selected-area electron diffraction
TGA	Thermal gravimetric analysis
NMR	Nuclear magnetic resonance
ppm	Parts per million
ICP-AES	Inductively coupled plasma atomic emission
	Spectroscopy
PVP	Polyvinylpyrrolidone
Furfural	2-furfuraldehyde
5-HMF	5-hydroxymethyl-2-furfural
5-MF	5-methyl-2-furfural
MFA	5-methyl-2-furfuryl alcohol
FDCA	Furan-2,5-dicarboxylic acid
DFF	2,5-diformylfuran
PET	Poly(ethylene terephthalate)
PBT	poly(butylene terephthalate)
HFCA	5-hydroxymethyl-2-furancarboxylic acid
FFCA	5-formylfuran-2-carboxylic acid

Nomenclature

a. u.	Arbitrary unit
0	Degree
λ	Wavelength
nm	Nanometre
°C	Degree Centigrade
mmol	Millimol
mL	Millilitre
μL	Microlitre
Μ	Molarity
α	Alfa
β	Beta
γ	Gamma
θ	Theta
cm	Centimetre
g	Gram
Chapter 1: Introduction and Background

1.1. Catalysis

In general, catalysis is a phenomenon where the tiny amount of a substance, called as the catalyst, alters the reaction rate without its consumption during the reaction. Catalysis has wide applications in academic research laboratories as well as in the different industries and gives a sustainable transformation of basic materials into different value-added products such as fuel components, pharmaceuticals, polymers, paint and much more require in our daily life.

1.1.1. Type of Catalysis

Depending upon catalyst phase, catalysis is broadly classified into two categories, homogeneous catalysis and heterogeneous catalysis.

1.1.1.1. Homogeneous Catalysis

Homogeneous catalysis is assigned to catalytic reactions where the catalyst and reactants are in the same phase [1, 2]. The homogeneous catalytic system offers an easy interaction between reactant and catalyst which results to superior and selective catalytic activity. These catalysts are associated with various advantages such as high selectivity, the better yield of product and high turnover numbers (TON). Moreover, catalysts could be tuned for different chemo-, stereo- and regio-selectivity by the simple structural modification in ligands which has high importance in medicine and in many others fields. Furthermore, high catalytic performance of homogeneous catalysts follows with their wide use in numerous commercial applications for various industries and research. Beside different applications of homogeneous catalysts, there are some limitations in the isolation and separation of catalyst from the reaction mixture.

1.1.1.2. Heterogeneous catalysis

In contrast to homogeneous catalysis, heterogeneous catalytic reactions involve the different phases of the catalyst and reactants where the catalyst is completely insoluble in the reaction medium [3, 4]. Heterogeneity for a catalyst can be attained by grafting of active material (metals or non-metal) through the covalent bond or using adsorption and incorporation of active material on the surface of any support. Due to insolubility of heterogeneous catalyst, these can be separated from the reaction mixture through an external force such as centrifugation and resulted in the high reusability. However,

heterogeneous catalysts are suffered from some disadvantages like in most of the cases, the active sites of catalyst are not completely approachable to reactant and the only bare surface participates in the catalytic reaction which resulted to a decrease catalytic performance of the catalyst. Furthermore, heterogeneous catalysts are faced leaching problem that also decreases the efficiency of the catalyst. These drawbacks could be overcome to large extent with the use of nanoparticles based catalysts (nano-catalyst). Nano-catalysts not only display high catalytic activity as well as selectivity like homogeneous catalysts but can also be recovering from the product after the reaction like heterogeneous catalysts.

1.2. Biomass-derived compounds

Concern towards fast depletion of fossil resources and its worldwide dependence have sparked current research to look an alternative stockpile for the production of fuels and different fine chemicals. In this direction lignocellulosic biomass, the most naturally abundant and low-cost carbon-rich material, is getting much more attention to substitute non-renewable fossil resources while its complex structure (cellulose, hemicellulose and lignin polymers) limits its direct use [5-12]. Therefore, different platform chemicals isolated or produced from lignocellulosic biomass such as sugars and furans are getting tremendous attention for the production of different industrially applicable chemicals and fuels components (Scheme 1.1) [13-16]. Furthermore, U. S. Department of Energy (DOE), in 2004, has reported twelve sugar-based building blocks those can be converted in various fine chemicals or materials [17].

1.2.1. Biomass-derived furans

Biomass-derived furans such as 2-furfuraldehyde (furfural), 5-hydroxymethyl-2-furfural (5-HMF) and others having highly reactive -CHO and/or -CH₂OH side chains with a furan ring, have taken enormous attention for the production of different value-added chemicals through diverse reactions [18-27]. These furans can be efficiently produced by the acid-catalyzed dehydration of sugars (pentose and hexose) [28-31]. Typically, furfural is produced from the xylose (a main part of hemicellulose) and it could be in top 30 in the DOE report published in 2004. Similarly, 5-HMF is efficiently produced by the dehydration of fructose with furanose structure [31]. It can also synthesize by the dehydration of glucose or directly from cellulose [31].



Scheme 1.1. Schematic representation for the transformation of lignocellulosic biomass to different valuable chemical *via* furan derivatives.

Further, fossil generated biofuels, biodiesel and bioethanol have highly established in the transportation area but have limited resources. These fuels have also suffered from many limitations to use in transportation as having corrosive nature, low stability towards oxidation as well as poor cold flow properties [15]. Transformation of biomass-derived furans such as furfural and 5-HMF to fuel components or fuel additive and different value-added chemicals is seemed as appealing approach to replace fossil or petroleum-based resources. Various fuel components produced from these furans such as 2,5-dimethylfuran (DMF), 2-methylfuran (2-MF), esters of levulinic acid (levulinic acid; LA), γ -valerolactone (GVL) and hydrocarbons have shown efficiency as high-quality fuels (Scheme 1.2) [15, 22-25]. Apart from various

applications in the production of fuel components, these furans have also shown high efficacy in the production of several C5, C6 or higher carbon containing valuable chemicals such as furan-2,5-dicarboxylic acid (FDCA), 2,5-diformylfuran (DFF), 2-furoic acid, ketones/diketone, 1,6-hexanediol, cyclopentanone, adipic acid, maleic anhydride, succinic acid and many more having wide application in several industries and pharmaceuticals (Scheme 1.2) [25-31].



Scheme 1.2. Transformation of furan derivatives to different potential industrially applicable chemicals.

1.3. Catalytic Upgradation of Biomass-derived furans

Various methodologies and catalysts have been explored to transform biomass-derived furan especially furfural and 5-HMF to different value-added chemicals and advanced materials [32-39]. In this regards, mainly transition metal-based catalysts involving noble and non-noble metals has efficiently used and are in high interest. In the upgradation of biomass-derived furans, homogeneous catalysts are getting significant attention to achieve high

selectivity of desired products. Moreover, different monometallic and bimetallic heterogeneous nanoparticles based catalysts have extensively explored in various catalytic reactions to achieve an efficient and selective production of several value-added chemicals.

1.3.1. Upgradation using homogeneous catalysts

In the recent years, homogeneous metal catalysts are receiving remarkable considerations in the transformation of biomass-derived furans to various fine chemicals (Figure 1.1). Different metal complexes based catalysts especially with Ir, Ru and Rh metals have been efficiently explored to achieve selective production of valuable chemicals from biomass-derived furans. In this upgradation, one pot catalytic transformation of 5-HMF to open ring ketones could be achieved using Cp*-Iridium(III) complexes [40-43]. The study revealed that Cp*-Iridium(III) complexes having bipyridine ligand displayed high catalytic efficiency towards the selective production of diketones, 1hydroxyhexane-2,5-dione (1-HHD), from 5-HMF via hydrogenation/hydrolytic furan ring opening [40]. The results inferred that Cp*-Iridium(III) complexes act as a bifunctional catalysts where complex catalyzed 5-HMF hydrogenation in the presence of H₂ gas followed by furan ring opening in the presence of *in-situ* generated acid. Furthermore, Xu et al. (2016) revealed that Cp*Ir complexes with bipyridine ligand having orthohydroxyl functional group (o-OH) and dimethyl amino (NMe₂) group exhibited superior catalytic activity as o-OH group enhanced Cp*Ir complex catalyzed heterolytic dissociation of H₂ molecule while dimethyl amino (NMe₂) group, having strong electron-donating affinity, promote the hydrogenation ability of Cp*Ir complex [41]. Wu et al. (2016) also studied $\mbox{Cp*Ir}^{\mbox{III}}$ half-sandwich complexes (having substituted bipyridine ligand) for the hydrogenation/hydrolytic ring opening of 5-HMF in formate buffer solution [42]. The study showed that pH of buffer solution highly influenced the ring opening and at pH = 2.5, 1-HHD was produced in highest yield while at pH >4.5 1-HHD was not observed and 2,5-bis-(hydroxymethyl)furan (BHMF) produced as a major product. Furthermore, substituents and their positions on bipyridine also influenced the catalytic performance of Ir catalyst as electron donating group enhanced the catalytic reaction at *p*-position in

comparison to at *o*-position which made steric hindrance. Ru-based catalysts have also exhibited high catalytic performance for the catalytic upgradation of furans [44-47]. In this way, *Pasini et al.* (2014) attained a selective hydrogenation of 5-HMF to BHMF with Ru-based shvo's catalyst [44]. Analogously, Ru(acac)₃/Ph₂P(CH₂)_nPPh₂ followed to an efficient catalytic hydrogenation of furfural to furfuryl alcohol under solvent-free reaction conditions [45].



Figure 1.1. Metal complexes reported for the catalytic upgradation of

1.3.2. Upgradation using heterogeneous Nano-catalysts

biomass-derived furans.

As heterogeneous nano-catalysts have shown high efficacy and stability in diverse reactions, these have also widely explored in the upgradation of biomass-derived furans [6-8]. In this way, transition metal-based catalysts involving non-noble as well as noble metals has efficiently employed and getting high-interest (as monometallic and bimetallic heterogeneous catalysts) in the different catalytic reactions to achieve a productive and selective transformation of furans to value-added chemicals [10, 28-31]. Furthermore, besides diverse catalytic activities exhibited by monometallic catalysts, the addition of second metal to form bimetallic catalyst have led to promote different catalytic reactions [4, 10]. The reports suggest that addition of

second metal may result to alter the catalytic activity by modifying the geometry of active sites present on the catalyst or by charge transfer from one metal to another which follows to change electron density on the active site of catalyst (Figure 1.2a) [48]. It may also result to minimize the deposition of carbonaceous matter on the catalyst surface that leads to enhancing the stability of the catalyst. Furthermore, synergistic interaction between two metals can facilitate the interaction of substrate and different reaction intermediates with the catalyst. Moreover, it has also reported that presence of two metals in a catalyst can be resulted to interact with two functional group of a substrate or intermediate and may lead to enhance the catalytic performance of catalyst (Figure 1.2b) [49].



Figure 1.2. Schematic representation for a) the electronic charge transfer from one metal to another metal (Reprinted with the permission from Ref. 48; Copyright 2016, Royal Society of Chemistry); b) interaction of bimetallic nanoparticles with two functional groups of furfural (Reprinted with the permission from Ref. 49; Copyright 2014, American Chemical Society).

Furthermore, in the enhancement of catalytic performance, the nature of support has also been shown promotional effect. In this regard, acidity or basicity associated with support may lead to facilitate the interaction of reactant and/or intermediates which can follow an enhanced catalytic performance (Figure 1.3) [50, 51].



Figure 1.3. Interaction of support with reactant and reaction intermediates (Reprinted with the permission from Ref. 50, 51; Copyright 2015 and 2017, American Chemical Society).

Diverse catalytic reactions involving hydrogenation, furan ring opening and oxidation of biomass-derived furans have been explored over different monometallic, bimetallic, supported and unsupported heterogeneous catalysts to achieve an efficient and selective production of desired products.

1.3.2.1. Hydrogenating upgradation

In the recent decades, different hydrogenated products produced from biomass-derived furans especially using furfural and 5-HMF (Scheme 1.3) has gained lot of consciousness towards the production of fuel components and different industrial applicable chemicals such as furfuryl alcohol has wide applications in the production of thermostatic resins while completely hydrogenated form of furfural, tetrahydro-2-furfuryl alcohol (THFAL), is a green, stable and degradable solvent [49]. Furthermore, DMF (hydrogenated products of 5-HMF) is one of the most high-quality biomass-derived fuel component having various superior factor such as moderate boiling point, very low miscibility with water and lower kinematic viscosity over fossil-derived fuels like bio-ethanol and bio-butanol that lead to an efficient alternative to gasoline with higher energy density [23]. Moreover, BHMF, produced by the selective hydrogenation of 5-HMF, is efficiently used in pharmaceuticals, resin and polymer industries [31].



Scheme 1.3. Schematic representation to the different hydrogenating transformations of biomass-derived furans.

Various metal based heterogeneous catalysts (mainly based on Pd, Au, Ru, Pd, Ir, Re, Rh, Ni, Cu and Co metals) have efficiently explored for the transformation of biomass-derived furans to several fine chemicals. Different variables for instance metallic surface, the presence of second metal, support, nature of solvent and hydrogen pressure have highly influenced catalytic hydrogenation of furans. In this way, Cu-based catalysts have shown high efficiency towards the hydrogenation of carbonyl group and C-O hydrogenolysis as compared to furan ring hydrogenation [38, 51-65]. The studies revealed that on the surface of Cu, the adsorption of furfural could not facilitate through the furan ring which resists the over hydrogenation of furans [38]. Further, DFT calculations suggested a strong repulsion between furan ring and Cu(111) surface which was presumed due to the overlapping of 3d band of Cu metal and antibonding orbital of furan ring [54]. Disparate from Cu-based catalysts, Ni catalysts displayed over hydrogenation and furan ring opening [38, 66-72]. In this regards, Nakagawa et al. (2012) achieved an efficient complete hydrogenation of furfural to THFAL from the gas phase hydrogenation of furfural over Ni/SiO₂ [66]. The study suggested that the hydrogenation of furfural to furfuryl alcohol preferentially occurred as compared to furfuryl alcohol to THFAL conversion which was due to the

strong adsorption of furfural over catalyst surface in comparison to furfuryl alcohol (Figure 1.4).



Figure 1.4. Proposed mechanistic pathway for the hydrogenation of (A) furfural and (B) furfuryl alcohol over Ni/SiO₂ (Reprinted with the permission Ref. 66, Copyright 2012, WILEY-VCH Verlag GmbH & Co).

Bimetallic Cu-Ni catalyst has also shown efficiency towards the total hydrogenation of furfural to THFAL. The study revealed that bimetallic Cu-Ni/CNT catalyst displayed higher activity towards furfural hydrogenation compared to the monometallic Ni/CNT while the selectivity of THFAL was more for Ni/CNT in contrast to Cu-Ni/CNT [71]. Analogously, Cu-Ni/ γ -Al₂O₃ (Cu/Ni = 1) exhibited higher catalytic performance for the hydrogenation of 5-HMF to DMF and furfural to 2-MF, in comparison to the monometallic Cu/ γ -Al₂O₃ and Ni/ γ -Al₂O₃ [72]. The results inferred that the increasing Ni content in Cu-Ni/ γ -Al₂O₃ led to an efficient Cu dispersion on γ -Al₂O₃. Furthermore, studies suggested that Cu has lower activity for H₂ dissociation while addition of Ni might assist to hydrogen in the form of atomic hydrogen and these resulted H-atoms diffused to Cu metal whereon the hydrogenation of carbonyl group occurred [73, 74].

Further, *Li et al.* (2016) developed N-doped carbon-supported Fe catalysts (prepared by the pyrolysis of Fe complexes having 1,10-phenanthroline, 2,2',6',2''-terpyridine, hemin, 2,2'-bipyridine or 8-hydroxyquinoline ligand) and employed for the catalytic transfer hydrogenation of furfural in 2-propanol [75]. The study suggested that the catalyst with the highest N···Fe atomic portion (prepared using Fe acetate and

1,10-phenanthroline) outperformed for the hydrogenation of furfural where N acted as Lewis-basic sites. Additionally, Lewis acidic sites were, probably, also developed because of N-doping on Fe that facilitated to the feasible adsorption of furfural. Sitthisa et al. (2011) observed that incorporation of Fe in Ni-Fe catalysts led to enhance the hydrogenation of furfural and C-O bond hydrogenolysis with the decrease in decarbonylation activity of Ni that followed to increase the yield of 2-MF [76]. For this, DFT calculations showed the remarkable difference in the selectivity of η^2 -(C,O) surface species on both monometallic and bimetallic catalysts which was higher over the bimetallic Ni-Fe catalyst in comparison to pure Ni. Furthermore, the oxyphilic behavior of Fe also led to strong interactions between carbonyl oxygen and Fe atoms which resulted in the increased hydrogenation of furfural to furfuryl alcohol followed by hydrogenolysis to 2-MF. Analogously, Audemar et al. (2015) achieved an efficient hydrogenation of furfural to furfuryl alcohol (88% yield) over Co/SBA-15 catalyst [77]. They observed that the oxidized form of Co, Co₃O₄, followed to lower furfural conversion with no production of furfuryl alcohol which indicated that Co in metallic form was crucial for the catalytic hydrogenation of furfural.

In the upgradation of furans, Pd-based catalysts have also exhibited high efficacy for the different hydrogenating reactions including hydrogenolysis and/or decarbonylation of furfural and 5-HMF [38, 78-89]. Sitthisa et al. (2011) observed decarbonylation of furfural to furan, a major product, over Pd/SiO₂ catalyst with a small amount of furfuryl alcohol as well as overhydrogenated products; tetrahydrofuran (THF) and THFAL [38]. In this context, Barteau et al. (1989, 1997) revealed that on the surface of Pd catalyst, aldehyde group form η^2 (C,O) surface intermediates which, in the presence of H₂, hydrogenated to alcohol while at high temperature transformed to highly stable acyl surface intermediate where C atom of carbonyl group strongly attached to the Pd surface that may lead to the decarbonylation of furfural to furan [90, 91]. Pd-based bimetallic nano-catalysts have also shown high performance towards the hydrogenation of furfural and 5-HMF [49, 92-95]. In this direction, Nakagawa et al. (2014) achieved total hydrogenation of biomass-derived furans, furfural and 5-HMF, over Pd-Ir/SiO₂ at low temperature and high H₂ pressure [49]. Their study inferred that the presence

of Ir in Pd-Ir/SiO₂ facilitated the total hydrogenation of furfural to THFAL whereas monometallic Pd/SiO_2 and Ir/SiO_2 resulted to a low furfural conversion. Moreover, a lower activity exhibited by the physical mixture of Pd/SiO_2 and Ir/SiO_2 further supported the possible synergistic interaction between Pd and Ir in the bimetallic Pd-Ir catalyst which followed to the higher catalytic activity of Pd-Ir/SiO₂. Further, Ir/SiO_2 could not facilitate the hydrogenation of furfuryl alcohol to THFAL when furfuryl alcohol was employed as a substrate. These observations showed that the presence of Ir metal in Pd-Ir/SiO₂ apparently assisted to the adsorption of C=O group along with the adsorption of furfur with the prevention of different side reactions.

Analogously, several Pt-based catalysts have shown selective production of different high-quality hydrogenated products from biomassderived furans [96-106]. In this direction, Chen et al. (2016) achieved chemoselective hydrogenation of furfural to furfuryl alcohol over Pt@TECN (TECN: carbon nitride nanosheets) [96]. The study inferred that the chemoselectivity for C=O bonds hydrogenation was due to the adsorption of furfural over Pt catalyst through C=O bond. Further, the observed results suggested a notable effect of solvent polarity on the catalytic hydrogenation reaction. As the highest conversion and selectivity to the desired product (furfuryl alcohol; >99%) was accomplished in water, usage of alcohols (ethanol and 2-propanol) resulted in the acetalization of furfural. Beside polar solvents, the non-polar solvents such as toluene and octane followed to a very poor furfural conversion. Analogously, Merlo et al. (2009) noticed the low conversion of furfural in non-polar solvents such as toluene and hexane over Pt/SiO₂ catalyst which was probably because of lower H₂ solubility in nonpolar solvents [97]. Luo et al. (2016) reported the role of H₂ gas pressure on the catalytic hydrodeoxygenation of furfural over Pt/C catalyst [98]. The study revealed that lower H_2 pressure led to decarbonylation of furfural to furan, however, at higher pressure hydrodeoxygenation dominated and resulted to the formation of 2-MF, which was assigned to the difference in the coverage of H_2 on the metal surface. In this context, the study suggested that in the presence of H₂ gas the adsorption configuration of furfural changed on the surface of metal catalyst where in the absence of H_2 , furfural preferentially adsorbed in a horizontal manner while it adsorbed perpendicularly in the presence of H_2 [107].

To upgrade biomass-derived furans, different monometallic and bimetallic heterogeneous Ru catalysts have also exhibited high efficacy for the hydrogenation [108-115]. Nagpure et al. furans (2015) explored hydrogenolysis of 5-HMF to DMF over Ru in different solvents such as protic (2-propanol), aprotic (THF and 1,2-dimethoxyethane) as well as non-polar (toluene) [109]. The study revealed the lowest hydrogenolysis of 5-HMF in toluene which was attributed due to the competitive adsorption of reactant as well as solvent on the surface of the catalyst. In this regards, reported studies suggested that this drawback of toluene can be resolved by controlling adsorption overlapping degree of π molecular orbitals of carbon with Ru dorbitals [116]. In the hydrogenating upgradation, Au sub-nano cluster supported on Al_2O_3 resulted to a selective hydrogenation of carbonyl group over ring hydrogenation of 5-HMF to BHMF where the amphoteric behavior of Al₂O₃ support followed to a high BHMF yield while acidic support resulted to furan ring opening [117]. Furthermore, results inferred that the small particles resulted in higher catalytic performance towards 5-HMF hydrogenation because of high unsaturated Au content associated with the small size Au cluster. Moreover, the observed high catalytic activity of Au catalyst for hydrogenation of 5-HMF was assigned to feasible adsorption of H₂ (enhanced by the unsaturated Au atoms) and facile C=O adsorption on Au clusters through π back donation. Similarly, *Li et al.* (2015) observed that the electron-rich Au particles in Au/Al_2O_3 catalyst resulted to enhance the selective hydrogenation of furfural to furfuryl alcohol [118].

Different furan ring-open products also have wide applications in diverse fields [119, 120]. LA, one of the most important open ring products, has shown diverse approaches in the production of several pharmaceuticals, liquid fuel, green solvents, and many more [25]. Furthermore, 1,2-pentanediol (1,2-PeD) is also accounted as an important leading chemical for the synthesis of polyesters and polyurethanes. Therefore, various catalysts involving different metals such as Pt, Pd, Ru, Ir, Re and Ni have explored for the production of diverse open ring products from biomass-derived furans [121-133]. Mizugaki et al. (2014) achieved an efficient transformation of furfural to

1,2-PeD over hydrotalcite supported Pt nanoparticles [123]. The study inferred that the high yield of open ring 1,2-PeD was due to the cooperation between Pt nanoparticles and hydrotalcite support, where basicity of hydrotalcite led to intense interactions between the hydroxyl group of the intermediate furfuryl alcohol and the support whereas furan ring interacted to Pt metal. *Jenness et al.* (2016) employed DFT and high-resolution electron energy loss spectroscopy (HR-EELS) to study the reaction path for hydrogenolysis of furans over Ir surface [124]. They observed that fully saturated furan ring resisted to hydrogenolysis kinetically while partially saturated furan ring at specific position facilitated hydrogenolysis for the selective production of diols. Moreover, the study revealed that selectivity of open ring diols, terminal or secondary, was controlled by the electron density on the aromatic π system which can be altered by the reduction or oxidation of side chains present on furan ring.

Besides furans, aldol adducts of furans have also been explored to produce long-chain alkanes (C_8 - C_{15}) and different value-added chemicals (Scheme 1.4) [134-144]. In this way, Sutton et al. (2013) attained one pot twostep selective conversion of furan aldol adducts to linear alkane over Pd/C and La(OTf)₃ where Pd catalyst assisted conversion of aldol adducts to polyketone in the presence of glacial acetic acid while La(OTf)₃ assisted to transform polyketone into alkane [135]. The study inferred that the acidic sites in the catalyst facilitated the removal of C=O bonds, a crucial step to produce alkanes, through diverse reaction paths (reduction, dehydration and hydrogenation). Similarly, Chatterjee et al. (2010) employed Pd-based catalysts for the transformation of furan/acetone aldol adducts to linear alkanes using supercritical carbon dioxide and 4 MPa H₂ at 80 °C [142]. The study inferred that the transformation of furan derivative to alkanes proceeded through furan rings hydrogenation [142]. Besides different Pd catalysts, Pt and Ru based catalysts have also displayed high efficacy towards the transformations of furan/acetone aldol adducts to high-quality chemicals. In this direction, Feba efficient et al. (2016)achieved an hydrogenation/hydrodeoxygenation of furfural/acetone aldol adducts to ntridecane over Pt/Al₂O₃ catalyst [143]. Further, Luska et al. (2016) observed that dilution of Ru catalyst by Fe followed to the formation of the highly active bimetallic FeRu@SILP catalyst (SILP: supported ionic liquid phase) which led to a selective hydrogenation of furfural/acetone aldol adduct at 100 $^{\circ}$ C and 20 bar H₂ [144]. The study revealed that the partial incorporation of Fe in Ru catalyst (FeRuNPs@SILP) led to enhance C=O bond hydrogenation over furan ring hydrogenation where the activity of FeRuNPs@SLIP was four times higher than the monometallic RuNPs@SILP catalyst [144].



Scheme 1.4. Schematic representation for the conversion of biomassderived furans to long chain hydrocarbons *via* condensed products.

1.3.2.2. Oxidative upgradation

Oxidative upgradation of biomass-derived furans is also one of the noteworthy approaches to produce different industrially applicable fine chemicals (Scheme 1.5). Among various oxidized products, FDCA is a prominent oxidized product of 5-HMF which has shown high potential in the production of bio-based polymers, cognate to polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) produced by petroleum-derived terephthalic acid [145, 146]. Moreover, DFF (a partially oxidized product of 5-HMF) is also a significant starting material to be used for the synthesis of drugs, polymers, fungicides and many other valuable chemicals [147-151].



Scheme 1.5. Schematic representation for the oxidation of 5-HMF.

Diverse reaction parameters such metal surface, particles size, nature of support, pH of the reaction mixture, solvent (polar or non-polar), oxygen pressure and others have highly influenced catalytic oxidation of furans. As Au has high affinity towards the oxidation reactions, different Au-based catalysts have been thoroughly studied for the oxidation of biomass-derived furans, particularly for the oxidation of 5-HMF [152-167]. For instance, Casanova et al. (2009) achieved an efficient oxidative esterification of 5-HMF to furan-2,5-dimethylcarboxylate (>99% selectivity) over Au nanoparticles supported on nanoparticulated ceria (Au/CeO₂) using 10 bar O₂ at 130 °C in methanol [153]. They observed a promotional role of CeO₂ support in Au/CeO₂ as compare to other supports (Fe₂O₃, TiO₂ or active carbon catalyst) which was due to an oxygen carrier behavior of CeO₂ through releasing and adsorbing oxygen atoms by Ce⁺⁴/Ce⁺³ redox reaction. Furthermore, Au/TiO₂ have also exhibited higher catalytic affinity for the oxidation of 5-HMF to FDCA among various explored catalyst (Pt/C, Au/TiO₂, Ru/C, Rh/C and Pd/C) [155]. The study inferred that pH of the reaction mixture and the surface of the metal catalyst has the significant effect on the catalytic oxidation reaction [155]. Results revealed that lower pH (\leq 7) favored the oxidation of alcoholic group of 5-HMF in comparison to the formyl group, however, higher pH (\geq 13) resulted in sluggish oxidation of alcoholic group. Furthermore, studies suggested that presence of base additives enhanced the FDCA production through obstructing of the catalyst deactivation which occurs due to the acid formation during the catalytic reaction [157, 158]. Ardemani et al. (2015) explored Au nanoparticles based catalyst supported on alkali-free Mg-Al hydrotalcite, Au/HT, for the oxidation of 5-HMF and observed the influence of the soluble base on the catalytic oxidation reaction *[159]*. The results inferred that the oxidation of 5-HMF over Au/HT in the absence of additional soluble base like NaOH followed to the oxidation of carbonyl group and resulted to 5-hydroxymethyl-2-furancarboxylic acid (HFCA). The study revealed that oxidation of alcoholic group and production of FDCA was very stagnant with Au/HT catalyst which was similar to different other Au-based catalysts *[160]*. Further, HT displayed a very small influence on the formation of FDCA, however, the addition of Mg(OH)₂ led to enhance the yield of FDCA. In the same way, increasing pH by NaOH remarkably increased the oxidation of 5-HMF and revealed a pivotal role of the soluble base to attain high yield of desired FDCA.

Further, Davis et al. (2012) studied the mechanistic path for the oxidation of 5-HMF to FDCA over Pt and Au catalysts with labelled reagents $^{18}\text{O}_2$ and H_2^{18}O [161]. The results inferred that there was no incorporation of ¹⁸O atom in HFCA (major product) when the catalytic oxidation of 5-HMF was carried out using ${}^{18}O_2$ in $H_2{}^{16}O$ over Au/TiO₂ catalyst while the absence of O₂ resulted to both oxidation and reduction of 5-HMF through Cannizzaro reaction and followed to the formation of HFCA and BHMF under basic reaction conditions. Furthermore, catalytic reaction carried out using ${}^{16}O_2$ and $H_2^{18}O$ resulted to the incorporation of two ¹⁸O atoms in HFCA and multiple ¹⁸O atoms in FDCA which inferred that the oxidation of 5-HMF pursued via the formation of germinal diol (Figure 1.5). Similarly, oxidation of 5-HMF over Pt/C exhibited no incorporation of labelled oxygen with ${}^{18}O_2$ and $H_2{}^{16}O$ in oxidized products (HFCA and FDCA); however, the presence of ${}^{16}O_2$ pressure in H₂¹⁸O resulted to the formation of HFCA with two ¹⁸O atoms and FDCA with four ¹⁸O atoms. These observations revealed a pivotal role of water in the oxidation reaction.

In the same direction, a base-free oxidation of 5-HMF to FDCA (94% selectivity) have efficiently explored over bimetallic Au-Pd nanoparticles supported on functionalized carbon nanotube under aqueous reaction conditions [164]. The study suggested that the organic support assisted to the adsorption of 5-HMF and other oxidized intermediates like DFF and 5-formyl-2-furancarboxylic acid (FFCA) where carbon nanotube (sp²-bonded carbon

surfaces) interacted with furan ring of the reactant or intermediates and followed to enhanced 5-HMF oxidation. Moreover, the study expected that functional groups on carbon nanotube surface (carbonyl/quinone and carboxyl groups) may also play an important role to adsorb 5-HMF and different intermediates which led to increasing the catalytic oxidation of 5-HMF. Analogously, Pt-based catalysts supported on functionalized activated carbon (oxygen containing functional groups such as carboxyl group) showed higher efficiency towards the oxidation of 5-HMF to FDCA [168].



Figure 1.5. Proposed mechanistic pathways for the oxidation of 5-HMF to FDCA in the presence of base (OH⁻) over Pt or Au catalyst under aqueous reaction conditions. (Reprinted with the permission from Ref. 161; Copyright 2012, Royal Society of Chemistry).

Although Au-based catalysts displayed high performance for the oxidative upgradation of 5-HMF and furfural, these also have gone through an easy deactivation due to organic compounds, particularly in the presence of carboxylic acid based products [167]. In this contrast, Pd catalysts have shown high efficacy and stability in the oxidation reaction of biomass-derived furans [169-177]. Siyo et al. (2014) achieved an efficient aerobic oxidation of 5-HMF to FDCA (90% yield) over PVP stabilized Pd nanoparticles (PVP-Pd NPs)

catalysts with NaOH to alkaline reaction conditions at 90 °C and 35 mL/min O_2 flow [169]. They observed that O_2 flow rate affect the catalytic reaction where high O_2 flow (115 mL/min) might result to deactivate Pd nanoparticle by the formation of metal oxide on the catalyst surface, however, a very low O_2 flow (4 mL/min) might deactivate Pd nanoparticles through irreversible adsorption of reaction intermediate like HFCA on the surface of catalyst. Further, *Siyo et al.* (2014) supported PVP stabilized Pd nanoparticle on the different oxide (TiO₂, γ -Al₂O₃, KF/Al₂O₃, and ZrO₂/La₂O₃) and attained a highly active and stable catalyst to the catalytic aerobic oxidation of 5-HMF [170]. Among all, Pd/ZrO₂/La₂O₃ displayed higher catalytic performance as well as stability in comparison to different other supports and resulted to higher selectivity to desired FDCA under alkaline aqueous reaction conditions using O₂ flow at 363 K. The superior activity assisted by ZrO₂/La₂O₃ support was assigned to obstruction of Pd nanoparticles aggregation in the presence of ZrO₂/La₂O₃.

Beside different catalysts, currently, magnetically separable catalysts have attained huge attention due to the easy separation through external magnet and reusability for forward catalytic reaction. In this way, different magnetically separable Pd-based catalysts have been explored for the catalytic oxidation of biomass-derived furans [171-173]. Mei et al. (2015) employed aerobic oxidation of 5-HMF over graphene oxide supported Pd nanoparticles (C-Fe₃O₄-Pd) and accomplished a high yield of FDCA where studied C-Fe₃O₄-Pd catalyst exhibited high stability and reusability under employed reaction conditions and could be separated using an external magnet from the reaction mixture after every catalytic run [171]. Similarly, *Zhang et al.* (2015) developed an efficient γ -Fe₂O₃@HAP-Pd(0) catalyst for the oxidation of 5-HMF to FDCA which showed high stability and recovery through magnetic separation and led to reuse of catalyst for five catalytic runs without any significant loss in the catalytic activity [172].

Analogous to Au and Pd, Pt-based catalysts have also exhibited high catalytic activity towards the oxidation reaction [178-181]. In this direction, an efficient oxidation of 5-HMF to FDCA (98% yield) was achieved over Pt nanoparticles supported on $Ce_{0.8}Bi_{0.2}O_{2-\delta}$ [181]. The Study showed an

important role of support in the catalytic oxidation reaction where Pt nanoparticles generate Pt-alkoxide intermediate that in the presence of OH⁻ ion led to β -H elimination while the presence of Bi in ceria increased the oxygen reduction and peroxide intermediate cleavage which assisted oxidation of 5-HMF to FDCA (Figure 1.6). Analogously, *Rass et al. (2013)* observed that addition of bismuth, *in-situ* or *ex-situ*, promoted the catalytic activity of Pt catalyst towards the oxidation of 5-HMF and inhibited to the deactivation of Pt catalyst *[168]*. The observed increased catalytic activity of Pt catalyst in the presence of Bi was assigned to the interaction between bismuth and π electrons of the furanic ring. Moreover, oxophilic nature of bismuth might also assist the adsorption of geminal diol intermediate on Pt catalyst surface for the dehydrogenation of hydroxymethyl side chain.



Figure 1.6. Proposed mechanism for the oxidation of 5-HMF under alkaline aqueous reaction. CeBi* illustrate oxygen vacancy incorporated with the bismuth. (Reprinted with the permission from Ref. 181; Copyright 2015, Royal Society of Chemistry).

Beside different metal catalyst, a highly selective catalytic oxidation of 5-HMF to DFF was attained over Ru clusters supported on activated carbon (Ru/C) [182]. Among various explored supports (activated carbon, Mg₂AlO_x, MgO, Al₂O₃, ZSM-5, TiO₂, CeO₂ and m-ZrO₂ having different acidity-basicity and redox surface properties), activated carbon with inert nature showed the highest selectivity to DFF as well as suppressed degradation and polymerization of 5-HMF. Furthermore, *Yi et al. (2016)* explored the oxidation of 5-HMF to FDCA over Ru/C and revealed that a strong base like NaOH resulted to the decomposition of 5-HMF and followed to lower yield of FDCA

while the presence of a weak base (CaCO₃) increased the yield of FDCA by neutralizing FDCA rather than involving as a base in the catalytic reaction *[183]*.

With the avail of the literature, we designed and developed highly efficient homogeneous as well as heterogeneous metal catalysts and explored to transform biomass-derived furans to different value-added chemicals.

1.4. Organization of thesis

In recent years, catalytic transformation of biomass-derived furans has taken much more considerations for the selective production of fuel components and different value-added chemicals. The aim of the works included in this thesis was to develop cost-effective high-performance metal catalysts (homogeneous and heterogeneous catalyst) for the upgradation of biomass-derived furans under simple and eco-friendly reaction conditions. This thesis is covered with different chapters as follows:

Chapter 1 includes a brief introduction about catalysis and biomass-derived compounds along with biomass-derived furans. The chapter is covered with background abridgment for catalytic upgradation of biomass-derived furans and the importance of different transformed compounds in the diverse fields.

Chapter 2 summarizes the instrumentation used in the studies those are included in this thesis.

Chapter 3 involves design and synthesis of water-soluble arene-ruthenium(II) complexes for catalytic transformation of biomass-derived furans to valuable ketoacid (levulinic acid; LA) and diketones (1-hydroxyhexane-2,5-dione; 1-HHD, 3-hydroxyhexane-2,5-dione; 3-HHD and hexane-2,5-dione; HD). The chapter is also included the mechanistic study for catalytic transformations.

Chapter 4 involves design and synthesis of bimetallic $Ni_{1-x}Pd_x$ ($0.10 \le x \le 0.75$) alloy nanoparticles for the catalytic aerial oxidation of biomass-derived furans. In this study, the effect of Ni/Pd molar ratio was also explored for the catalytic oxidative upgradation.

Chapter 5 involves design and synthesis of M-Pd (M = Ni, Cu or Co) nanocatalyst supported on *in situ* generated Mg(OH)₂ nanoflakes for the catalytic aerial oxidation of 5-hydroxymethyl-2-furfural (5-HMF) to furan-2,5dicarboxylic acid (FDCA) without any external base additive. The study included the effect of support (acidic or basic) and Ni/Pd molar ratio on the catalytic oxidation of 5-HMF. The synthesized FDCA was further explored for the preparation of different furan diesters; precursors for bio-based polymers and plastics materials.

Chapter 6 involves room temperature catalytic hydrogenation of biomassderived furans and furan-acetone aldol adducts over bimetallic Ni-Pd alloy nano-catalyst. The chapter also covers the effect of Ni/Pd molar ratio on the catalytic hydrogenation of furans.

Chapter 7 summarizes the work included in this thesis, importance and future scope of the work.

1.5. References

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Chapter 2: Materials and Instrumentation

2.1. Introduction

In this chapter, materials and instruments employed in the different projects of the thesis are discussed.

2.2. Materials

All furans [2-furfural (99%), 5-hydroxymethyl-2-furfural (99%), 5-methyl-2furfural (99%), 3-furfural (>97%), 2-furfuryl alcohol (98%), 2,5dimethylfuran (99%)], metal salts [Ruthenium(III) chloride hydrate (99.98%), Potassium tetrachloropalladate(II) (98%), Nickel(II) chloride hexahydrate (98%)], deuterated solvents [Chloroform-d (99.8%), Acetone-d6 (99.9%), sulfoxide-d6 (≥99%), Deuterium oxide Dimethyl (99.9%)] and Polyvinylpyrrolidone (average mol. wt. 40,000) used in the studies included in this thesis were purchased from Sigma Aldrich. Sodium borohydride, fructose, and formic acid were purchased from Alfa Aesar. All solvents were purchased from Merck and SD Fine.

2.3. Instrumentation

2.3.1. NMR Spectroscopy

¹H NMR (400 MHz), and ¹³C NMR (100 MHz) spectra were recorded on Bruker Avance 400 spectrometer at 298 K using tetramethylsilane (TMS) as an external standard and Chloroform-d (CDCl₃), Acetone-d6, Dimethyl sulfoxide-d6 (DMSO-d6) or Deuterium oxide (D₂O) as a solvent. Chemical shifts in ¹H and ¹³C spectra were reported in parts per million (ppm). In ¹H NMR, chemical shifts are reported relative to the residual solvent peak (CDCl₃; singlet at 7.26 ppm, Acetone-d6; center of quintet at 2.04 ppm, DMSO-D6; center of quintet at 2.49 ppm, D₂O; singlet at 4.75 ppm). ¹³C NMR chemical shifts are also reported relative to the solvent residual peak (CDCl₃; center of triple at 77.0 ppm, Acetone-d6; center of Septet at 29.80 ppm, DMSO-d6; center of Septet at 39.50 ppm). Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), quint (quintet), sep (septet) and the coupling constants *J*, are given in Hz.

2.3.2. Mass Spectrometry

High resolution mass spectra (HRMS) and electrospray ionization mass spectra (ESI-MS) were recorded on Brucker-Daltonics, microTOF-Q II mass spectrometer using positive and negative mode electrospray ionizations.

2.3.3. UV-vis Spectroscopy

UV-Vis absorption spectra were recorded in a quartz cuvette (10×10 mm) using a Varian UV-Vis spectrophotometer (Carry 100 Bio) and were corrected using solvent absorption as the baseline.

2.3.4. Single Crystal X-ray Diffraction Studies

Single crystal X-ray structural studies were executed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Using graphite-monochromated Mo K α radiation ($\lambda \alpha = 0.71073$ Å) based diffraction, data were collected at 150(2) K by the standard 'phi-omega' scan techniques, then scaled and reduced using CrysAlisPro RED software. The extracted data were evaluated using the CrysAlisPro CCD software. The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on *F2* [1]. The positions of all the atoms were determined by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2*Ueq* of their parent atoms. Crystal structures were drawn with the help of ORTEP-3. The CCDC numbers for reported Ru-complexes are 1401711 and 1402536.

2.3.5. Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) measurements are performed on the dried particles using a Rigaku SmartLab, Automated Multipurpose X-ray Diffractometer at 40 kV and 30 mA using CuK α radiation ($\lambda = 1.5418$ Å).

2.3.6. Transmission Electron Microscopic (TEM)

Transmission Electron Microscopic (TEM) imaging was carried out using PHILIPS CM 200 with operating voltages 20-200kv and resolution 2.4 Å.

High-resolution transmission electron microscopic (HR-TEM) imaging, Elemental mapping and energy dispersive X-ray spectroscopy (EDS) analysis were performed on FEI Tecnai G2, F30 TEM with operating voltage of 200 kV.

2.3.7. Scanning electron microscopy (SEM)

Scanning electron microscopic (SEM) images and elemental mapping data were collected with a Supra55 Zeiss (operating voltage 5 kV) equipped with an Oxford instrument EDS X-ray spectrometer.

2.3.8. Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were performed on the Metler Toledo thermal analysis system. The measurements were done at heating rate of 10 °C/minute and heated upto 800 °C.

2.3.9. Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

ICP-AES analyses were carried out on ARCOS, simultaneous ICP spectrometer of SPECTRO analytical instruments.

2.3.10. X-ray photoelectron spectroscopy (XPS)

XPS analyses were performed over Kratos Analytical, UK (SHIMADZU group), Model: AXIS Supra, having Two chamber ultra-high vacuum system, Analysis chamber (< 2.0 x 10^{-9} Torr) and Sample load-lock chamber (< 5.0 x 10^{-8} Torr), automated sample transfer mechanism with five-axis sample manipulator and monochromatic (Al K α) 600 W X-ray source; 1486.6 eV. The binding energies acquired from the XPS study were analyzed relative to the standard C 1s binding energy as the reference at 284.8 eV.

2.3.11. Gas chromatography-mass spectrometry (GC-MS)

GC-MS analysis was performed on Shimadzu GCMS-QP2010 Ultra with EI source in MS using Rtx-5MS column and Helium as a carrier gas. For the GC-MS analysis injection temperature was 280 °C with injection in spilt mode,

column oven temperature held at 40 °C for 5 min and then increased upto 280 °C at the rate of 20 °C/min and kept hold for 13 min at 280 °C.

2.4. References

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3.1 Introduction

The development of new methodologies and catalysts for the transformation of biomass and biomass-derived compounds into biofuel components is highly desirable to reduce the global dependence on fossil fuel resources. Moreover, these transformations of biomass can also produce several value-added chemicals for potential applications in the chemical industries. However, direct usage of biomass is considered unsuitable so far [1-7]. In this regard, furans, an important feedstock of biomass obtained by the selective dehydration of hexose and pentose sugars, are considered as an important resource for the production of bio-based chemicals [8-18]. Furan derivatives such as 5-HMF, furfural and 5-MF are used as valuable C5/C6 resources for the synthesis of different valuable chemicals and fuel components based on Levulinic acid (LA), succinic acid, ketones, 1,6-hexanediol, cyclopentanone, adipic acid, caprolactam, caprolactone, furoic acid and so on [19-35]. Moreover, C5-C15 alkanes can also be produced by the hydrolytic ring opening and complete hydrogenation of furans and their aldol adducts [35-37]. Ketoacids and diketones have been successfully used to produce several value-added fine chemicals such as esters, alcohols, lactones, amines and cycloketones [38-40]. According to the US-DOE, LA (ketoacid) has been identified as one of the 12 important target chemicals in their biomass programme [41]. Due to the presence of a carbonyl group, a carboxylic group and α -H in LA, various types of compounds can be synthesized by different types of reactions such as halogenation, esterification, hydrogenation, condensation etc. that can be used in drugs, agriculture, food, cosmetics and spice industries (Scheme 3.1) [40]. Looking into the pharmaceutical applications of LA, derivatives of LA, δ -aminolevulinic acid or 5aminolevulinic acid and acyloxyalkyl ester prodrugs of 5-aminolevulinic acid have been engaged in photodynamic therapy (PDT) of tumor like human meningioma (Scheme 3.1) [42-44]. Moreover, the calcium salt of levulinic acid, calcium levulinate has been identified as a new supplement for calcium [40]. δ -Aminolevulinic acid has also been used as a harmless, highly environment compatible, selective and biodegradable photoactivation weedicide which has a vital agricultural application [40]. Levulinates, α angelica lactone and γ -valerolactone, can be employed as perfume materials

and food additives [40]. LA can also be used for the production of liquid hydrocarbon fuels by decreasing oxygen contents through dehydration/hydrogenation and increasing molecular weight through ketonization (Scheme 3.1) [45]. Alternatively, LA can be upgraded to high energy density compounds such as γ -valerolactone or methyltetrahydrofuran for blending with gasoline (Scheme 3.1).



Scheme 3.1. Schematic representation for the transformation of furan derivatives to ketoacid and diketones for potential industrial applications.

Various processes and catalysts have been developed for the transformation of furans into open ring products, but only a few are active at low temperature with high selectivity of the desired product in aqueous medium. For instance, *Girisuta et al. (2006)* reported a kinetic study of acid,

H₂SO₄, catalyzed decomposition of 5-HMF to levulinic acid in the 98-181 °C temperature range [46]. The transformation of furfural, 5-HMF and furfuryl alcohol to LA and its esters was studied by Hu et al. (2013-2015) in the presence of the Amberlyst 70 catalyst in water and methanol at 170 °C [47-49]. They reported that in aqueous medium, polymerization dominates over ring opening; even in the presence of Pd/Al_2O_3 with Amberlyst 70, a lower amount of furfural was converted to methyl levulinate and levulinic acid using 70 bar H₂ at 165 °C in methanol [47-49]. Hydrogenation/hydrolytic ring opening of 5-HMF to the corresponding diketones was reported using Au nanoparticles in the presence of H₃PO₄ [30]. A similar kind of 5-HMF transformation to diketones was also reported over the Pd/C catalyst using CO₂/H₂O at 120 °C [31]. Tuteja et al. (2014) achieved hydrogenolytic ring opening of 5-HMF to 1,6-hexanediol over Pd/ZrP at 140 °C using formic acid as a hydrogen source [33]. However, Gorbanev et al. (2011) studied the conversion of 5-HMF using O_2 with 2.5 bar pressure in the presence of the Ru(OH)_x/Al₂O₃ catalyst and achieved 25% LA at 140 °C [50]. Furthermore, Xu et al. (2015) investigated the catalytic transformation of biomass-derived 5-HMF and its derivatives to diketones using Cp*-Ir(III) complex based catalysts under 20 bar pressure of H₂ gas and 110 °C [51]. The above results inferred that so far the hydrogenation/ring opening of furans was acquired under strident reaction conditions such as usage of H_2 gas with high pressure and high temperature. Therefore, new catalytic processes have to be optimized to achieve high activity and selectivity for the desired product under moderate reaction conditions.

Over a period of years, arene-ruthenium(II) complexes have been established as an efficient and active type of catalyst for the hydrogenation of carbonyl groups in ketones, aldehydes, esters and C-N double bonds in imines [52-56]. Among several H-donor sources used for the hydrogenation reaction, formic acid offers unique properties. Being a non-toxic organic acid, formic acid not only served the demand of a H-donor for hydrogenation, but also it can tune the acidity by delivering H^+ ions. Moreover, the usage of water as a solvent facilitated the hydrolytic ring opening of furans as well as offered green and clean reaction conditions. Acquainted with the available facts, in this study we investigated highly efficient, recyclable and water-soluble homogeneous 8-aminoquinoline coordinated arene-ruthenium(II) complexes for the catalytic transformation of furan derivatives such as furfural, 5-HMF and 5-MF to a ketoacid; LA, and diketones; 1-hydroxyhexane-2,5-dione (1-HHD), 3-hydroxyhexane-2,5-dione (3-HHD) and hexane-2,5-dione (HD) in the presence of subsidiary amount of formic acid under moderate reaction conditions (Scheme 3.2). Moreover, time-scaled UV-visible spectroscopic studies were performed to observe the progress of the catalytic transformation reaction. Using ¹H NMR spectroscopic studies and several other experiments, attempts were made to identify the key intermediate of the catalytic reaction. Herein, we also reported the structural characterization of the highly active 8-aminoquinoline coordinated arene-ruthenium(II) complexes engaged with the catalytic transformation of furan derivatives using single-crystal X-ray diffraction studies.



Scheme 3.2. Catalytic transformation of furans to ketoacid and diketone based open ring compounds by arene-ruthenium(II) catalysts.

3.2. Results and discussion

3.2.1. Synthesis of arene-ruthenium complex based catalysts

To perform ruthenium catalyzed transformation of furans in water, we first synthesized highly water soluble arene-ruthenium(II) complexes containing a chelating 8-aminoquinoline ligand (Scheme 3.3). The 8-aminoquinoline coordinated arene-ruthenium(II) complexes $[(\eta^6\text{-arene})\text{RuCl}(8\text{-}aminoquinoline)]\text{Cl}$, **[Ru]-1** ($\eta^6\text{-arene} = \eta^6\text{-benzene}$) and **[Ru]-2** ($\eta^6\text{-arene} = \eta^6\text{-p-cymene}$) were obtained, using the reported process with some

modifications [56], in quantitative yield from the reaction of arene-ruthenium dimer precursors $[{(\eta^6-\text{benzene})\text{RuCl}_2}_2]$ and $[{(\eta^6-p-\text{cymene})\text{RuCl}_2}_2]$, respectively, with 8-aminoquinoline in methanol for 4 h at room temperature. The analogous of **[Ru]-2** were also synthesized $[(\eta^6-p-\text{cymene})\text{Ru}(\text{PPh}_3)(8-\text{aminoquinoline})]2\text{Cl}([$ **Ru]-3** $), <math>[(\eta^6-p-\text{cymene})\text{RuCl}(2,2'-\text{bipyridine})]\text{Cl}([$ **Ru]-4** $) and <math>[(\eta^6-p-\text{cymene})\text{RuCl}(8-\text{hydroxyquinoline})]([$ **Ru]-5**) [56-58].



Scheme 3.3. Schematic representation for the synthesis of areneruthenium(II) complexes.

The water soluble red-brown and orange-brown colored complexes [Ru]-1 and [Ru]-2, respectively, were characterized by ¹H and ¹³C NMR spectroscopy, elemental analysis and ESI-MS techniques. The ¹H NMR spectra of [Ru]-1 and [Ru]-2 depicted a downfield shift of the protons of 8aminoquinoline in comparison to the free uncoordinated ligand, which is consistent with the coordination of 8-aminoquinoline with the Ru center [59, 60]. Structural characterization of the complexes [Ru]-1 and [Ru]-2 was further confirmed by single-crystal X-ray diffraction of the most appropriate crystals of both the complexes (Figure 3.1; Table 3.1 and 3.2). The geometry around the ruthenium center in both [Ru]-1 and [Ru]-2 complexes is pseudooctahedral where the n^6 -coordinated arene ring is in the apical position and the remaining three vertices are occupied by two nitrogen atoms of the bidentate ligand 8-aminoquinoline and a chlorine atom [61-63]. The Ru-nitrogen bond distances for the coordinated 8-aminoquinoline are 2.097 Å and 2.094 Å for Ru-N(quinoline) and 2.126 Å and 2.134 Å for Ru-NH₂ in [Ru]-1 and [Ru]-2, respectively [64]. The Ru-Cl bond distances are 2.4085 Å and 2.3984 Å for complexes [Ru]-1 and [Ru]-2 respectively [64]. The Ru-C bond distances are also comparable with other similar complexes [64]. The N1-Ru-N2 bite angles in complexes [**Ru**]-1 and [**Ru**]-2 were found to be 78.66° and 78.71°, respectively [65-67].



Figure 3.1. ORTEP view of the η^6 -arene ruthenium(II) complex **[Ru]-1** and **[Ru]-2** (50% probability thermal ellipsoids). Chloride counteranion and hydrogen atoms (except those of $-NH_2$) are omitted for clarity.

Table	3.1.	Single	crystal	X-ray	refinement	data	for	complexes	[Ru]-1
and [R	u]-2								

	[Ru]-1	[Ru]-2	
Empirical formula	$C_{15}H_{14}CIN_2Ru$	$C_{19}H_{22}Cl_2N_2Ru$	
Formula weight (g mol ⁻¹)	358	450.36	
Temperature (K)	150(2)	150(2)	
Wavelength (Å)	1.5418	1.5418	
Crystal system	Triclinic	Monoclinic	
Space group	<i>P</i> -1	<i>P</i> 21/c	
Crystal size (mm)	0.33 x 0.26 x 0.21	0.33 x 0.26 x 0.21	
<i>a</i> (Å)	7.6680(5)	17.0720(2)	
<i>b</i> (Å)	8.3022(6)	12.30860(10)	
<i>c</i> (Å)	13.5405(6)	9.10130(10)	
α (°)	83.606(5)	90	
β (°)	81.922(5)	100.9000(10)	
γ (°)	70.403(6)	90	
V (Å ³)	802.11(9)	1877.97(3)	
Z	2	4	
$\rho_{\rm calcd} ({\rm g \ cm}^{-3})$	1.76	1.593	

$\mu ({\rm mm}^{-1})$	11.044	9.382
<i>F</i> (000)	424	912
θ range, (°)	3.30 to 72.68	4.46 to 71.35
Index ranges	-9<=h<=6;	-19<=h<=20;
	-9<=k<=10;	-14<=k<=13;
	-16<=l<=16	-11<=l<=9
Completeness to θ_{max}	94.6%	98.4 %
No. of data	4800 / 3022 [<i>R</i> (int) =	11844 / 3586
collected/unique data	0.0300]	[R(int) = 0.0199]
Absorption correction	Semi-empirical from	Semi-empirical
	equivalents	from equivalents
No. of	3022 / 0 / 208	0.2433 and 0.1478
parameters/restraints		
Refinement method	full-matrix least-squares	full-matrix least-
	on F^2	squares
		on F^2
Goodness of fit on F^2	1.093	1.057
R1 [$I > 2\sigma(I)$]	R1 = 0.0489	0.0267
wR2 [$I > 2\sigma(I)$]	0.1363	0.0705
R indices (all data)	R1 = 0.0493, wR2 =	R1 = 0.0271, wR2
	0.1368	= 0.0709
Largest diff peak and hole, e Å ⁻³	2.989 and -4.032	0.628 and -0.723

Table 3.2. Selected bond lengths (Å) for complex [Ru]-1 and [Ru]-2

[Ru]-1		[Ru]-2	
Ru(1)-N(1)	2.097(4)	Ru(1)-N(1)	2.0940(18)
Ru(1)-N(2)	2.126(4)	Ru(1)-N(2)	2.1336(18)
Ru(1)-C(12)	2.164(5)	Ru(1)-C(15)	2.164(2)
Ru(1)-C(14)	2.175(5)	Ru(1)-C(13)	2.167(2)
Ru(1)-C(11)	2.184(5)	Ru(1)-C(16)	2.189(2)
Ru(1)-C(10)	2.186(5)	Ru(1)-C(12)	2.193(2)
Ru(1)-C(13)	2.195(5)	Ru(1)-C(14)	2.198(2)
Ru(1)-C(15)	2.201(5)	Ru(1)-C(11)	2.223(2)
N(2)-H(2A)	2.4085(11)	Ru(1)-Cl(1)	2.3984(6)
N(2)-H(2B)	1.322(7)	N(1)-C(1)	1.325(3)
C(1)-C(2)	1.376(6)	N(1)-C(9)	1.375(3)
C(2)-C(3)	1.443(6)	N(2)-C(8)	1.452(3)

C(3)-C(4)	0.9200	N(2)-H(1N)	0.91(4)
C(4)-C(5)	0.9200	N(2)-H(2N)	0.93(4)
C(4)-C(9)	1.415(7)	C(1)-C(2)	1.408(3)
C(5)-C(6)	1.358(8)	C(2)-C(3)	1.359(4)
C(6)-C(7)	1.404(8)	C(3)-C(4)	1.412(4)
C(7)-C(8)	1.417(8)	C(4)-C(9)	1.411(3)
C(8)-C(9)	1.418(7)	C(4)-C(5)	1.414(4)
C(10)-C(11)	1.374(9)	C(5)-C(6)	1.362(5)
C(10)-C(15)	1.399(8)	C(6)-C(7)	1.412(4)
C(11)-C(12)	1.374(7)	C(7)-C(8)	1.360(3)
C(12)-C(13)	1.411(7)	C(8)-C(9)	1.404(3)
C(13)-C(14)	1.393(9)	C(10)-C(11)	1.498(4)
C(14)-C(15)	1.406(9)	C(11)-C(16)	1.408(4)
	1.409(8)	C(11)-C(12)	1.419(4)
	1.407(8)	C(12)-C(13)	1.405(4)
	1.415(8)	C(13)-C(14)	1.426(4)
	1.403(8)	C(14)-C(15)	1.402(4)
		C(14)-C(17)	1.512(3)
		C(15)-C(16)	1.421(3)
		C(17)-C(19)	1.509(5)
		C(17)-C(18)	1.511(4)

3.2.2. Catalytic transformation of furans into a ketoacid and diketones

One pot catalytic transformation of furans into a ketoacid and diketones was attempted by employing ruthenium catalysts, **[Ru]-1** and **[Ru]-2**, in water under moderate reaction conditions. Initially furfural, an agricultural by-product and readily available furan derivative, was chosen as a model substrate for its transformation into LA in the presence of **[Ru]-1** catalyst. The reaction of furfural with the **[Ru]-1** catalyst (1 mol%) in the presence of 24 equivalents of formic acid gave an excellent conversion with >99% selectivity for LA in 24 h at 80 °C (Table 3.3, entry 1). However, decreasing the reaction temperature to 60 °C or lower (40 °C) resulted in a drastic decrease in the catalytic conversion of furfural (Table 3.3, entries 2 and 3). Interestingly,

complete conversion of furfural to LA was also achieved in the reaction performed with lower formic acid content (12 equiv.) at 80 °C in 24 h. However, further decrease in the formic acid content or the reaction time resulted in lower catalytic conversion of furfural to LA (Table 3.3, entries 5 and 6).

Table 3.3. Optimization of reaction conditions for the catalytic transformation of furfural by arene-ruthenium(II) complexes in aqueous condition. Reaction condition: furfural (1.0 mmol), formic acid (as specified), ruthenium catalyst (1 mol %), water (10 mL).

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	Furfural	τ (°C)	LAÖ	
Entry	Catalyst	HCOOH (equiv.)	$T(^{\circ}C)/t(h)$	Conv./Sel. (%)
1	[Ru]-1	24	80/24	>99/>99
2	[Ru]-1	24	60/24	8/>99
3	[Ru]-1	24	40/24	6/>99
4	[Ru]-1	12	80/24	>99/>99
5	[Ru]-1	6	80/24	46/>99
6	[Ru]-1	12	80/16	68/>99
7	[Ru]-1	12	60/16	2.5/>99
8	[Ru]-2	12	80/16	>99/>99
9	[Ru]-2	12	60/16	23/>99
10	[Ru]-2	12	90/12	>99/>99
11	[Ru]-2	12	100/7	>99/>99
12	[Ru]-2	8	80/16	85/93
13	[Ru]-2	4	80/16	37/91
14	[Ru]-2	2	80/16	21/82
15	[Ru]-2	1	80/16	5/56
16 ^{<i>a</i>}	[Ru]-2	12	80/16	57/>99
17^{b}	[Ru]-2	12	80/16	28/>99
18 ^c		12	80/16	d
19	[Ru]-2	0	80/16	е

^{*a*}0.5 mol % catalyst. ^{*b*}0.25 mol %. ^{*c*}Reaction performed without catalyst. ^{*d*}Unidentified polymeric compounds. ^{*e*}No conversion.

In contrast to the [Ru]-1 catalyst, the [Ru]-2 catalyst appeared to be more efficient (Figure 3.2), as complete catalytic transformation of furfural to LA was achieved with the **[Ru]-2** catalyst at 80 °C in 16 h (Table 3.3, entry 8). Even at 60 °C, the activity of [Ru]-2 was found to be much higher than that of [Ru]-1 under analogous conditions (Table 3.3, entries 7 and 9). Moreover, increasing the reaction temperature to 90 or 100 °C, the reaction completion time can be reduced to 12 and 7 h, respectively (Table 3.3, entries 10 and 11). The lower activity of the benzene complex [Ru]-1 compared with that of the *p*-cymene complex **[Ru]-2** is consistent with the beneficial effect of the donor groups at the arene ligand [56]. Further, an analogous catalytic turnover can be achieved when performing the catalytic reaction with a lower catalyst amount of **[Ru]-2**, TOFs 7.0 h⁻¹ (0.25 mol%), 7.1 h⁻¹ (0.5 mol%) and 6.2 h⁻¹ (1 mol%) (Table 3.3, entries 16 and 17). It is worth mentioning here that the presence of both the ruthenium catalyst and formic acid was found to be essential for the efficient conversion of furfural to LA, as the reaction cannot proceed or end with humin formation, if any of these (the ruthenium catalyst and formic acid) was absent (Table 3.3, entries 18 and 19).



Figure 3.2. Influence of temperature on the catalytic transformation of furfural to LA in the presence of [Ru]-1 and [Ru]-2 catalysts.

3.2.2.1. Effect of catalyst structure on the catalytic transformation of furfural to LA. To further investigate the influence of unique structural advantages of **[Ru]-2** catalysts on its catalytic efficiency, its catalytic activity was compared by performing the reaction using structurally analogous

ruthenium catalysts having 2,2'-bipyridine ([Ru]-4) and 8-hydroxyquinoline ([Ru]-5) ligands, in the place of 8-aminoquinoline, for the catalytic transformation of furfural under the optimized reaction conditions. Interestingly, replacing the 8-aminoquinoline with 2,2'-bipyridine and 8hydroxyquinoline in ruthenium complexes [Ru]-4 and [Ru]-5, respectively, demonstrated a decrease in the catalytic activity in the following order: [Ru]-2 >[Ru]-5 > [Ru]-4 for the catalytic transformation of furfural to LA (Figure 3.3). These results clearly depicted the role of N-H moiety in the observed superior catalytic activity of [Ru]-2 catalysts [56], where, presumably, N-H moiety form hydrogen bonds to bring the furfural in close proximity to the ruthenium center as well as transfer a H^+ ion to a formyl group to assist in the formic acid driven transfer hydrogenation of furfural to furfuryl alcohol [68]. Moreover, replacing the labile chloro group by bulky PPh₃ in [**Ru**]-3 resulted in a significant decrease in the catalytic activity (17%) suggesting that under the reaction conditions the chloro group in the ruthenium catalyst is detached to provide a vacant site for the coordination of water or the formate anion (Figure 3.3).



Figure 3.3. Influence of catalyst on the catalytic transformation of furfural to LA in the presence of different arene-ruthenium(II) complexes. Reaction Conditions: furfural (1.0 mmol), catalyst (1 mol %), formic acid (12 equiv.) and water (10 mL), T = 80 °C.

3.2.2.2. Reaction kinetics and identification of reaction intermediates. A time-scaled UV-visible spectroscopic experiment (0-16 h) was performed to monitor the progress of the catalytic transformation reaction of furfural to LA with the **[Ru]-2** catalyst (1 mol%) in the presence of formic acid (12 equiv.) at

80 °C in water (Figure 3.4). As time progressed, the intensity of the absorption band at 274 nm corresponding to furfural also decreased, which inferred the consumption of furfural. A linear relationship between $\ln(C_t/C_0)$ and the reaction time (on the basis of the absorbance for furfural at 274 nm) was obtained which indicated that the catalytic transformation of furfural to LA followed pseudo-first-order kinetics (rate constant = 3.7×10^{-5} s⁻¹).



Figure 3.4. Time-scaled UV-visible spectra (inset: kinetics profile) for the catalytic transformation reaction of furfural to LA in the presence of **[Ru]-2** (1 mol %) and formic acid (12 equiv.) at 80 °C in water.

Interestingly, during ¹H NMR spectral studies of the catalytic reaction performed with varying content of formic acid (1-12 equiv.) along with the expected product LA furfuryl alcohol, a key intermediate for the catalytic transformation of furfural to LA was also observed. As shown in Figure 3.5, with an increase in the content of formic acid, the relative selectivities for furfuryl alcohol and LA from furfural also varied, where the selectivity towards LA increases while that of furfuryl alcohol decreases. The identification of furfuryl alcohol further strengthened the fact that the catalytic transformation of furfural to LA was proceeding through an initial ruthenium catalyzed hydrogenation of furfural to furfuryl alcohol using formic acid as a hydrogen source. Moreover, the decrease in the selectivity of furfuryl alcohol with increasing formic acid contents indicated that presumably the intermediate furfuryl alcohol underwent formic acid promoted hydrolytic ring opening/hydrogenation to LA.



Figure 3.5. Influence of formic acid (equivalent to furfural) on the [Ru]-2 catalyzed transformation of furfural to LA and identification of the intermediate, furfuryl alcohol.

To further investigate whether the formation route of LA is from furfuryl alcohol hydrolytic ring opening, a new set of experiments was performed under the optimized reaction conditions in the absence of the ruthenium catalyst using furfuryl alcohol as the starting material. Interestingly, a complete conversion of furfuryl alcohol to LA was achieved even in the absence of any ruthenium catalyst (Table 3.4, entry 2). These observations further inferred that the hydrogenation of furfural to furfuryl alcohol is a crucial step to initiate the catalytic transformation of furfural to LA (Scheme 3.4).

Furthermore, to examine whether the activation of formic acid by the ruthenium catalyst has an impact on the observed high conversion of furfural to LA, we examined the decomposition of formic acid using the **[Ru]-2** catalyst in water, without furfural, at 60, 80 and 100 °C. Results indeed inferred that the **[Ru]-2** catalyst activates formic acid and complete conversion of formic acid to H₂ was achieved in 6 and 3 h at 80 and 100 °C, respectively, whereas poor conversion was observed at 60 °C. The observed trend is well in accordance with the activity of the ruthenium catalyst towards furfural transformation to LA (Table 3.3, entries 8, 9 and 11). However, to examine whether the *in situ* generated hydrogen assists the hydrogenation of furfural to furfuryl alcohol, we performed an experiment for the transformation of

furfural using the [**Ru**]-2 catalyst in the presence of H_2 gas at 80 °C under optimized reaction conditions. In contrast to the high activity achieved in the presence of formic acid, replacing formic acid with H_2 gas resulted in no conversion of furfural. This result further supported that the formation of a metal-hydride bond in the presence of formic acid and the –NH moiety of the 8-aminoquinoline ligand facilitated the transfer hydrogenation for the conversion of furfural to furfuryl alcohol.



Scheme 3.4. Plausible reaction pathway for the catalysed transformation of furfural to LA on the basis of ¹H NMR studies.

Moreover, using other short chain organic acids, acetic acid, instead of formic acid, resulted in only traces of conversion even after 16 h at 80 °C. Furthermore, using organic acids with increasing carbon chain, propionic acid, or the bulky organic acid, iso-butyric acid was also found inactive for the conversion of furfural to LA under the optimized reaction conditions. These observations inferred that these acids could not contribute to metal catalyzed transfer hydrogenation. However, the slight conversion was presumably due to the acid catalyzed protonation/hydrolytic ring opening process of furan [69]. Moreover, a facile transformation of furfuryl alcohol to LA with formic acid or even with acetic acid in the absence of ruthenium clearly inferred that the transfer hydrogenation of furfural to furfuryl alcohol is a crucial step which

can take place in the presence of formic acid but not with other organic acids or H_2 gas under our optimized reaction conditions. Furthermore, screening of the formic acid amount (1-12 equiv.) showed that the amount of formic acid also plays an important role in the complete transformation of furfural to LA (Table 3.3, entries 8 and 12-15). Moreover, formic acid played a dual role by acting as a H-donor to facilitate the hydrogenation reaction and by populating H^+ ions in the reaction mixture to promote the hydrolytic ring opening of the intermediate furfuryl alcohol to LA (Scheme 3.4) [70]. Furthermore, water provided an additional advantage as the ruthenium catalysts [**Ru**]-1 and [**Ru**]-2 displayed high aqueous solubility.

3.2.2.3. Catalytic transformation of furan derivatives. The activities of both [Ru]-1 and [Ru]-2 catalysts were further evaluated for the catalytic transformation of other furans having different substituents at 2 and 5 positions such as 5-HMF and 5-MF under the optimized reaction conditions. The results are shown in Table 3.4. Notably, poor conversion of 5-HMF (7% and 31%) to open ring compounds was observed after 16 h with both [Ru]-1 and [Ru]-2 catalysts (Table 3.4, entry 4). However, higher conversion (>99%) of 5-HMF to the corresponding open-ring compounds, 1-HHD, LA and 3-HHD was achieved using [Ru]-2 after 48 h with the relative selectivities of 52% (1-HHD), 21% (LA) and 27% (3-HHD). Although the transformation of 5-HMF to 1-HHD was also reported earlier using other catalysts like Pd/C [32] and Cp*-Ir(III) complexes [51] with elevated temperature (110-120 °C) and/or high H_2 pressure (20 bar), our reported ruthenium catalysts [**Ru**]-1 and [Ru]-2 also facilitated the formation of other important compounds such as 3-HHD and LA, along with 1-HHD, under mild reaction conditions. Analogous to furfural, 5-MF also underwent facile catalytic transformation to the corresponding open ring components in the presence of **[Ru]-2** catalyst (Table 3.4, entry 5). Higher conversion (89%) of 5-MF to 3-HHD and HD with relative selectivities of 92% and 8%, respectively, was achieved with the [Ru]-2 catalyst in 16 h. One of the major products of 5-MF conversion, 3-HHD, also known as Henze's ketol, was previously identified in plant extracts and is also known for its role in human biochemistry [71]. Moreover, the catalytic transformation of 5-HMF and 5-MF was also performed at 100 °C in

the presence of **[Ru]-2** catalyst and it was observed that the reaction time can be considerably reduced.

Table 3.4. Conversion and products distribution for the catalytic transformation of furan derivatives in aqueous medium. Reaction Conditions: furans (1.0 mmol), catalyst (1 mol %), formic acid (12 equiv.) and water (10 mL), T = 80 °C.

Entry	Furans	Time (h)	Products	Conv./ Sel. (%)	Conv./ Sel. (%)
		~ /		[Ru]-1	[Ru]-2
1		16	ОН	68/>99	>99/>99 47 ^a , [62] ^{a, b, c}
2	О	12	ОН	>99	$0/>99^{d}$
3		6		>99	0/>99 ^d
4	но	16	HO O a	7/27:33:40 (a:b:c)	31/27:18:55 (a:b:c)
		48	о он	14/31:41.5: 27.5	>99/52:21:27 (a:b:c)
			O OH c O	(a:b:c)	>99/54:23:23 ^{b,e} (a:b:c)
5		16		30/>99 (a)	89/92:8 (a:b) 67 ^{<i>a</i>} , [75] ^{<i>a, b, c</i>} (a)

^{*a*}Isolated yield. ^{*b*}T = 100 °C. ^{*c*}Time = 7 h. ^{*d*}Reaction performed without catalyst. ^{*e*}Time = 30 h

Studies for the conversion of furan derivatives to open ring compounds have been done particularly in an autoclave using H₂ gas with high pressure and high temperature. *Hu et al.* (2015) investigated that in the presence of Amberlyst 70 furfural convert to polymer in water as well as methanol [47]. They also proposed a mechanism for the synthesis of insoluble polymer from furfural in the presence of acid under aqueous medium [48]. Even in the presence of Pd/Al₂O₃ with Amberlyst 70, only 23.1% and 2.4% yield of methyl-levulinate and levulinic acid was achieved from furfural using 70 bar H₂ at 165 °C in methanol [49]. Furthermore, *Gorbanev et al.* (2011) studied the conversion of 5-HMF in the presence of Ru(OH)_x/Al₂O₃ catalyst and achieved 25% (TOF = 0.8 h⁻¹) to LA at 140 °C [50]. Discrete from these results, we achieved complete conversion of furfural to LA with yield up to 62% (TOF = 8.85 h⁻¹) using 8-aminoquinoline coordinated areneruthenium(II) complexes in water under open atmospheric conditions at 80-100 °C.

3.2.2.4. Thermal stability of ruthenium catalyst. We performed ¹H NMR experiments and thermal gravimetric analysis (TGA) measurements to study the thermal stability of the ruthenium catalysts. In the course of catalyst recyclability test (discussed in a later section), the remarkable stability towards air and water with an extended time period was observed for the [Ru]-2 catalyst. Further to explore the robust activity of the catalyst, thermal stability of ruthenium catalysts, **[Ru]-1** and **[Ru]-2**, in D₂O was tested in a NMR tube. The decomposition of the catalyst was monitored by ¹H NMR taken at certain time intervals (0, 24, 48 and 72 h). Ruthenium catalysts displayed high thermal stability and only traces of decomposition were observed after 72 h of heating at 80 °C, whereas at elevated temperature 100 °C, decomposition of the ruthenium catalyst started even after 24 h. Moreover, the respective TGA graphs of catalysts [Ru]-1 and [Ru]-2 inferred that both the catalysts are stable up to 200 °C (Figure 3.6). The first loss of ~29% from the **[Ru]-2** catalyst in the temperature range 211-304 °C, corresponds to the loss of *p*-cymene ring. Analogously, [Ru]-1 showed the elimination of the benzene ring corresponding to the loss of $\sim 20\%$ in the temperature range 196–299 °C. In view of the high thermal stability and catalytic activity shown by the [Ru]-2





Figure 3.6. Thermal gravimetric analysis (TGA) graph of a) [Ru]-1 and b) [Ru]-2.

3.2.2.5. Recovery and recyclability of ruthenium catalyst. Even if the homogeneous catalyst provides various advantages, catalyst recovery from the reaction limitations. mixture has some However, synthesized 8aminoquinoline coordinated arene-ruthenium(II) complexes having high solubility in water, offered us an opportunity to easily recover the catalyst from the reaction mixture and to reuse it in the further transformation of furfural without any significant loss of the catalytic activity. After individual catalytic run, organic components were extracted from the reaction mixture using an appropriate organic solvent while catalyst remained in the aqueous phase. The aqueous layer was further used for next catalytic run by adding appropriate amount of distilled water, for making the reaction volume 10 mL, furfural and formic acid. Figure 3.7 depicted a high recyclability of [Ru]-2 for the catalytic conversion of furfural to LA up to 4 catalytic runs without any significant loss in the catalytic activity.


Figure 3.7. Recyclability of **[Ru]-2** catalyst for the catalytic transformation of furfural to LA.

3.3. Conclusions

To summarize, we successfully explored the high catalytic performance of 8aminoquinoline coordinated arene-ruthenium(II) complexes, [Ru]-1 and [Ru]-2, for the transformation of biomass-derived furans such as furfural, 5-HMF and 5-MF to ketoacid (LA) and diketones (1-HHD, 3-HHD and HD) based value-added chemicals in the presence of formic acid, as a hydrogen source, under moderate reaction conditions. In the studied ruthenium catalyst, [Ru]-2 catalyst, outperformed and facile catalytic transformation of furfural to LA was achieved with excellent selectivity (>99%) in the presence of formic acid at 80 °C in water. Exploring the catalytic activity of several structural analogues of *p*-cymene ruthenium complex, [Ru]-2 catalyst, with different ligands suggested a unique structure-activity relationship in [Ru]-2, due to the presence of N-H moiety and a labile chloro group, which contributes to the superior catalytic activity of [Ru]-2 catalyst. A plausible catalytic reaction pathway for the conversion of furfural to LA was reasonably proposed on the basis of ¹H NMR results and several other experiments which showed that the formation of furfuryl alcohol, a key intermediate, is a crucial step for the transformation of furfural to LA. Moreover, high aqueous solubility and stability of the studied ruthenium catalysts offered high recyclability of the catalyst. We believe that this study could provide perceptions towards the synthesis of a simple but active catalyst for the transformation of biomassderived compounds to precious chemicals and bio-fuel components, and can be applicable for many other catalytic reactions.

3.4. Experimental Section

3.4.1. General procedure for the synthesis of complexes

3.4.1.1. Arene-ruthenium dimers: Dichloro bridged arene-ruthenium dimers, $[\{(\eta^6\text{-benzene})\text{RuCl}_2\}_2]$ and $[\{(\eta^6\text{-}p\text{-}cymene)\text{-}\text{RuCl}_2\}_2]$, used as precursors for the synthesis of [Ru]-catalysts, were synthesized according to the literature procedures [72,73].

3.4.1.2. Preparation of complex [(η^6 -benzene)**RuCl(8-aminoquinoline**)]**Cl** ([**Ru**]-1): The studied complexes were synthesized using the reported procedure with some modification [56]. In a round bottom flask [{(η^6 -benzene)**RuCl**₂}₂] (0.250 g, 0.5 mmol) and 8-aminoquinoline (0.144 g, 1.0 mmol) were dissolved in methanol (50 mL). The reaction mixture was stirred for 4 h at room temperature. Solution volume was reduced and the red-brown crystals of complex [**Ru**]-1 were grown in solution of methanol and diethyl ether (1:10 v/v). Yield = 85%. ¹H NMR (400 MHz, D₂O): δ (ppm) = 9.57 (d, 1H, J = 8Hz), 8.45 (d, 1H, J = 12Hz), 7.84 (d, 1H, J = 8Hz), 7.75 (d, 1H, J = 4Hz), 7.66-7.57 (m, 2H), 5.96 (s, 6H), ¹³C NMR (100 MHz, D₂O): δ (ppm) = 156.20, 145.30, 139.40, 137.88, 129.27, 128.24, 128.10, 127.12, 123.79, 84.74. MS (ESI) m/z calculated for [(η^6 -benzene)RuCl(8-aminoquinoline)]⁺: 358.9 [M⁺], found 358.0 [M⁺], [(η^6 -benzene)Ru(8-aminoquinoline)]²⁺: 324.0 [M⁺], found 323.0 [M⁺]. Anal. Calcd. for [**Ru**]-1: C, 45.70; H, 3.58; N, 7.11. Found: C, 45.30; H, 4.01; N, 6.90.

3.4.1.3. Preparation of complex $[(\eta^6-p\text{-cymene})\text{RuCl}(8\text{-aminoquinoline})]\text{Cl}$ ([**Ru**]-2): Under the analogous conditions of [**Ru**]-1 preparation, $[(\eta^6-p\text{-}cymene)\text{RuCl}(8\text{-aminoquinoline})]\text{Cl}$ ([**Ru**]-2) complex was synthesized by the reaction of $[\{(\eta^6-p\text{-cymene})\text{RuCl}_2\}_2]$ (0.306 g, 0.5 mmol) and 8-aminoquinoline (0.144 g, 1.0 mmol) in 50 mL of methanol. Yield = 87%. ¹H NMR (400 MHz, D₂O): δ (ppm) = 9.55 (d, 1H, J = 4Hz), 8.51 (d, 1H, J = 8Hz), 7.89 (d, 1H, J = 8Hz), 7.81 (d, 1H, J = 4Hz), 7.72 (m, 1H), 7.65 (t, 1H, J = 8Hz), 6.03 (d, 1H, J = 4Hz), 5.91 (d, 1H, J = 4Hz), 5.80 (d, 1H, J = 4Hz), 5.71 (d, 1H, J = 4Hz), 2.65-2.58 (m, 1H), 2.10 (s, 3H), 1.05 (d, 3H, J = 8Hz), 0.90 (d, 3H, J = 4Hz), ¹³C NMR (100 MHz, D₂O): δ (ppm) = 156.12, 145.27, 139.46, 137.83, 129.27, 128.47, 128.29, 127.36, 124.11, 103.17, 100.83, 84.87, 83.30, 82.68, 82.08, 30.40, 21.19, 21.07, 17.77. MS (ESI) m/z calculated for $[(\eta^6-p-\text{cymene})\text{RuCl}(8\text{-aminoquinoline})]^+$: 415.0 [M⁺], found 415.1 [M⁺], $[(\eta^6-p\text{-cymene})\text{Ru}(8\text{-aminoquinoline})]^{2+}$: 380.0 [M⁺], found 379.1 [M⁺]. Anal. Calcd. for [**Ru**]-2: C, 50.67; H, 4.92; N, 6.22. Found: C, 50.21; H, 4.54; N, 5.96.

 $[(\eta^6-p-\text{cymene})\text{RuPPh}_3(8-$ 3.4.1.4. **Preparation** of complex aminoquinoline)]2Cl ([Ru]-3): Complex [Ru]-3 was synthesized using [Ru]-2. For that 0.050 g (0.081 mmol) of [Ru]-2 and 0.022 g (0.081 mmol) of PPh₃ were dissolved in 20 mL methanol and stirred for 4 h. Yield= 85% ¹H NMR (400 MHz, D₂O): δ (ppm) = 8.39 (d, 1H, J = 4Hz), 8.32 (d, 1H, J = 8Hz), 7.72 (d, 1H, J = 8Hz), 7.68 (d, 1H, J = 8Hz), 7.58-7.50 (m, 2H), 7.44-7.40 (m, 3H),7.26-7.18 (m, 12H), 6.44 (d, 1H, J = 8Hz), 6.34 (d, 1H, J = 8Hz), 6.27 (d, 1H, *J* = 8Hz), 5.21 (d, 1H, *J* = 8Hz), 2.28-2.22 (m, 1H), 1.74 (s, 3H), 1.01 (d, 3H, *J* = 8Hz), 0.42 (d, 3H, J = 8Hz). ³¹P NMR (162 MHz, D₂O): δ (ppm) = 41.27. MS (ESI) m/z calculated for $[(\eta^6-p-\text{cymene})\text{RuPPh}_3(8-\text{aminoquinoline})]^{2+}$: 642.1 [M⁺], found 641.2 [M⁺], $[(\eta^6 - p - \text{cymene})\text{Ru}(8 - \text{aminoquinoline})]^{2+}$: 380.0 [M⁺], found 379.1 [M⁺]

3.4.2. General procedure for the catalytic transformation of furans to ketoacid and diketones: The catalytic transformation of furans was carried out in open atmospheric conditions. For this, furan derivative (1 mmol) was added to an aqueous solution (10 mL) of arene-ruthenium(II) complex (1 mol %) in a round bottom flask and then formic acid (12 equiv.) was added. Reaction mixture was stirred for a desired time at 80 °C in an oil bath. The progress of reaction was monitored by thin layer chromatography (TLC). After the reaction, reaction mixture was extracted with ethylacetate (5 × 10 mL), organic layer was dried over anhydrous Na₂SO₄ and then solvent was evaporated under reduced pressure to get the desired product. The reaction products were identified by ¹H NMR, ¹³C NMR, HRMS and GC-MS. The conversion and selectivities of the products were obtained by ¹H NMR. Isolated yield of the products was also calculated. The aqueous portion of the

reaction mixture, containing arene-ruthenium(II) catalyst, was further used for recyclability experiments.

3.4.3. Spectral data of products obtained by catalytic transformation of biomass-derived furans

ОН

Levulinic acid (**LA**): ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 2.73 (t, 2H, J = 8 Hz), 2.59 (t, 2H, J = 8 Hz), 2.17 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 206.65, 177.53, 37.69, 29.78, 27.64. HRMS (ESI) m/z: calculated 139.04 [C₅H₈O₃ + Na⁺], found 139.036 [C₅H₈O₃ + Na⁺].



3-Hydroxyhexane-2,5-dione (3-HHD): ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.33-4.30 (m, 1H), 3.75 (br, 1H) 2.95 (dd, 1H, $J_1 = 16$ Hz, $J_2 = 4$ Hz), 2.82 (dd, 1H, J = 16 Hz, $J_2 = 4$ Hz), 2.22 (s, 3H), 2.18 (s, 3H), ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 209.15, 207.09, 73.76, 46.11, 30.81, 25.38. HRMS (ESI) m/z: calculated 153.05 [C₅H₁₀O₃ + Na⁺], found 153.05 [C₅H₁₀O₃ + Na⁺].



1-Hydroxyhexane-2,5-dione (1-HHD): ¹H NMR (400MHz, CDCl₃): δ (ppm) = 4.31 (s, 2H), 2.82 (t, 2H, *J* = 8 Hz), 2.61 (t, 2H, *J* = 8 Hz), 2.17 (s, 3H).

Hexane-2,5-dione (HD): ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 2.69 (s, 4H), 2.18 (s, 6H).

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3.5. References

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Chapter 4: Catalytic aerial oxidation of biomass-derived furans to furan carboxylic acids in water over bimetallic Ni-Pd alloy nanoparticles

4.1. Introduction

The conversion of biomass into fuel and chemicals has been developed in the last few decades as an efficient methodology to substitute, partial or full, the fossil fuel and petroleum products [1-12]. Huge efforts are currently devoted towards the development of new and efficient methodologies to achieve the maximum yield of platform chemicals from biomass or biomass-based chemicals [7-12]. In this context, biomass-based chemicals such as furans, 2furfuraldehyde (furfural), 2-furfuryl alcohol (furfuryl 5alcohol), hydroxymethyl-2-furfural (5-HMF), 5-methyl-2-furfural (5-MF) and 5methyl-2-furfuryl alcohol (MFA) have received attention. Particularly, 5-HMF is regarded as the most promising key platform substrate for the production of value-added fine chemicals and fuel components in several catalytic processes [13-30]. One of the important transformations includes the selective oxidation of furfural and its derivatives to obtain important chemicals such as 2-furoic acid, furan-2,5-dicarboxylic acid (FDCA) and 2,5-diformylfuran (DFF) (Scheme 4.1), for diverse applications in the food, pharmaceuticals and polymer industries [31-37]. For example, 2-furoic acid is widely used as a preservative and flavouring agent [32-34]. FDCA, obtained from the selective oxidation of 5-HMF, has been identified as the top-12 value-added chemicals from biomass [35]. FDCA has shown potential to serve as a bio-based polymer building block by replacing petroleum-derived terephthalic acid for the production of crucial polymers such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) [36].



Scheme 4.1. Schematic representation of the oxidation of biomass-derived furans to furan carboxylic acids.

Au-nanoparticles-based catalysts have been widely used in oxidation reactions because of their high affinity towards oxygen [38, 39]. Therefore, several groups have explored monometallic Au and bimetallic Au-Cu and Au-Pd catalysts for the selective oxidation of 5-HMF to FDCA [40-47]. As the Au catalysts showed some deactivation in the presence of carboxylate products,

most of these reactions were performed under the high pressure (20 bar) of O₂ gas and in several cases with strong base, NaOH, to achieve high selectivity to FDCA [39-47]. Other than Au catalysts, Pt-, Ru- and Pd-based catalysts were also reported in the oxidation of 5-HMF. In this direction, Pt-based catalysts have exhibited high efficiency for the complete oxidation of 5-HMF to FDCA, however, in the presence of a strong base and high pressure of O_2 or air [39, 48-55]. For example, recently Han et al. (2016) explored the oxidation of 5-HMF to FDCA over Pt/C-O-Mg catalyst at 110 °C and 1.0 MPa O₂ gas [55]. On the other side, Ru catalyst also showed selective oxidation of 5-HMF to DFF at 110 °C with high pressure of O₂, 2.0 MPa, in organic solvents while usage of water resulted in the synthesis of FDCA [56, 57]. Similarly to Au, Pd catalysts displayed high activity towards the oxidation of alcohols and carbonyl compounds [58-60]. Several Pd nanoparticle catalysts were reported for the catalytic aerobic oxidation of 5-HMF to FDCA [41-44, 61-65]. In particular, Pd/PVP (PVP=polyvinylpyrrolidone) catalyst (1.8 nm) showed higher yield for FDCA at 90 °C in the presence of 1.25 equivalents of NaOH [61]. Interestingly, for Pd nanoparticle catalysts the content of oxygen was reported to be crucial, as at low O₂ flow by-products may block the surface active sites, whereas under higher O_2 content atomic oxygen may block the surface [61]. Moreover, alkaline solution decreases the stability of Pd nanoparticles and, therefore, it is difficult to recycle Pd nanoparticles [62]. By alloying Pd with Au in Au₈Pd₂/AC (AC=activated carbon) catalyst, higher activity for 5-HMF oxidation to FDCA, in quantitative yield, was obtained but only in the presence of two equivalents of NaOH under 3 MPa O₂ at 60 °C [43]. Au-Pd/CNT (CNT=carbon nanotube), catalysed 5-HMF to FDCA under base-free oxidation conditions, but only at 100 °C under 0.5 MPa O₂ or 1.0 MPa of air after 12 h [44]. Notably, the presence of Pd in the Au-Pd catalyst enhanced the oxidation of the hydroxyl group of 5-HMF, and therefore higher selectivity was achieved for FDCA than with the Au catalyst, which preferentially catalysed 5-HMF to 5-hydroxymethyl-2-furancarboxylic acid (HFCA) [44]. Although the Au or Pd catalyst showed higher catalytic activity, they also suffered from several drawbacks such as the requirement of a strong base, high reaction temperature and high air or O₂ pressure for the oxidation reaction. Hence, there is a thrust to search for other highly active catalysts that can activate aerial oxygen even at atmospheric pressure, cost-effective and highly stable under the reaction conditions. In this context, we have developed a highly active low-cost Ni-Pd nanoparticle catalyst for Suzuki-Miyaura reaction *[66-68]*. This catalyst showed high synergistic interaction by promoting the electronic charge transfer between Ni and Pd to achieve high catalytic activity with low Pd leaching and high recyclability. We anticipated that such strong synergistic interaction of Ni and Pd in Ni-Pd alloy catalysts could be beneficial for the catalytic oxidation reaction.

In our continuous effort towards the upgrading of biomass-derived furans [13, 14], herein, we report bimetallic Ni_{1-x}Pd_x ($0.10 \le x \le 0.75$) alloy nanoparticles for the aerial oxidation of biomass-derived furans (furfural and its derivatives, e.g., 5-HMF). High catalytic conversion of these furans selectively into the corresponding furan carboxylic acids was achieved by using the Ni_{0.90}Pd_{0.10} nanoparticle catalyst at lower temperature, 80 °C. The studied catalyst, Ni_{0.90}Pd_{0.10}, showed high stability in water under aerial oxygen atmosphere and thus displayed high recyclability. Using time-scaled ¹H NMR and UV/Vis spectroscopic studies, attempts were made to gain more insight in the reaction pathway.

4.2. Result and Discussion

4.2.1. Synthesis and characterisation of bimetallic Ni-Pd alloy nanoparticles

Bimetallic Ni_{0.90}Pd_{0.10} alloy nanoparticles were prepared by aqueous-phase coreduction of an aqueous solution of potassium tetrachloropalladate(II) and nickel(II) chloride hexahydrate salts, using NaBH₄ as a reducing agent in the polyvinylpyrrolidone [66-68]. presence of $Ni_{1-x}Pd_x$ (x=0.25-0.75)nanoparticles with varying Ni/Pd ratios were also synthesised accordingly. Nanoparticles were collected by centrifugation, dried under vacuum at room temperature and used for the characterisation. Transmission electron microscopic (TEM) images of bimetallic Ni_{0.90}Pd_{0.10} nanoparticles revealed the particle size in the range of 2-4 nm (Figure 4.1). Moreover, transmission electron microscopic energy-dispersive X-ray spectrometry (TEM-EDS), elemental mapping and point analysis revealed the presence of both Ni and Pd metals in alloy Ni_{0.90}Pd_{0.10} and suggested a uniform distribution of both metals in the bimetallic Ni-Pd nanoparticles (Figure 4.1). Furthermore, The TEM-EDS and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of Ni_{0.90}Pd_{0.10} nanoparticles showed the ratio of Ni to Pd to be approximately 9:1.



Figure 4.1. a,b) TEM image of fresh (a) and used (b) $Ni_{0.90}Pd_{0.10}$ nanoparticles. c) SAED pattern. d) EDS analysis. e) FEG-TEM images and f,g) their corresponding EDS elemental mapping showing Pd (red) and Ni (green) for fresh $Ni_{0.90}Pd_{0.10}$ nanoparticles.

The powder XRD diffraction pattern of Ni_{0.90}Pd_{0.10} nanoparticles showed a major peak at $2\theta = 40^{\circ}$, which can be indexed to the (111) lattice plane (Figure 4.2.). Shifting towards a higher 2θ value than that of Pd(111) and a lower 2θ value as compare to Ni(111) diffraction pattern suggested an alloy composition of Ni_{0.90}Pd_{0.10} nanoparticles. Consistent with the XRD results, the



selected area electron-diffraction (SAED) pattern also revealed the presence of fcc (111) lattice plane (Figure 4.1).

Figure 4.2. Powder XRD pattern of studied bimetallic Ni-Pd nanoparticles and monometallic Ni and Pd nanoparticles.

4.2.2. Catalytic aerial oxidation of biomass-derived furans

Catalytic aerial oxidation of biomass-derived furans was performed over $Ni_{1-x}Pd_x$ (x=0.10-0.75) nanoparticles under moderate reaction conditions in an aqueous medium using furfuryl alcohol as the model substrate. Furfuryl alcohol was used for the initial optimisation of the reaction, because the direct

conversion of a primary alcohol to carboxylic acid is often more difficult to achieve than that of the formyl group (as in furfural). All catalytic reactions were performed by using freshly prepared Ni-Pd nanoparticles, obtained from the reduction of the respective metal salts (in specified Ni/Pd molar ratio) by NaBH₄, without further purification. To our delight, complete conversion of furfuryl alcohol to 2-furoic acid was achieved in 4 h with >99% selectivity in the presence of 5 mol% Ni_{0.90}Pd_{0.10} nanoparticles in water under continuous air bubbling at 80 °C (Table 4.1, entry 1).

Decreasing the reaction temperature to 60 °C or increasing to 100 °C led to the complete conversion of furfuryl alcohol to 2-furoic acid in 8 h and 3 h, respectively (Table 4.1, entries 2-4). Complete conversion of furfuryl alcohol with approximately 99% selectivity for 2-furoic acid was also achieved at 80 $^{\circ}$ C in 3 h (Table 4.1, entry 5). The reaction performed without air bubbling through external source, but in open atmospheric conditions, was found to be very slow and only 40% conversion was achieved at 80 °C in 3 h, suggesting the decisive role of aerial oxygen in the catalytic oxidation reaction (Table 4.1, entry 6). Notably, very poor conversion (~1%) was observed under Ar atmosphere (Table 4.1, entry 7). However, the reaction performed in the absence of catalyst could not proceed (Table 4.1, entry 8). Contrary to the high catalytic activity of the bimetallic Ni_{0.90}Pd_{0.10} nanoparticles catalyst, the monometallic Ni nanoparticles catalyst was not active at all (Table 4.1, entry 9). Complete conversion of furfuryl alcohol was achieved with 5 mol% Pd, but in the reaction performed with 0.5 mol% Pd nanoparticles (the amount of Pd was equivalent to that in 5 mol% Ni_{0.90}Pd_{0.10} nanoparticles) only 24% conversion was achieved (Table 4.1, entries 10 and 11). Moreover, only ~20% conversion of furfuryl alcohol was observed for the reaction performed by using a physical mixture of Ni and Pd nanoparticles (Table 4.1, entry 12). It is reported in the literature that furfural and furfuryl alcohol decompose or polymerise in the presence of acid and water, however, we achieved a considerable good yield of 2-furoic acid in aqueous medium using the Ni_{0.90}Pd_{0.10} nanoparticle catalyst [69-71].

Interestingly, the reaction performed using $Ni_{1-x}Pd_x$ nanoparticles with varying Ni/Pd ratio also resulted in the complete conversion of furfuryl alcohol, but not with complete selectivity for 2-furoic acid (Table 4.1, entries 13-15).

Among all the studied $Ni_{1-x}Pd_x$ nanoparticles, $Ni_{0.90}Pd_{0.10}$ displayed the highest turnover frequency (TOF, 65.3 h⁻¹) with complete selectivity for 2-furoic acid, which was 10 times higher than the TOF of Pd nanoparticles (6.4 h⁻¹, Figure 4.3). Hence, further catalytic reactions were performed using the highperforming $Ni_{0.90}Pd_{0.10}$ nanoparticle catalyst.

Table 4.1. Reaction optimization for the catalytic oxidation of furfuryl alcohol over $Ni_{1-x}Pd_x$ nanoparticle catalysts in water.^{*a*}

Entry	Catalyst	T (°C)/	Conv.	Sel. (%	Sel. (%)	
		Time (h) ^(%)		(2-furoic acid)	(furfural)	
1	Ni _{0.90} Pd _{0.10}	80/4	>99	>99		
2	Ni _{0.90} Pd _{0.10}	60/4	67	>99		
3	Ni _{0.90} Pd _{0.10}	60/8	>99	93	7	
4	Ni _{0.90} Pd _{0.10}	100/3	>99	>99		
5	Ni _{0.90} Pd _{0.10}	80/3	>99	98.5	1.5	
6 ^{<i>b</i>}	Ni _{0.90} Pd _{0.10}	80/3	40	33	67	
7^c	Ni _{0.90} Pd _{0.10}	80/3	1.3		>99	
8	without catalyst	80/3				
9	Ni	80/3				
10^d	Pd	80/3	24	>99		
11	Pd	80/3	>99	97.5	2.5	
12^e	Ni +Pd	80/3	19	98	2	
13	Ni _{0.75} Pd _{0.25}	80/3	>99	99	1	
14	Ni _{0.50} Pd _{0.50}	80/3	>99	97	3	
15	Ni _{0.25} Pd _{0.75}	80/3	>99	96	4	

^{*a*}Reaction conditions: furfuryl alcohol (1.0 mmol), catalyst 5 mol%, air bubbling, water (10 mL), ^{*b*}under open atmosphere (without air bubbling), ^{*c*}under Ar atmosphere, ^{*d*}0.5 mol% catalyst, ^{*e*}physical mixture of Ni and Pd monometallic nanoparticles (9:1).



Figure 4.3. Catalytic activity of various nanoparticle catalysts (5 mol%) in the oxidation of furfuryl alcohol to 2-furoic acid under air bubbling at 80 °C for 3 h in water. ^{*a*}0.5 mol% Pd nanoparticles, ^{*b*}physical mixture of Ni and Pd nanoparticles in 9:1 molar ratio.

The kinetics of the catalytic reaction was studied by using time-scaled UV/Vis and ¹H NMR spectroscopy, to gain more insight into the reaction progress and the reaction pathway for the catalytic aerial oxidation of furfuryl alcohol to 2-furoic acid in the presence of Ni_{0.90}Pd_{0.10} nanoparticle catalyst. The UV/Vis spectrum (Figure 4.4) was recorded for the Ni_{0.90}Pd_{0.10} catalysed aerial oxidation of furfuryl alcohol to 2-furoic acid under the optimised reaction conditions, for a period of 0-4 h. The initial highly intense absorption band at 215 nm, corresponding to furfuryl alcohol, showed a continuous fall in intensity with the progress of the catalytic reaction, consequently, a new band at 277 nm, corresponding to furfural, appeared over a period of 0-45 min. Further, with the progress of the reaction, the intensity of the absorption band at 277 nm decreased continuously with the appearance of a new absorption band at 246 nm, corresponding to 2-furoic acid. Concurrently, after 4 h only one prominent band at 246 nm was left, suggesting the complete conversion of furfuryl alcohol to 2-furoic acid and that the oxidation reaction proceeded via the furfural intermediate.



Figure 4.4. Time-scaled UV-visible spectra for the catalytic aerial oxidation of furfuryl alcohol to 2-furoic acid in the presence of $Ni_{0.90}Pd_{0.10}$ nanoparticle catalyst.

Analysing the catalytic reaction by ¹H NMR spectroscopy at different time intervals revealed a continuous decrease in the intensity of the peaks assigned to furfuryl alcohol with the appearance of peaks corresponding to furfural and 2-furoic acid (Figure 4.5). Peak identification of furfural during ¹H NMR studies further reinforced that the catalytic oxidation reaction of furfuryl alcohol to 2-furoic acid proceeded through the formation of furfural.



Figure 4.5. Time-dependent ¹H NMR study for the catalytic aerial oxidation of furfuryl alcohol to 2-furoic acid in the presence of $Ni_{0.90}Pd_{0.10}$ nanoparticle catalyst.

Notably, using NaBH₄ to synthesize Ni-Pd nanoparticles in situ was advantageous, because during the reduction process, the NaBH₄ generated sodium metaborate (NaBO₂), which further facilitated (as a base) the catalytic oxidation of furfuryl alcohol to 2-furoic acid. The effect of the base was found to be crucial, because for the reaction in the presence of washed $Ni_{0.90}Pd_{0.10}$ nanoparticles, free from NaBO₂, only 5% conversion of furfuryl alcohol to 2furoic acid was achieved under the optimised reaction conditions. Furthermore, using other bases (0.25 equiv.) such as sodium carbonate, sodium tert-butoxide and sodium hydroxide, complete conversion of furfuryl alcohol to 2-furoic acid over the $Ni_{0.90}Pd_{0.10}$ nanoparticle catalyst was also achieved, but with higher yields of 2-furoic acid than that with the in situ generated NaBO₂ (Table 4.2). Increasing the amount of base to 0.5 equivalents could not enhance the yield, therefore, we further explored the catalytic oxidation reaction using Na₂CO₃ (0.25 equiv.). Furthermore, earlier reports revealed the effect of solvent polarity on the oxidation of 5-HMF and showed a high conversion to FDCA in water relative to that in organic solvents (63,64]. Likewise, we also observed a higher activity for $Ni_{0.90}Pd_{0.10}$ nanoparticle catalyst in the oxidation of furfuryl alcohol in water than that in organic solvents such as toluene, ethanol and methanol (Table 4.3).

Table 4.2. Influence of base on the catalytic aerial oxidation of furfuryl
alcohol to 2-furoic acid in the presence of $Ni_{0.90}Pd_{0.10}$ nanoparticles in
water. ^a

Entry	Base	Time (h)	Conv./Sel. (%)	Isolated yield (%)
1	b	4	>99/>99	38
2	Na ₂ CO ₃	4	>99/>99	46 (47) ^c
3	NaO ^t Bu	4	>99/>99	42
4	NaOH	3	>99/>99	48

^{*a*}Reaction conditions: fufuryl alcohol (1.0 mmol), 5 mol% Ni_{0.90}Pd_{0.10}, air bubbling, base (0.25 equiv.), Temp. 80 °C, water (10 mL). ^{*b*}Sodium metaborate (NaBO₂), produce from sodium borohydride after the reduction of metal salts in the synthesis of metal nanoparticles, act as a base. ^{*c*}0.5 equiv. Na₂CO₃.

F	o urfuryl al	OH ————————————————————————————————————	Ni _{0.90} Pd _{0.10} air bubbling, 2CO ₃ (0.25 equiv 80 °C, 4h	→ OH V.), 2-furoic acid	+ U furfural
ĺ	Entry	Solvent	Conv.	Sel. (%)	Sel. (%)
			(%)	(2-furoic acid)	(furfural)
	1	water	>99	>99	
	2	methanol	8	>99	
	3	ethanol			
_	4	toluene			

 Table 4.3. Influence of solvent polarity on the catalytic oxidation of furfuryl alcohol.

The catalytic activity of Ni_{0.90}Pd_{0.10} nanoparticles was further explored for the aerial oxidation of several other furan derivatives, such as furfural, 5-MF, MFA and 5-HMF, under the optimized reaction conditions of 5 mol% Ni_{0.90}Pd_{0.10} and 0.25 equivalents of Na₂CO₃ at 80 °C in water. It was reported earlier that the presence of a strong base, for example NaOH, decomposes or degrades furans (such as 5-HMF), whereas with a mild base the degradation of furans can be avoided and even higher yields of the oxidized product (such as FDCA from 5-HMF) can be achieved [62]. Moreover, a strong base may also adversely affect the stabilizing effect of PVP, which led to agglomeration and decreased catalytic activity [61]. Interestingly, complete conversion of furfural to 2-furoic acid was achieved in 1 h, suggesting that the oxidation of formyl group to carboxylic acid is a facile process (Table 4.4, entry 2). Analogous to furfural and furfuryl alcohol, aerial oxidation of 5-methyl-2-furfural (5-MF) and 5-methylfurfuryl alcohol (MFA) selectively to 5-methyl-2-furoic acid (MFCA) was also accomplished in 1.5 h and 4 h, respectively over $Ni_{0.90}Pd_{0.10}$ nanoparticle catalyst (Table 4.4, entries 3, 4).

High reactivity towards the catalytic oxidation of 5-HMF was also observed with the $Ni_{0.90}Pd_{0.10}$ nanoparticle catalyst, for which, because of the availability of an alcoholic and a formyl group, several oxidized intermediate products were observed (Figure 4.6 and Table 4.4, entry 5). The $Ni_{0.90}Pd_{0.10}$ nanoparticle-catalyzed aerial oxidation of 5-HMF with 0.25 equivalents of Na₂CO₃ was found to be slow and only 58% conversion was achieved with 5formylfuran-2-carboxylic acid (FFCA) as the major product (59% selectivity). The slow conversion of 5-HMF was presumably caused by the low amount of base, which led to competition between 5-HMF and its products, HFCA and FFCA, for their further oxidation to FDCA. Furthermore, the increase in the Na_2CO_3 content to 0.50 and 0.75 equivalents significantly increased the conversion of 5-HMF to 85% and >99%, respectively, but the selectivities towards FDCA were only 14 and 69%, respectively. Notably, using one equivalent of Na₂CO₃ resulted in the complete conversion of 5-HMF with 86% selectivity for FDCA (70% isolated yield, Table 4.4, entry 5). Using more than one equivalent of Na₂CO₃ or performing the catalytic reaction at 100 °C could not increase the selectivity for FDCA significantly. The observation of several intermediate oxidized products during the catalytic oxidation of 5-HMF suggested a stepwise oxidation of 5-HMF with the oxidation of the formyl group to carboxylic acid (step a) and then of the alcohol to carboxylic acid via a formyl group (steps b and c, Scheme 4.2).



Scheme 4.2. Schematic illustration of the plausible reaction pathway for the catalytic aerial oxidation of 5-HMF to FDCA.

Entry	Furans	Time (h)	Products	Conv./Sel.(%)
1	Он	4	ОН	>99/>99 (46) ^b
2		1	ОН	>99/>99 (42) ^b
3		1.5	ОН	>99/>99 (47) ^b
4	О	4	ОН	>99/>99 (54) ^b
5 ^c	но	4	HO OH (FDCA) HO (HFCA)	>99/86:11:3 (FDCA:HFCA:FF CA) {70 (FDCA)} ^b
			HO O (FFCA)	

Table 4.4. Catalytic aerial oxidation of furan derivatives overNi_{0.90}Pd_{0.10} nanoparticle catalyst.^a

^{*a*}Reaction conditions: furans (1.0 mmol), air bubbling, Na₂CO₃ (0.25 equiv.) water (10 mL), 80 °C. ^{*b*} isolated yield. ^{*c*} reaction with 1 equiv. of Na₂CO₃.



Figure 4.6. Effect of Na₂CO₃ amount on the catalytic aerial oxidation of 5-HMF.

4.2.2.1. Stability, recovery and recyclability of the Ni_{0.90}Pd_{0.10} **nanoparticle catalyst.** Impressively, the highly active Ni_{0.90}Pd_{0.10} nanoparticle catalyst also showed high stability in water and air. Therefore, the recyclability test of Ni_{0.90}Pd_{0.10} nanoparticle catalyst was attempted for the catalytic oxidation of furfuryl alcohol to 2-furoic acid in the presence of 0.25 equivalents of Na₂CO₃ under the optimised reaction conditions. Notably, the Ni_{0.90}Pd_{0.10} nanoparticle catalytic runs without any significant loss in conversion and selectivity (Figure 4.7). ICP-AES analysis showed no significant leaching of Ni or Pd for the Ni_{0.90}Pd_{0.10} nanoparticle catalyst during the catalytic oxidation reaction. Furthermore, SEM-EDS analysis of the spent Ni_{0.90}Pd_{0.10} nanoparticle catalyst was also recycled for six catalytic runs for the catalytic oxidation of 5-HMF to FDCA.



Figure 4.7. Recyclability of the $Ni_{0.90}Pd_{0.10}$ nanoparticle catalyst for the oxidation of furfuryl alcohol to 2-furoic acid.



Figure 4.8. a) SEM image of fresh $Ni_{0.90}Pd_{0.10}$ nanoparticles and b) corresponding EDS analysis (Ni/Pd = 9:1). c) SEM image of spent $Ni_{0.90}Pd_{0.10}$ nanoparticles and d) corresponding EDS analysis (Ni/Pd = 9:1).

We also attempted the direct catalytic transformation of fructose to FDCA (and other furan carboxylic acid products) in the presence of the $Ni_{0.90}Pd_{0.10}$ nanoparticle catalyst (Scheme 4.3). In a one-pot two-step catalytic reaction, initially fructose was treated with 0.5 equivalents of NH₄Cl in 2-propanol at

80 °C for 12 h [72]. Thereafter, to the reaction mixture, water (8 mL) and 1.5 equivalents of Na₂CO₃ were added and the mixture was stirred again for another 8 h at 80 °C with air bubbling in the presence of 5 mol% Ni_{0.90}Pd_{0.10} nanoparticle catalyst. ¹H NMR analysis of the reaction mixture inferred the formation of HFCA and FDCA as the major products with 74 and 22% selectivities, respectively, whereas FFCA (2.5%) and 5-HMF (1.5%) also appeared as minor products. Importantly, the formation of the reaction product FDCA, analogous to that obtained from 5-HMF, suggesting the direct transformation of fructose to furan carboxylic acids (FDCA, HFCA or FFCA) *via* 5-HMF, can be achieved by using Ni_{0.90}Pd_{0.10} nanoparticle catalyst under suitably tuned one-pot reaction conditions.



Scheme 4.3. One-pot transformation of fructose to furan carboxylic acids.

The observed high catalytic activity and recyclability displayed by the studied bimetallic Ni_{0.90}Pd_{0.10} nanoparticle catalyst towards aerial oxidation of biomass-derived furans in water is significant, because most of the earlier reported catalysts showed oxidation of furans only at high temperature and/or with high O₂ gas or air pressure. Moreover, earlier studies also showed that Pd catalysts displayed high catalytic activity, mostly in the presence of O₂ rather than air [63]. Further, the Pd/PVP catalyst was active for the oxidation of 5-HMF to FDCA only at 90 °C with 1.25 equivalents of NaOH [61]. Notably, the studied Ni_{0.90}Pd_{0.10} nanoparticles catalyst displayed a higher TOF (35 h⁻¹, with respect to the Pd content in the Ni_{0.90}Pd_{0.10} nanoparticles catalysts (~5 h⁻¹) in the oxidation of 5-HMF to FDCA [44, 61-65].

4.2.2.2. Catalytic reaction pathway for the oxidation of biomass-derived furans. The high catalytic-performance and reusability exhibited by Ni_{0.90}Pd_{0.10} nano-catalyst (having the lowest Pd content) were manifested to the strong synergistic interaction between Ni and Pd metals. The reported studies revealed that O2 required least adsorption energy (-0.85 eV) to adsorb on the surface of Pd(111) nanomaterial as compare to Pt(111), Ag(111) and Au(111); -0.70, -0.12 and -0.05 eV, respectively [73]. The adsorbed O₂ features a longer O-O bond [73, 74], where Pd(111) displayed highest O-O bond distance (1.36 Å) than Pt, Ag, Au (1.34, 1.27, and 1.25 Å, respectively) and free molecular O_2 (1.23 Å) [73]. The elongation of O-O bond is followed by the decrease O₂ bond order, which resulted due to the transfer of electrons from the metal to π^* antibonding orbital of O₂ at the time of adsorption [73, 74]. The study further revealed that the activation or dissociation of O_2 on the surface of Pd(111) is thermodynamically and kinetically favoured which facilitate to the oxidative activity of Pd(111) while on Au(111) and Ag(111), it is kinetically disfavoured and followed to lower activity at low temperatures (activity order: $Pd(111) > Pt(111) \gg Au(111)$, Ag(111)) [73]. Consequent to earlier reports, we anticipated that the electronic charge transfer from Pd to oxygen may result to partially oxidized or slightly positive Pd centre and a highly negative charged Pd centre may be a favourable site for the facile activation of O_2 (even in the presence of a very low content of O_2 , for example, as in air). Further, our earlier reported DFT calculations suggested an electronic charge transfer from Ni (having lower ionisation energy than Pd) to Pd in the bimetallic Ni/Pd alloy nanoparticles which followed to more electron rich Pd centre [66-68]. Moreover, high Ni content in bimetallic Ni/Pd alloy nanoparticles $(Ni_{0.90}Pd_{0.10})$ may retain the Pd centre electron rich (in its active form) even after adsorption of O_2 and lead to high activity and stability of Ni_{0.90}Pd_{0.10} catalyst as compare to the catalysts having high Pd content and monometallic Pd nanoparticles with no significant leaching of Pd metal during the catalytic oxidation reaction. Therefore, the high TOF achieved with bimetallic Ni_{0.90}Pd_{0.10} alloy catalyst as compared to monometallic Ni and Pd nanoparticles, can be attributed to synergistic interactions between Ni and Pd metals. Beside O_2 activation, Pd(111) surface also facilitate the adsorption of furan ring where surface hydroxyalkyl intermediate favoured dehydrogenation of furfuryl alcohol [75]. Furthermore, the soluble base also assists the oxidation reaction through the activation of –OH group of adsorbing intermediate and stability of catalyst by the neutralization of synthesized acid which may deactivate the metal catalyst [76, 77].

4.3. Conclusions

We explored various bimetallic Ni_{1-x}Pd_x ($0.1 \le x \le 0.75$) alloy nanoparticle catalysts for the aerial oxidation of biomass-derived furans, furfural, furfuryl alcohol, 5-hydroxymethyl-2-furfural (5-HMF), 5-methyl-2-furfural (5-MF) and 5-methylfurfuryl alcohol (MFA), to their corresponding carboxylic acid products, 2-furoic acid, furan-2,5-dicarboxylic acid (FDCA) and 5-methyl-2furoic acid (MFCA), in the presence of a mild base at 80 °C under aqueous reaction conditions. Among the bimetallic Ni_{1-x}Pd_x (0.10 $\leq x \leq 0.75$) nanoparticles, along with monometallic Ni and Pd nanoparticles and a physical mixture of Ni and Pd monometallic nanoparticles, the bimetallic Ni_{0.90}Pd_{0.10} nanoparticle catalyst outperformed over others and achieved a high catalytic turnover to the corresponding furan carboxylic acids. Moreover, the Ni_{0.90}Pd_{0.10} nanoparticle catalyst displayed excellent stability towards air and water and could be recycled up to ten catalytic runs of the aerial oxidation of furfuryl alcohol without significant loss in catalytic activity. Experiments revealed that the catalytic oxidation of 5-HMF proceeds through the initial oxidation of the formyl group to carboxylic acid, and subsequently the conversion of alcohol to carboxylic acid via the formyl group to form FDCA. Furthermore, the high catalytic activity of Ni_{0.90}Pd_{0.10} nanoparticle catalyst was also explored in the one-pot direct transformation of fructose to furan carboxylic acid products (such as FDCA). We demonstrated a significant synergy between Ni and Pd to achieve high catalytic activity (turnover frequency) for the aerial oxidation of biomass-derived furans to the corresponding furan carboxylic acids. We believe that this study on low-cost high-performing bimetallic Ni-Pd nanoparticle catalysts for the selective aerial oxidation of biomass-derived furans could provide perceptions towards the development to highly active catalysts for several other important catalytic transformations including biomass transformation to value-added chemicals and others.

4.4. Experimental Section

4.4.1. General procedure for preparation of Ni_{1-x}Pd_x (0.10 \leq x \leq 0.75) **nanoparticle catalysts:** Bimetallic Ni_{0.90}Pd_{0.10} nanoparticles were prepared following our previously reported aqueous-phase co-reduction process of Ni²⁺ and Pd²⁺ salts using polyvinylpyrrolidone (PVP), as a stabilizer *[66-68]*. Typically, an aqueous solution of NaBH₄ (0.0125 g in 5 mL water) was added dropwise to the 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) in water (5 mL) at room temperature. The content of the flask was sonicated for 10 min that resulted in a black suspension of nanoparticles. Analogously, other bimetallic Ni_{1-x}Pd_x alloy nanoparticles with different molar ratios of Ni and Pd, as well as monometallic Ni and Pd nanoparticles were prepared using their corresponding metal salts. A physical mixture of Ni + Pd nanoparticles in 9:1 molar ratio.

4.4.2. General procedure for the catalytic aerial oxidation of furan derivatives: In a two neck round bottom reaction flask, having freshly prepared 10 mL aqueous suspension of 5 mol% nanoparticles (based on metal salts), 1 mmol of furan derivative was added. The reaction mixture was stirred at 80 °C with a continuous flow of air in an oil bath for a desired reaction time. The progress of the reaction was monitored by thin layered chromatography (TLC). After the completion of the reaction, catalyst was recovered from the reaction mixture by centrifugation at 6000 rpm x 2 for 10 min. To the reaction mixture, 5 mL of brine solution and 3 mL of 1.2 M HCl was added and then extracted using diethyl ether (5 x 10 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered off and then solvent was evaporated under reduced pressure. The oxidized products of 5-HMF were obtained from the reaction mixture using 5 mL brine and 10 mL of 1.2 M HCl followed by extraction with diethyl ether (10 x 10 mL) and evaporation under reduced pressure. Resulted products were identified by ¹H NMR, ¹³C NMR, HRMS and GC-MS. Conversion and selectivities of the products were obtained by ¹H NMR. Purification of FDCA, obtained by the oxidation of 5-HMF, was done using column chromatography with a mixture of dichloromethane and methanol, from 99.9:0.1 to 99:1 as an elute.

Recyclability of $Ni_{0.90}Pd_{0.10}$ nano-catalyst was performed under the optimized reaction conditions, where catalyst was recovered from the reaction mixture by centrifugation (6000 rpm x 2 for 10 min), washed with ethanol (2 mL x 1) and distilled water (2 mL x 2), and then dispersed in 10 mL distilled water for next catalytic run.

4.4.3. Spectral data of products obtained by catalytic oxidation of biomass-derived furans



2-Furoic acid: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.65 (s, 1H), 7.32 (d, 1H, J = 4 Hz), 6.56-6.57 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 162.81, 147.08, 143.47, 119.76, 111.95. HRMS (ESI) m/z: calculated 112.0110, 111.0077 [C₅H₄O₃ – H], found 112.0144, 111.0111 [C₅H₄O₃ – H].

5-methyl-2-furoic: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.23 (d, 1H, *J* = 4 Hz), 6.17 (d, 1H, *J* = 4 Hz), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 163.69, 158.87, 142.49, 121.99, 109.28, 14.37. HRMS (ESI) m/z: calculated 126.0267, 125.0233 [C₆H₆O₃ – H], found 126.0245, 125.0193 [C₆H₆O₃ – H].



furan-2,5-dicarboxylic acid: ¹H NMR (400 MHz, DMSO- d_6): δ (ppm) = 7.28 (s, 2H). ¹³C NMR (100 MHz, DMSO- d_6): δ (ppm) = 158.91, 147.04, 118.42. HRMS (ESI) m/z: calculated 156.0009, 154.9975 [C₆H₄O₅ - 1H], found 156.0031, 154.9995 [C₆H₄O₅ - 1H]

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Chapter 5: Catalytic aerial oxidation of 5hydroxymethyl-2-furfural (5-HMF) to furan-2,5-dicarboxylic acid (FDCA) over Ni-Pd nanoparticles supported on Mg(OH)₂ nanoflakes for the synthesis of furan diesters

5.1. Introduction

Fast depletion of fossil resources and environment impacts have stimulated current research to utilize renewable biomass resources for the production of fuel and different fine chemicals [1-8]. 5-Hydroxymethyl-2-furfural (5-HMF), produced from cellulose or cellulose derived carbohydrates, is a potential platform compound for the sustainable synthesis of various pharmaceuticals and industrial applicable chemicals [9-23]. A complete aerial oxidation of 5-HMF to furan-2,5-dicarboxylic acid (FDCA) is one of the most appealing transformation, as FDCA has wide applications in textiles, coating, packaging. Because FDCA, is an important building block for the production of biomass-based polymers to replace petroleum-derived terephthalite (PET) and polybutylene terephthalate (PBT) (Scheme 5.1) [24-30]. Therefore, it is not surprising that FDCA has been listed in top-12 valuable chemicals derived from biomass, according to the U. S. Department of Energy Report [31].



Scheme 5.1. Schematic representation for the transformation of biomass-derived compound (5-HMF) to FDCA and further to industrially valuable molecules.

In recent past, partial or complete oxidation of 5-HMF has been explored over various catalysts based on Au, Pd, Pt and Ru metals, but in most of the cases presence of strong base (NaOH) and high pressure of O_2 is required. As Au has good affinity towards the oxidation reactions, Au nanoparticles based catalysts have been extensively investigated as an highly active catalyst for the oxidation of 5-HMF [32-44], however, in the presence of organic products like carboxylic acid Au have shown an easy deactivation [44,45]. Furthermore, Pd nanoparticles catalysts have also displayed high affinity for the oxidation of 5-HMF [46-50]. Moreover, it has been noticed that the usage of strong base like NaOH led to the decomposition of 5-HMF. Also, the presence of strong base adversely affects the stabilizing capacity of the stabilizers like PVP, and resulted in the agglomeration of nanoparticles and subsequently loss in the catalytic activity [46, 47]. To avoid the usage of base additive, basic solid supports have efficiently assist a complete oxidation of 5-HMF, as most of the reported catalysts are inactive for the oxidation reaction in the absence of basic support or base additives.

Furthermore, alloying Pd with other metals such as Au could be advantageous to enhance the catalytic activity and stability of the catalyst to the oxidation of 5-HMF [40-44]. In this way, bimetallic Au-Pd alloy nanoparticles supported on different supports, such as activated carbon and functionalized carbon nanotubes, have shown higher catalytic activity towards the oxidation of 5-HMF to FDCA, under base-free reaction conditions but in the presence of high pressure of O_2 or air (0.5 M Pa O_2 or 1 M Pa air) [40-44]. In contrary to Au and Pd based catalysts, Pt nanoparticles catalysts supported on the supports like TiO₂ and γ -A1₂O₃ required high amount of base for the oxidation of 5-HMF to FDCA [51-58]. Although Ru nanoparticles supported on activated carbon only displayed partial oxidation of 5-HMF to 2,5-diformylfuran (DFF) in toluene with 2.0 MPa O₂ at 110 °C [59], a complete oxidation of 5-HMF to FDCA was also achieved with 0.2 MPa O₂ at 120 °C in water [60]. Despite the higher catalytic activity exhibited by Au, Pd, Pt and Ru based catalysts for the oxidation of 5-HMF, these metal catalysts suffered from several drawbacks including high cost, necessity of strong base or solid supports prepared under unpleasant reaction conditions, and high pressure of air or O₂. Therefore highly active, low-cost and stable catalysts, which can trigger aerial oxygen for the oxidation reaction, are essentially required for the efficient transformation of biomass-derived furans to value added products, such as FDCA. Previously, we have explored simple and cost effective bimetallic Ni-Pd alloy nanoparticles catalyst for the coupling reactions, where the significant synergistic cooperation between Ni and Pd driven by an electronic charge transfer from Ni to Pd resulted in the formation of highly active catalyst [61-63].

With our sustained efforts to upgrade biomass-derived furans [14-16], herein, we explored bimetallic $M_{0.90}Pd_{0.10}$ (M = Ni, Co or Cu) alloy

nanoparticles supported on simple and low-cost in situ prepared $Mg(OH)_2$ nanoflakes for the catalytic aerial oxidation of biomass-derived 5-HMF without any base additive added externally. Using the synthesized Ni_{0.90}Pd_{0.10}/Mg(OH)₂ catalyst, optimized catalytic reaction conditions were established for an efficient transformation of 5-HMF to FDCA. To explore the effect of Ni to Pd ratio, various Ni_{1-x}Pd_x/Mg(OH)₂ catalysts along with the monometallic Ni and Pd as well as the physical mixture, Ni/Mg(OH)₂ + Pd/Mg(OH)₂, were explored for the catalytic reaction. Exploration of different supports (SiO₂, Al₂O₃, ZnO and Mg(OH)₂) revealed that basicity of Mg(OH)₂ presumably exhibited a pivotal role in the oxidation of 5-HMF. Unlike earlier reports, where $Mg(OH)_2$ from MgO and other magnesium salts like $Mg(NO_3)_2$ were synthesized at high temperature and/or in the presence of strong base [64-69], we presented here a facile room temperature easy transformation of MgO to Mg(OH)₂ nanoflakes. Moreover, this transformation led us to synthesize NiPd/Mg(OH)₂ catalyst via in situ transformation of MgO to $Mg(OH)_2$ during the synthesis of NiPd/Mg(OH)₂ catalyst, where the basic support favors the catalytic oxidation of 5-HMF to FDCA. Furthermore, synthesized FDCA was also employed successfully for the synthesis of several furan diesters, such as bis(2-hydroxyethyl), dimethyl, diethyl, dipropyl and dibutyl furan-2,5-dicarboxylate, as precursors of biomass-based polymers and different value-added chemicals, in high yields.

5.2. Results and Discussion

5.2.1. Synthesis and Characterization of Ni_{0.90}Pd_{0.10}/Mg(OH)₂ catalyst. was prepared using pre-synthesized bimetallic $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ Ni_{0.90}Pd_{0.10} alloy nanoparticles and MgO, dispersed in a water-ethanol (3:1 v/v) solution, under vigorous stirring at room temperature in argon atmosphere $Ni_{0.90}Pd_{0.10}/Mg(OH)_{2}$ nanoparticles were protection. collected bv centrifugation, washed, purified and dried under vacuum at room temperature before using it further for the characterization. P-XRD pattern of presynthesized Ni_{0.90}Pd_{0.10} nanoparticles showed a dominant peak at $2\theta = 40^{\circ}$ which can attributed to fcc (111) lattice plane. Moreover, shifting in the 2θ value towards lower side relative to Ni (111), inferred the alloy composition of Ni_{0.90}Pd_{0.10} nanoparticles (Figure 5.1). Furthermore, P-XRD pattern of Ni_{0.90}Pd_{0.10} loaded on *in situ* prepared Mg(OH)₂ showed the presence of a prompt peak at $2\theta = 38^{\circ}$, corresponding to the (101) lattice plan, whereas the signature peak of pure MgO at $2\theta = 43^{\circ}$ was absent (Figure 5.2 k).



Figure 5.1. Powder X-ray diffraction pattern of unsupported bimetallic Ni_{0.90}Pd_{0.10} alloy nanoparticles and monometallic Ni and Pd nanoparticles.

Careful examination revealed the *in situ* transformation of MgO to $Mg(OH)_2$. This was indeed the case, as MgO stirred in the solution of water and ethanol under argon atmosphere for 4 h, also showed the complete transformation of MgO to Mg(OH)₂, even in the absence of Ni_xPd_{1-x} nanoparticles. Moreover, SEM images of the freshly prepared Mg(OH)₂ displayed the flakes like morphology (Figure 5.2 b). Worthy to mention that this procedure represent one of the easiest way to transform MgO to Mg(OH)₂ at room temperature [64-69]. Thus formed Ni_{0.90}Pd_{0.10}/Mg(OH)₂ could also be synthesize by using freshly prepared Mg(OH)₂ and then stabilized presynthesize Ni_{0.90}Pd_{0.10} nanoparticles over it. However, we preferred to synthesize Ni_{0.90}Pd_{0.10}/Mg(OH)₂ by using pre-synthesized Ni_{0.90}Pd_{0.10} stabilized over it. Moreover, SEM images of Ni_{0.90}Pd_{0.10}/Mg(OH)₂ also showed that Ni_{0.90}Pd_{0.10} nanoparticles are stabilized on Mg(OH)₂ nanoflakes (Figure 5.2 c).

HR-TEM images of bimetallic $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ nanoparticles revealed the formation of ~4 nm size of nanoparticles supported on $Mg(OH)_2$ nanoflakes (Figure 5.2. d,e). Furthermore, TEM-EDS elemental mapping and point analysis showed the presence of Ni, Pd and Mg metals in $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ and suggesting a uniform distribution of $Ni_{0.90}Pd_{0.10}$ over $Mg(OH)_2$ support (Figure 5.2 j and Figure 5.3). With steady to the P-XRD diffraction pattern, the observed ring in the selected area electron diffraction (SAED) can also assigned to (101) lattice plan for $Mg(OH)_2$ supported $Ni_{0.90}Pd_{0.10}$ (Figure 5.2. f) [66]. Furthermore, TEM-EDS and ICP analyses of the supported bimetallic $Ni_{0.90}Pd_{0.10}$ alloy nanoparticles are well in agreement with the expected Ni to Pd ratio of 9:1.



Figure 5.2. SEM image of (a) pure MgO, (b) freshly prepared Mg(OH)₂ and (c) freshly prepared Ni_{0.90}Pd_{0.10}/Mg(OH)₂. (d,g) TEM images, (e,h)

HR-TEM images and (f,i) SAED pattern of fresh and used Ni_{0.90}Pd_{0.10}/Mg(OH)₂. (j) EDS point analysis for fresh Ni_{0.90}Pd_{0.10}/Mg(OH)₂. (k) P-XRD analyses.



Figure 5.3. a) FEG-TEM image, b-d) their corresponding EDS elemental mapping showing b) Mg (green), c) Ni (blue) and d) Pd (red) for freshly prepared $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$.

Consistent with the P-XRD and SAED pattern, XPS analysis of $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ revealed the characteristic binding energy peaks for Mg [1s], Mg [2p] and O [1s] at 1302.63, 48.46 and 130.06 eV, respectively, which confirm the presence of Mg(OH)_2 in Ni_{0.90}Pd_{0.10}/Mg(OH)_2 [70]. Furthermore, in the XPS analysis of Ni_{0.90}Pd_{0.10}/Mg(OH)_2, signals corresponding to the metallic Ni [2p_{3/2}] (854.88 eV) was observed, but the signals for Pd [3d] were hardly detected by XPS analysis, presumably due to the very low content of Pd (0.005 mmol of Pd) in Ni_{0.90}Pd_{0.10}/Mg(OH)_2 (Figure 5.4) [61]. However, alloy composition of Ni and Pd in Ni_{0.90}Pd_{0.10} was further authenticated by XPS analysis of the unsupported Ni_{0.90}Pd_{0.10}, which was later supported on Mg(OH)_2, where characteristic signals for metallic Pd [3d_{5/2}] and Ni [2p_{3/2}] were appeared at 335.50 and 854.79 eV, respectively (Figure 5.5) [61].



Figure 5.4. XPS analysis of Ni_{0.90}Pd_{0.10}/Mg(OH)₂.



Figure 5.5. XPS analysis of unsupported bimetallic Ni_{0.90}Pd_{0.10} nanoparticles.

5.2.2. Catalytic aerobic oxidation of 5-HMF

5.2.2.1. Optimization of reaction conditions. Catalytic aerobic oxidation of 5-HMF was carried out using freshly prepared bimetallic $M_{0.90}$ -Pd_{0.10}/Mg(OH)₂ (M = Ni, Co, Cu) and monometallic Ni/Mg(OH)₂ and Pd/Mg(OH)₂ in water. Catalytic aerial oxidation reaction of 5-HMF was first initiated over Ni/Mg(OH)₂ at 80 °C with a continuous flow of air, but resulted with no conversion of 5-HMF (Table 5.1, entry1). As Pd nanoparticles have shown its activity for the oxidation of alcohols and aldehydes including oxidation of 5-HMF [*16*, *46-50*], we also observed the catalytic affinity of

 $Pd/Mg(OH)_2$ towards the oxidation of 5-HMF. Unlike Ni/Mg(OH)₂ which was inactive, bimetallic Ni_{0.90}Pd_{0.10}/Mg(OH)₂, having a low Pd content (10% as compare to Ni), displayed high activity for the oxidation of 5-HMF (conv. 92%) to FDCA (as a major product 49%), along with 5-hydroxymethyl-2furancarboxylic acid (HFCA, 24%) and 5-formyl-furan-2-carboxylic acid (FFCA, 27%) at 80 °C in 10 h (Table 5.1, entry 2). Under analogous reaction conditions, Co_{0.90}Pd_{0.10}/Mg(OH)₂ and Cu_{0.90}Pd_{0.10}/Mg(OH)₂ also exhibited good activity for the oxidation reaction with 86% and 90% conversion of 5-HMF, respectively (Table 5.1, entry 3 and 4). Furthermore, increasing the reaction temperature to 100 °C was found to be advantageous, as complete conversion of 5-HMF was achieved over Ni_{0.90}Pd_{0.10}/Mg(OH)₂ and the selectivity of FDCA was significantly increased from 49% to 76%. Unlike Ni_{0.90}Pd_{0.10}/Mg(OH)₂ catalyst, Co based catalyst showed only marginal enhancement, whereas for Cu_{0.90}Pd_{0.10}/Mg(OH)₂ catalyst, loss in the catalytic activity was observed at 100 °C (Table 5.1, entries 5-7). Furthermore, increasing the amount of the support to double (0.100 g) in Ni_{0.90}Pd_{0.10}/Mg(OH)₂ also resulted to an enhancement in the selectivity of FDCA to 88% at 100 °C in 10 h (Table 5.1, entry 10). Further, selectivity of FDCA upto 94% could also be achieved after 16 h of the reaction (Table 5.1, entry 12). However, further increasing in the amount of support resulted to the decrease in conversion of 5-HMF (Table 5.1, entry 13).

Table 5.1. Optimization of reaction conditions for the oxidation of 5-HMF.^a



Entry	Catalyst	MgO	T (° C)	Conv.	Sel. (%)			
		(g)	/ <i>t</i> (h)	(%)	FDCA	HFCA	FFCA	DFF
1	Ni/Mg(OH) ₂	0.050	80/10					
2	$\frac{Ni_{0.90}Pd_{0.10}}{Mg(OH)_2}$	0.050	80/10	92	49	24	27	
3	$\frac{Co_{0.90}Pd_{0.10}}{Mg(OH)_2}$	0.050	80/10	86	34	26	40	
4	$\begin{array}{l} Cu_{0.90}Pd_{0.10} / \\ Mg(OH)_2 \end{array}$	0.050	80/10	90	57	35	8	
5	$\frac{Ni_{0.90}Pd_{0.10}}{Mg(OH)_2}$	0.050	100/10	>99	76	7	17	
6	$\frac{Co_{0.90}Pd_{0.10}}{Mg(OH)_2}$	0.050	100/10	94	46	12	42	
7	$\frac{Cu_{0.90}Pd_{0.10}}{Mg(OH)_2}$	0.050	100/10	81	41	45	14	
8	$Ni_{0.90}Pd_{0.10}/Mg(OH)_2$	0.050	100/16	>99	78	10	12	
9	$\frac{Ni_{0.90}Pd_{0.10}}{Mg(OH)_2}$	0.100	80/10	>99	77	11	12	
10	$\frac{Ni_{0.90}Pd_{0.10}}{Mg(OH)_2}$	0.100	100/10	>99	88 (78%) ^b	6	6	
11 ^c	$Ni_{0.90}Pd_{0.10}/Mg(OH)_2$	0.100	100/10	>99	57	12	31	
12	$\frac{Ni_{0.90}Pd_{0.10}}{Mg(OH)_2}$	0.100	100/16	>99	94 (86%) ^b	4	2	
13	$Ni_{0.90}Pd_{0.10}/Mg(OH)_2$	0.150	100/10	98	70	9	21	
14 ^{<i>d</i>}	Pd/ Mg(OH) ₂	0.100	100/10	35	4	27	62	7
15 ^e	$Ni_{0.90}Pd_{0.10}/Mg(OH)_2$	0.100	100/10	27	4	34	62	
16 ^f			100/10					
17^{g}	MgO	0.100	100/10					
18^h	Mg(OH) ₂	0.100	100/10					
19 ⁱ	$\frac{Ni_{0.90}Pd_{0.10}}{Mg(OH)_2}$		100/10	>99	83 (74%) ^b	4	13	

^{*a*}Reaction Conditions: 5-HMF (1 mmol), H₂O (10 mL), Ni_{1-x}Pd_x (0.05 mmol with respect to metal salts) supported over *in situ* prepared Mg(OH)₂. ^{*b*}isolated yield. ^{*c*}one time used Ni_{0.90}Pd_{0.10}/Mg(OH)₂. ^{*d*}0.005 mmol Pd nanoparticles, amount present in Ni_{0.90}Pd_{0.10}, supported in Mg(OH)₂. ^{*e*}reaction without air bubbling. ^{*f*}without catalyst. ^{*g*}only MgO without nanoparticles. ^{*h*}freshly prepared Mg(OH)₂. ^{*i*}Ni_{0.90}Pd_{0.10} supported on freshly prepared Mg(OH)₂.

5.2.2.2. Effect of different supports. Catalytic oxidation of 5-HMF performed over bimetallic Ni_{0.90}Pd_{0.10} alloy nanoparticles supported on different supports (SiO₂, Al₂O₃, ZnO or Mg(OH)₂) revealed that support plays an important role in the oxidation reaction. Among several supports used for the stabilization of bimetallic Ni_{0.90}Pd_{0.10} alloy nanoparticles, those supported on Mg(OH)₂ showed highest catalytic activity for the oxidation of 5-HMF, whereas other supports could not facilitate complete oxidation of 5-HMF to FDCA (Figure 5.6). Moreover, Ni_{0.90}Pd_{0.10}/MgO, prepared by calcination of Ni_{0.90}Pd_{0.10}/Mg(OH)₂, exhibited very low activity towards the oxidation of 5-HMF and only 22% conversion of 5-HMF to HFCA was observed, under the optimized reaction. These observation clearly revealed the crucial role of Mg(OH)₂ for the oxidation of 5-HMF to FDCA. Moreover, earlier reports demonstrated that the presence of soluble base, due to the leaching of support or additionally added base, may tune the selectivity towards the desired product [39]. For instance, Ardemani et al. (2015) showed that the selectivity towards FDCA can be significantly enhanced by performing the catalytic oxidation of 5-HMF over Au/hydrotalcites in presence of a soluble base (NaOH), where soluble base facilitate an easy activation of R-OH bond over the catalyst and thus enhanced selectivity for FDCA [39]. Analogous behavior was also observed with $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst, where ICP-AES analysis of the reaction mixture showed the presence of Mg^{2+} in the solution due to the leaching of the $Mg(OH)_2$ support, which advantageously tune the selectivity towards FDCA over Ni_{0.90}Pd_{0.10}/Mg(OH)₂ catalyst. Notably, air bubbling is one of the crucial factor for the oxidation of 5-HMF, as without conversion of 5-HMF bubbling only 27% was achieved over $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ (Table 5.1, entry 15). Furthermore, reaction could not proceed in the absence of the catalyst, or only with MgO or freshly prepared Mg(OH)₂ nanoflakes (Table 5.1, entry 16-18).



Figure 5.6. Effect of different supports on the catalytic aerial oxidation of 5-HMF at 100 °C in 10 h. (■) unreacted 5-HMF, (■) selectivity of FDCA, (■) selectivity of HFCA, (■) selectivity of FFCA and (■) selectivity of DFF, after the catalytic oxidation reaction.

5.2.2.3. Effect of Ni/Pd molar ratio present in Ni_{1-x}Pd_x/Mg(OH)₂ catalysts. After establishing the optimized reaction with $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$, we further investigated the effect of Ni to Pd ratio in $Ni_{1-x}Pd_x/Mg(OH)_2$ catalyst. Results inferred that Ni_{0.90}Pd_{0.10}/Mg(OH)₂ exhibited high catalytic activity analogous to that as observed with Ni_{1-x}Pd_x/Mg(OH)₂ with high Pd content (x > 0.10) (Table 5.2, entries 2-7). Considering the content of Pd, $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ displayed highest TON, which is ~ 10 times higher than that of Pd/Mg(OH)₂ (Figure 5.7). Moreover, Ni_{0.90}Pd_{0.10}/Mg(OH)₂, while having only 0.005 mmol of Pd, exhibited higher turnover frequency (TOF = 15.6 h^{-1}) in comparison to Pd/Mg(OH)₂ (TOF = 1.7 h^{-1} ; Pd content 0.05 mmol). Also, TOF (h^{-1}) for Ni_{0.90}Pd_{0.10}/Mg(OH)₂ was observed to be increasing constantly for the reaction performed at 5, 8 and 10 h, whereas $Pd/Mg(OH)_2$ exhibited only poor TOF (h⁻¹). Analogously, the selectivity for FDCA over Pd/Mg(OH)₂ was only 19%, whereas 25% selectivity of FDCA was achieved with $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst after 5 h (Table 5.2). Notably, $Ni/Mg(OH)_2$ is inactive for the oxidation of 5-HMF. Moreover, Pd/Mg(OH)₂, having Pd content equivalent to the Pd content present in

 $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$, also exhibited poor catalytic activity (conv. 35%) for the oxidation of 5-HMF, with a TOF of merely 0.28 h⁻¹ (Table 5.2, entry 8), further support that the presence of Ni in alloy nanoparticles is advantageous to achieve higher catalytic activity. Moreover, poor catalytic activity exhibited by the physical mixture of Ni/Mg(OH)₂ and Pd/Mg(OH)₂ (Ni/Pd = 9:1), further revealed that the alloy composition of Ni and Pd is crucial for the higher activity of Ni-Pd/Mg(OH)₂ catalyst and not the mere presence of Ni and/or Pd (Table 5.2, entry 9).

Table 5.2. Catalytic oxidation of 5-HMF over Ni/Mg(OH)₂, Pd/Mg(OH)₂ and Ni_{1-x}Pd_x/Mg(OH)₂ catalysts.^{*a*}

но о 5-нм	O Ni _{1-x} Pd _x /Mg(OH 100 °C, H ₂ O air bubbling 10h	^{I)} 2 HO → HO F	о он но dca	O HFCA	он но	O FFCA	o O O DFF
Entry	Catalyst	Conv.		Isolated			
		(%)	FDCA	HFCA	FFCA	DFF	FDCA (%)
1	Ni/Mg(OH) ₂						
2	$Ni_{0.90}Pd_{0.10}/Mg(OH)_2$	>99	88 (25) ^d	6	6		78 (17) ^{d,e}
3 ^{<i>b</i>}	$Ni_{0.90}Pd_{0.10}/Mg(OH)_2$	>99	94	4	2		86
4	$Ni_{0.75}Pd_{0.25}/Mg(OH)_2$	>99	95	3	2		87
5	$Ni_{0.50}Pd_{0.50}/Mg(OH)_2$	>99	98	1	1		89
6	$Ni_{0.25}Pd_{0.75}/Mg(OH)_2$	>99	95	3	2		85
7	Pd/ Mg(OH) ₂	>99	94 (19) ^d	3	3		85(15) ^{<i>d,e</i>}
8 ^{<i>c</i>}	Pd/Mg(OH) ₂	35	4	27	62	7	n.d.
9	Ni/Mg(OH)+ Pd/Mg(OH) ₂	38	5	30	60	5	n.d.

^{*a*}Reaction Conditions: 5-HMF (1 mmol), H_2O (10 mL), $Ni_{1-x}Pd_x$ (0.05 mmol with respect to metal salts) supported on *in situ* prepared Mg(OH)₂. ^{*b*}reaction time 16h. ^{*c*} 0.005 mmol of Pd nanoparticles supported on *in situ* prepared Mg(OH)₂. *n.d.* not determined. ^{*d*} 5 h. ^{*e*}nmr yields.



Figure 5.7. Comparative catalytic activities of $Ni_{1-x}Pd_x/Mg(OH)_2$ (x = 0.10 to 1) catalysts for the oxidation of 5-HMF to FDCA at 100 °C for 10 h. ^aPhysical mixture of Ni/Mg(OH)₂ and Pd/Mg(OH)₂ (Ni/Pd molar ratio 9:1). ^b0.005 mmol Pd nanoparticles (content of Pd equivalent to that present in $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$).

These findings demonstrated that decreasing the Pd content (with increasing Ni content) resulted in the formation of highly active Ni₁. _xPd_x/Mg(OH)₂ catalyst. As mentioned in our earlier report (Chapter 4) [16], studies shows that the adsorption of O_2 on the surface of Pd nanoparticles requires less energy and adsorb strongly on the Pd surface, which is followed by the lengthening of O-O bond in comparison to free O₂ [73,74]. Lengthening of O-O bond distance is due to the filling of $O_2 \pi^*$ antibonding orbital with the electrons transferred from metal during the adsorption. Therefore, Pd nanoparticles with more negative charge could be highly active for the activation of O_2 and therefore even the lower content of O_2 in air can be utilized for oxidation reactions. Furthermore, in our earlier reported studies [62], DFT calculations revealed an electronic charge transfer from Ni (having less ionization energy as compare with Pd) to the Pd center in the bimetallic Ni-Pd nanoparticles which makes Pd center more electron rich as compare to monometallic Pd nanoparticles. Thus electron rich Pd center resulted to an easy adsorption of O₂ on the surface of Pd and an enhanced catalytic activity of Ni_{0.90}Pd_{0.10}/Mg(OH)₂ towards the oxidation of 5-HMF in comparison to

monometallic Pd/Mg(OH)₂ nanoparticles (having similar Pd content as present in Ni_{0.90}Pd_{0.10}/Mg(OH)₂). Moreover, in the absence of Ni, a high amount of Pd (almost 10 times) was required in Pd/Mg(OH)₂ to achieve analogous conversion or selectivity as observed with Ni_{0.90}Pd_{0.10}/Mg(OH)₂, under optimized reaction conditions. Therefore, the presence of Ni was found to be advantageous, where with the decrease in Pd/Ni ratio in Ni_xPd_{1-x}/Mg(OH)₂ catalyst resulted in an enhancement in the catalytic activity, which is further reflected in the decrease in TON with the decrease in Pd content (Figure 5.7).

5.2.2.4. Leaching, poisoning and recyclability experiments. To further investigate the nature of the catalytic species, leaching and catalyst poising experiments were performed for the highly active $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst. Under the optimized reaction conditions, 5-HMF was treated with $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ (S/C = 20) and after 5 h, reaction mixture was centrifuged to separate the catalyst. The supernatant was divided into two portions; the first was analyzed by ¹H NMR to evaluate the conversion, whereas the second portion was extended for an additional 5 h under the optimized reaction conditions. ¹H NMR analysis of the second portion, showed no remarkable enhancement in the conversion of 5-HMF suggesting that the $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ is indeed heterogeneous in nature during the catalytic reaction (Figure 5.8). Unlike the above observation, complete conversion of 5-HMF was achieved with Ni_{0.90}Pd_{0.10}/Mg(OH)₂ catalyst in 10 h. Moreover, ICP-AES analysis of reaction mixture showed no significant leaching of Ni and Pd metals from the catalyst and the Ni/Pd ratio remains constant before and after the catalytic reaction. Also, TEM images of the Ni_{0.90}Pd_{0.10}/Mg(OH)₂ recovered after the catalytic oxidation of 5-HMF, inferred no significant change in the particles size (Figure 1g-i). Furthermore, catalyst poisoning experiment with CS₂ showed a significant quenching in the catalytic activity which further support the heterogeneous nature of Ni_{0.90}Pd_{0.10}/Mg(OH)₂ catalyst (Figure 5.8) [71,72]. The above observations ensure that there is no significant deformation in the catalyst and the heterogeneity of the catalyst is retained during the catalytic reaction, which is consistent with the observed catalytic activity achieved with the recovered catalyst for the catalytic oxidation of 5-HMF (Table 1, entry 11). Moreover, recycling experiments for the catalytic conversion of 5-HMF to FDCA over



 $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ exhibited that the catalyst can be reused for three consecutive catalytic runs.

Figure 5.8. Leaching and poisoning experiments. (1) Catalytic aerial oxidation of 5-HMF over $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ at 100 °C for 10 h, optimized reaction conditions. (2a-2b) Leaching experiments: catalytic aerial oxidation of 5-HMF over (2a) $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ at 100 °C for 5 h, and afterwards (2b) reaction mixture was centrifuged to separate the catalyst and reaction was extended for another 5 h at 100°C (without catalyst). (3) CS₂ poisoning experiment.

5.2.2.5. Gram-scale oxidation of 5-HMF. Most importantly, the optimized reaction methodology was further explored for a gram-scale oxidation of 5-HMF over $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst at 100 °C, where complete conversion of 5-HMF with high selectivity (76%) for FDCA (66% isolated yield) was be achieved after 48 h.

Catalytic activity manifested by $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ towards the aerial oxidation of 5-HMF without any base additive in aqueous medium is significant and encouraging, as most of the earlier studies were performed under harsh reaction conditions, such as high pressure of air and O₂, use of strong base additives and so on. In comparison to reports with monometallic and bimetallic catalysts based on Pd, Au, Pt and Ru, herein investigated $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst, having a very low amount of Pd (Ni/Pd molar

ratio of 9/1), exhibited high catalytic activity for the aerial oxidation of 5-HMF, with high selectivity for FDCA. Affinity of Pd towards O_2 [73, 74] was further enhanced by getting a negatively charged Pd center, favored by a negative charge transfer from Ni to Pd [61-63]. Therefore, an easy activation of O_2 molecule and subsequently high catalytic activity for the oxidation of 5-HMF was achieved over Ni_{0.90}Pd_{0.10}/Mg(OH)₂ catalyst. Moreover, *in situ* transformation of MgO to Mg(OH)₂ nanoflakes was found to be advantageous, as the basic nature of the support Mg(OH)₂ in the Ni_{0.90}Pd_{0.10}/Mg(OH)₂ catalyst further promoted the oxidation of 5-HMF without using an external base additive.

5.2.3. Synthesis of furan diesters. FDCA, synthesized by the catalytic oxidation of 5-HMF, was successfully utilized for the synthesis of a wide range of furan diesters (bis(2-hydroxyethyl), dimethyl, diethyl, dipropyl and dibutyl furan-2,5-dicarboxylate) with HCl using respective alcohol (Table 5.3, entries 1-5). Results inferred that furan diesters were obtained in high selectivity (>99%) and yield (>90%). FDCA displayed a unique structural analogy with terephthalic acid and an efficient synthesis of furan diesters from FDCA could further be explored as a model procedure for the synthesis of polyethyl furan dicarboxylate (PEFDC) as an alternative of polyethyl terephthalate (PET).

Table 5.3. Synthesis of furan diesters from catalytically sythesized FDCA.^a

Entry	-R	T (°C)/	Conv.	Sel.	Isolated yield of
		<i>t</i> (h)	(%)	(%)	Turan diester (%)
1	-CH ₃	70/12	>99	>99	92
2	-CH ₂ CH ₃	70/12	>99	>99	90
3	$-CH_2CH_2CH_3$	70/12	>99	>99	91
4	$-CH_2CH_2CH_2CH_3$	70/12	>99	>99	89
5	-CH ₂ CH ₂ OH	100/24	>99	>99	90
^a Reaction conditions: FDCA (0.5 mmol), R-OH (2 mL), HCl (12 M, 0.200 mL).					



5.3. Conclusions

We demonstrated an easy and one-pot transformation of MgO to Mg(OH)₂ nanoflakes at room temperature in water-ethanol mixture. This procedure was successfully explored to synthesize catalysts based on Ni_{1-x}Pd_x ($0.1 \le x \le 1$) nanoparticles supported on *in situ* generated Mg(OH)₂ nanoflakes. Synergistic cooperation between Ni and Pd in $Ni_{1-x}Pd_x/Mg(OH)_2$ catalysts was attributed to the achieved high catalytic activity for the aerobic oxidation of 5-HMF with high selectivity for FDCA. Notably, catalytic activity displayed by Ni_{0.90}Pd_{0.10}/Mg(OH)₂ catalyst was significant (TON: 156), as it was as par with the activity of $Ni_{1-x}Pd_x/Mg(OH)_2$ catalysts having higher Pd content (x > 0.10, TON: 22). Furthermore, poor activity observed with the physical mixture of Ni/Mg(OH)₂ and Pd/Mg(OH)₂, strongly support that atomic level mixing of Ni and Pd is crucial to achieve higher catalytic activity. Using $Mg(OH)_2$ as a basic support is advantageous, as it not only facilitate the oxidation reaction, but also avoid the use of a base additive. Therefore, the electron charge transfer from Ni to Pd in the bimetallic $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst and the presence of the basic Mg(OH)₂ nanoflakes support essentially contribute in the observed higher catalytic activity for the aerial oxidation of 5-HMF with high selectivity for FDCA (>94%). Furthermore, this methodology was explored for the gram scale transformation of 5-HMF to FDCA. Subsequently, the synthesized FDCA further transformed to a series of furan diesters (bis(2hydroxyethyl), dimethyl, diethyl, dipropyl and dibutyl furan-2.5dicarboxylate) in high selectivity (>99%) and yield (>90%). We believe, the investigated methodology could be a pathway for facile transformation of biomass derived 5-HMF to diesters or even bio-compatible plastics.

5.4. Experimental Section

5.4.1. Synthesis of bimetallic $M_{0.90}Pd_{0.10}$ (M = Ni, Co or Cu) alloy nanoparticles supported on Mg(OH)₂ nanoflakes

5.4.1.1. General procedure for the synthesis of NiPd/Mg(OH)₂ catalysts. In a typically synthesis procedure [16,61-63]; a solution of NaBH₄ (0.0125 g in 5 mL water) was added dropwise to a 5 mL aqueous solution of potassium tetrachloropalladate (II) (0.0016 g, 0.005 mmol), nickel (II) chloride

hexahydrate (0.0107 g, 0.045 mmol) and PVP (0.025 g) at room temperature. The content of the flask was sonicated for 10 min to obtain a black suspension which was collected by centrifugation at 6000 rpm x 2 for 10 min. Freshly prepared bimetallic $Ni_{0.90}Pd_{0.10}$ alloy nanoparticles were dispersed in a 10 mL solution of distilled water and ethanol (3:1 v/v) followed by the addition of appropriate amount of MgO support. Content of the flask was stirred for 4 h under argon atmosphere and then centrifuged at 6000 rpm x 2 for 10 min to collect bimetallic Ni_{0.90}Pd_{0.10} alloy nanoparticles supported on *in situ* prepared Mg(OH)₂ nanoflakes. The obtained Mg(OH)₂ supported Ni_{0.90}Pd_{0.10} nanoparticles were washed twice with 2 mL distilled water and used for the catalytic reactions. Similarly, other bimetallic Ni-Pd nanoparticles having different molar ratio of Ni/Pd and mono metallic Ni and Pd nanoparticles were prepared with suitable metal salts. Monometallic Ni/Mg(OH)₂ and $Pd/Mg(OH)_2$ nanoparticles were synthesized using the above method by using only the respective metal salts and MgO. Moreover, a physical mixture of $Ni/Mg(OH)_2$ and $Pd/Mg(OH)_2$, was obtained by mixing separately synthesized monometallic Ni and Pd nanoparticles (in 9:1 molar ratio) and MgO.

5.4.1.2. General procedure for the synthesis of $Co_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst. Under analogues reaction conditions used for $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$, bimetallic $Co_{0.90}Pd_{0.10}$ alloy nanoparticles were prepared using cobalt (II) chloride hexahydrate (0.0107 g, 0.045 mmol) and potassium tetrachloropalladate (II) (0.0016 g, 0.005 mmol), followed by the stabilization of bimetallic alloy nanoparticles over *in situ* prepared Mg(OH)₂ nanoflakes.

5.4.1.3. General procedure for the synthesis $Cu_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst. Similarly, $Cu_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst was prepared using copper (II) chloride dihydrate (0.0076 g, 0.045 mmol) and potassium tetrachloropalladate (II) (0.0016 g, 0.005 mmol), followed by the stabilization of bimetallic $Cu_{0.90}Pd_{0.10}$ alloy nanoparticles over *in situ* prepared Mg(OH)₂ nanoflakes.

5.4.2. Synthesis of $Mg(OH)_2$ nanoflakes. For the synthesis of $Mg(OH)_2$ nanoflakes, MgO (0.100 g) was dispersed in the solution of 10 mL water and ethanol (3:1 v/v) and content of the flask was stirred for 4 h under Ar atmosphere. The synthesized $Mg(OH)_2$ nanoflakes were collected by centrifugation at 6000 rpm x 2 for 10 min and washed twice with 2 mL of distilled water.

5.4.3. General procedure for the catalytic aerial oxidation of 5-HMF. Catalytic oxidation of 5-HMF was performed in a two necked 50 mL round bottom reaction flask, which was charged with 10 mL aqueous suspension of freshly prepared mono-/bimetallic alloy nanoparticles supported on in situ Mg(OH)₂ nanoflakes, as described above, followed by the addition of 1 mmol of 5-HMF (S/C = 20). The reaction mixture was stirred in an oil bath at desired temperature with the continuous flow of air. Progress of oxidation reaction was monitored by thin layered chromatography (TLC). After completion, reaction mixture was centrifuged at 6000 rpm for 10 min to recover the catalyst. To the reaction mixture 5 mL of brine solution and 10 mL of 1.2M HCl was added and then extracted using diethyl ether (10 x 10 mL). Combined organic fractions were dried over anhydrous Na₂SO₄, filtered off and then solvent was removed under reduced pressure. The obtained solid were characterized by ¹H NMR, ¹³C NMR and HRMS to confirm the identity of the products. Conversion and selectivity of the products were confirmed by ¹H NMR. Purification of FDCA was done using column chromatography with a mixture of dichloromethane and methanol, from 99.9:0.1 to 99:1 as an elute. For recyclability experiments, catalyst was recovered from the reaction mixture by centrifugation at 6000 rpm for 10 min, washed by ethanol (1 x 2 mL) and distilled water (2 x 2 mL), and then dispersed in 10 mL of distilled water for next catalytic run.

5.4.4. General procedure for the synthesis of Furan diesters. Furan diesters were synthesized using 0.5 mmol of FDCA and 0.200 mL of 12 M HCl in 2 mL of respective alcohol. Reaction mixture was stirrer in an oil bath at desired temperature for appropriated time. After the reaction, mixture was neutralized with saturated sodium hydroxide and dried under reduced pressure. Product were recovered by dissolution in acetone (5 mL) and characterized by NMR and mass spectroscopy.

5.4.5. Gram-scale catalytic conversion of 5-HMF. A gram-scale oxidation of 5-HMF was achieved in a 100 mL two neck round bottom flask which was charged with 1.008 g (8 mmol) of 5-HMF and freshly prepared $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst (S/C = 40) dispersed in 40 mL water. The whole mixture was stirred in an oil bath at 100 °C with the continuous flow of air for 48 h. After the completion of catalytic reaction, catalyst was recovered from

the reaction mixture by centrifugation at 6000 rpm for 10 min. To the reaction mixture 20 mL of brine solution and 40 mL of 1.2M HCl was added and then extracted using diethyl ether (20 x 20 mL). Organic layer was dried over anhydrous Na₂SO₄, filtered off and then solvent was removed under reduced pressure. Purification of FDCA was carried out with column chromatography using a mixture of dichloromethane and methanol, from 99.9:0.1 to 99:1 as an elute.

5.4.6. Poisoning experiment. To confirm the heterogeneity of $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst for the oxidation of 5-HMF, 10 mL aqueous suspension of $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ was stirred for 30 min with 5 mmol of CS₂ at optimized reaction temperature (100 °C), cool and collected by centrifugation at 6000 rpm for 10 min. The recovered $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ was re-dispersed in 10 mL distilled water and used for the oxidation of 5-HMF (1 mmol), under the flow of air at 100 °C for 10 h.

5.4.7. Spectral data of furan-2,5-dicarboxylic Acid (FDCA) transformed by the catalytic aerial oxidation of 5-hydroxymethyl-furfural (5-HMF).



2,5-furandicarboxylic acid: ¹H NMR (400 MHz, DMSO- d_6): δ (ppm) = 7.28 (s, 2H), 13.59 (b, 2H). ¹³C NMR (100 MHz, DMSO- d_6): δ (ppm) = 118.39, 147.01, 158.88. HRMS (ESI) m/z: calculated 154.9975 [C₆H₄O₅ – 1H], found 154.9980 [C₆H₄O₅ – 1H].

5.4.8. Spectral data of Bis(2-hydroxyethyl)furan-2,5-dicarboxylate and Dialkylfuran-2,5-dicarboxylates synthesized from FDCA (obtained by catalytic aerial oxidation of 5-HMF).

Bis(2-hydroxyethyl)furan-2,5-dicarboxylate: ¹H NMR (400 MHz, Acetoned₆): δ (ppm) = 3.84 (t, 4H, J = 4.76 Hz), 4.18 (b, 2H), 4.38 (t, 4H, J = 4.76 Hz), 7.34 (s, 2H). ¹³C NMR (100 MHz, Acetone-d₆): δ (ppm) = 60.54, 67.80, 119.38, 147.74, 158.55. HRMS (ESI) m/z: calculated 267.0475 [$C_{10}H_{12}O_7$ + 1Na], found 267.0483 [$C_{10}H_{12}O_7$ + 1Na].



Dimethyl furan-2,5-dicarboxylate: ¹H NMR (400 MHz, Acetone-d₆): δ (ppm) = 3.88 (s, 6H), 7.30 (s, 2H). ¹³C NMR (100 MHz, Acetone-d₆): δ (ppm) = 52.55, 119.26, 147.51, 158.82. HRMS (ESI) m/z: calculated 207.0264 [C₈H₈O₅ + 1Na], found 207.0264 [C₈H₈O₅ + 1Na].



Diethyl furan-2,5-dicarboxylate: ¹H NMR (400 MHz, Acetone-d₆): δ (ppm) = 1.34 (t, 6H, J = 7.04 Hz), 4.33-4.38 (q, 4H, J = 7 Hz), 7.30 (s, 2H). ¹³C NMR (100 MHz, Acetone-d₆): δ (ppm) = 14.45, 62.00, 119.14, 147.79, 158.41. HRMS (ESI) m/z: calculated 235.0577 [C₁₀H₁₂O₅ + 1Na], found 235.0586 [C₁₀H₁₂O₅ + 1Na].



Dipropyl furan-2,5-dicarboxylate: ¹H NMR (400 MHz, Acetone-d₆): δ (ppm) = 0.98 (t, 6H, J = 7.24 Hz), 1.71-1.80 (m, 4H), 4.27 (t, 4H, J = 6.52 Hz), 7.31 (s, 2H). ¹³C NMR (100 MHz, Acetone-d₆): δ (ppm) = 10.50, 22.63, 67.40, 119.14, 147.77, 158.47. HRMS (ESI) m/z: calculated 263.0890 [C₁₂H₁₆O₅ + 1Na], found 263.0890 [C₁₀H₁₂O₅ + 1Na].



Dibutyl furan-2,5-dicarboxylate: ¹H NMR (400 MHz, Acetone-d₆): δ (ppm) = 0.95 (t, 6H, *J* = 7.28 Hz), 1.40-1.49 (m, 4H), 1.69-1.76 (m, 4H), 4.31 (t, 4H, J = 6.8 Hz), 7.31 (s, 2H). ¹³C NMR (100 MHz, Acetone-d₆): δ (ppm) = 13.90, 19.71, 31.36, 65.72, 119.14, 147.80, 158.47. HRMS (ESI) m/z: calculated 291.1203 [C₁₄H₂₀O₅ + 1Na], found 291.1195 [C₁₀H₁₂O₅ + 1Na].

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5.5. References

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Chapter 6: Bimetallic Ni-Pd alloy nanoparticles: An efficient catalyst for the room temperature hydrogenation of biomass-derived furans and furan/acetone aldol adducts

6.1. Introduction

Continuous depletion and increasing dependence on fossil resources has stimulated current research to look forward for an alternative source. In this way, lignocellulosic biomass (one of the most naturally abundant low-cost carbon-rich materials) has received tremendous attention to substitute nonrenewable fossil resources [1-5]. However, the complex structure of lignocellulosic biomass (having cellulose, hemicellulose and lignin polymers) restricts its direct usage; whereas biomass derived small fragments are generally used as starting material for the efficient production of various fine chemicals [6-8]. Recently, biomass-derived furans such as 2-furfuraldehyde (furfural), 2-furfuryl alcohol (1), 5-hydroxymethyl-2-furfural (5-HMF), 5methyl-2-furfural (5-MF) and their aldol adducts are extensively in use to produce fuel and different valuable compounds [9-14]. Fuel components produced from these furans like 2,5-dimethylfuran, 2-methylfuran, γ valerolactone (GVL) and hydrocarbons have shown high efficiency as highquality fuel [15-17]. However, due to the short carbon chain, these are not suitable for the direct use of fuels (due to low boiling points and insufficient specific energy density). Furthermore, aldol condensation of furans (furfural, 5-MF, and others) with acetone is one of the best ways to increase the carbon chain length to produce various valuable chemicals.

In this way, hydrogenated products of furan/acetone aldol adducts such as 4-(tetrahydrofuran-2-yl)butan-2-ol (4c), 1,5-bis(tetrahydrofuran-2yl)pentan-3-ol (5c) and others have wide applications in the production of long chain (C8-C13) hydrocarbon-based fuel components [18-20]. These hydrogenated products have diverse industrial applications, for instance 4c is one of the most important precursors for the synthesis of 1-octanol and ethyloctylether, important chemicals in perfume industries [18-20]. Moreover, tetrahydrofurans derivatives are also explored for 1,4rearrangement-ring expansion to produce oxocanes, the appealing chemicals for natural product synthesis [21].

Various Pd, Ru, Rh, Ir, Ni and Pt metal-based catalysts have been extensively explored for the hydrogenation of furans and their aldol adducts *[22-36]*. Among these, hydrogenation of furan derivatives has efficiently explored over Pd based catalysts, but most of the studies are at high temperature with high

H₂ pressure [23-33]. In this direction, Nakagawa et al. (2010) employed Ni- Pd/SiO_2 (Ni/Pd = 7) catalyst for the hydrogenation of furan derivatives, where total hydrogenation could be achieved in the presence of acetic acid and 8 MPa H₂ at 313 K [26]. Moreover, the reported Ni-Pd/SiO₂ catalyst displayed poor recyclability due to the significant amount of Ni leaching [26]. Li et al. (2014) explored hydrogenation of furfural/acetone aldol adduct over Pd/CN@MgO and attained hydrogenation of furan ring and olefins at 393 K using 1.0 MPa H₂ [27]. Similarly, Huber et al. (2005) achieved hydrogenation of furfural/acetone aldol adducts over Pd/Al₂O₃ at 393 K using 55 bars H₂ pressure in methanol [28]. Furthermore, the hydrogenation of aldol adducts of furfural or 5-HMF with acetone over Pd/MgO-ZrO₂ could also accomplished at 393 K with 55 bar H₂ [29]. Wegenhart et al. (2014) explored hydrogenation of different furoins using Pd/C with co-catalyst, amberlyst-15 or ZnCl₂, at 120 °C with high H_2 pressure (20-40 bar) in ethanol [30]. Analogously, hydrodeoxygenation of biomass-derived compounds was also attained over Pd/Nb₂O₅/SiO₂ catalyst, while at 170 °C with 2.5 MPa H₂ pressure [31]. Moreover, Chatterjee et al. (2010) studied the hydrogenation of furan aldol adducts over different Pd catalyst at 80 °C with 4 MPa H₂ as well as 14 MPa CO_2 and revealed that the formation of alkane proceeded through the reaction intermediate having hydrogenated furan rings [34]. Pt-based catalysts studied for hydrogenation and hydrodeoxygenation of furfural/acetone aldol adducts also required very high temperature and H₂ pressure (220 °C and 5.5 MPa) [35]. Similarly, Luska et al. (2016) employed bimetallic Fe-Ru nanoparticles immobilized on a supported ionic liquid phase (FeRuNPs@SILP) for the hydrogenation of substituted aromatic compounds including furfural/acetone aldol adduct and achieved hydrogenation of branch C=C and C=O bonds at 373 K and 20 bar H_2 [36]. The above rich literature reports revealed that most of the explored catalysts till date require high temperature and high H₂ pressure to achieve efficient hydrogenation of furan/furan-acetone aldol adducts, and hence the search for highly efficient hydrogenation catalysts for low temperature hydrogenation is of prime importance.

After successful exploration of various pathways for the upgradation of biomass-derived furans [37-40], herein, we report an efficient catalytic route for the room temperature total hydrogenation of different furans and

furan/acetone aldol adducts over bimetallic Ni-Pd alloy catalysts in water using H₂ gas.

6.2. Results and Discussions

6.2.1. Characterization of bimetallic Ni-Pd alloy nanoparticles. A simple co-reduction process was employed for the synthesis of bimetallic Ni-Pd alloy nanoparticles [41, 42]. Powder X-ray diffractogram of Ni_{0.90}Pd_{0.10} nanoparticles displayed a 2θ value of 40° corresponding to (111) lattice plane (Figure 6.1). A similar characteristic face centered cubic (fcc) structure was also observed during the powder X-ray diffraction (PXRD) analysis of all the NiPd nanoparticles, where a shifting towards higher 2θ value in contrast to Pd(111) and lower 2θ value as compared to Ni(111) diffraction indicates the formation of NiPd alloy (Figure 6.1). High resolution-Transmission electron microscopic (HR-TEM) images of the bimetallic Ni_{0.90}Pd_{0.10} nanoparticles revealed the particle size in the range of 2-4 nm (Figure 6.2a-b). Furthermore, energy dispersive X-ray spectroscopic (EDS) analyses and elemental mapping show the presence and a uniform distribution of both Ni and Pd metals in Ni_{0.90}Pd_{0.10} nanoparticles (Figure 6.2c and Figure 6.2e-g). Moreover, selected area electron diffraction (SAED) pattern for Ni_{0.90}Pd_{0.10} nanoparticles is revealed the presence of fcc (111) lattice plane (Figure 6.2d). The fringes with d-spacing of 0.214 nm as shown in the HR-TEM image of the Ni_{0.90}Pd_{0.10} nanoparticle (Figure 6.3) corresponds to the (111) planes of the NiPd alloy (dspacing for monometallic Pd and monometallic Ni are 0.225 nm (JCPDS 461043) and 0.205 nm (JCPDS 040850), respectively). Steady with the PXRD and SAED, X-ray photoelectron spectroscopic (XPS) analysis of Ni_{0.90}Pd_{0.10} displays characteristic signals for both metallic Pd [3d_{5/2}] and Ni $[2p_{3/2}]$ at 335.50 and 854.79 eV, respectively, which further supports alloy composition of Ni and Pd in Ni_{0.90}Pd_{0.10} (Figure 5.5, Chapter 5). Furthermore, ICP-AES, TEM-EDS, and SEM-EDS analyses of Ni_{0.90}Pd_{0.10} nanoparticles inferred the Ni to Pd atomic ratio of approximately 9:1.



Figure 6.1. Powder X-ray diffraction pattern of bimetallic Ni-Pd alloy nanoparticles and monometallic Ni and Pd nanoparticles.



Figure 6.2. (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. (f-g) their corresponding elemental mapping showing Pd (green) and Ni (red) for fresh Ni_{0.90}Pd_{0.10} nanoparticles.



Figure 6.3. HR-TEM image and corresponding d-spacing (in nm) for fresh Ni_{0.90}Pd_{0.10} nanoparticles.

6.2.2. Optimization of catalytic hydrogenation reaction conditions. The catalytic hydrogenation of compound 1 was initiated over monometallic Ni nanoparticles using H_2 gas at room temperature, where Ni nanoparticles were found inactive towards the hydrogenation of C=C bonds of furan ring (Table 6.1, entry 1). Interestingly, incorporation of a small amount of Pd (10 mol% Pd) in Ni to form bimetallic Ni_{0.90}Pd_{0.10} alloy nanoparticles, resulted in 66% conversion of compound **1** to the hydrogenated product, tetrahydro-2-furfuryl alcohol (1a) with >99% selectivity at room temperature in 6 h (Table 6.1, entry 2). Moreover, a complete conversion of compound 1 with >99%selectivity for the product 1a (79% isolated yield) was achieved in 12 h, under similar reaction conditions (Table 6.1, entry 3). In contrary to $Ni_{0.90}Pd_{0.10}$, monometallic Pd nanoparticles also resulted in the furan ring opening to produce 5-hydroxypentan-2-one (1b) in 39% selectivity along with the desired product **1a** (in 61% selectivity) in 6 h (Table 6.1, entry 4). The ring opening of compound 1 to 1b over Pd surface might be due to the multiple catalytic reactions involving hydrodeoxygenation of furfuryl alcohol to 2-methylfuran followed by furan ring opening to 1b, which is in accordance with previous reports [43-47]. Moreover, DFT calculations for furan hydrogenation and ring opening over Pd(111) surface suggested that hydrofuran is a reactive intermediate for both hydrogenation as well as ring opening pathways to form the respective tetrahydrofuran and ring open products [44]. Study suggested that furan ring opening is thermodynamically favored while ring hydrogenation is kinetically driven, and hence tetrahydrofuran is formed as a major product at low temperature. This was consistent with our findings with Pd nanoparticles (Table 6.1, entry 4), where the hydrogenated product tetrahydro-2-furfuryl alcohol (1a), was the major product over the open ring product (5-hydroxypentan-2-one; 1b) [44]. To get more insight into the mechanistic aspect, hydrogenation of 2-methylfuran was performed over monometallic Pd nanoparticles under optimized reaction conditions, resulted in the formation of the product 1b. These findings were in accordance with the previous reports suggesting that the ring opening presumable occurs via the hydrodeoxygenation of furfuryl alcohol over the Pd surface [43-47]. Interestingly with the Ni_{0.90}Pd_{0.10} alloy nanoparticles, any such open chain products (such as 1b) were not observed and only the desired product 1a remained the major dominating product even after extending the reaction time to 24 h or 48 h. The above observation suggested that the presence of Ni may tune the selectivity of the NiPd alloy towards ring hydrogenation over hydrodeoxygenation, presumably by tuning the interaction of furfuryl alcohol with the catalyst surface. Further the facile hydrogenation of furan ring over Pd nanoparticles was also in accordance with the previous reports, which suggest that the strong interaction of hydrogen with Pd surface and low activation barrier for H₂ dissociation on the surface of Pd, presumably made Pd to catalyze hydrogenation reactions even at room temperature [48-50]. Furthermore, a favorable interaction of furan ring to the Pd catalyst surface might also contribute in a facile hydrogenation under mild reaction condition [32, 44, 51]. In this regard, Li et al. (2017) also reported an efficient hydrogenation of furans (2-furfuryl alcohol) to total hydrogenated products (tetrahydro-2-furfuryl alcohol) over Pd nanoparticles based catalyst under room temperature conditions using H₂ gas at atmospheric pressure in 2propanol [33]. They proposed that the high catalytic activity for the hydrogenation of furan ring was due to the strong interaction of Pd surface with furan ring which was also in agreement with the observation of Nakagawa et al. (2014) [32, 33].

Notably, reactions performed without catalyst but in the presence of H₂ gas or the hydrogenating agent NaBH₄ could not lead to any conversion under

the optimized reaction conditions (Table 6.1, entry 5 and 6). Although a complete conversion of compound 1 was attained using 5 mol% Pd nanoparticles, reaction performed with 0.5 mol% Pd nanoparticles (equivalent to the amount of Pd present in $Ni_{0.90}Pd_{0.10}$ catalyst) resulted in only 30% conversion, which clearly depicts that the presence of Ni in bimetallic $Ni_{0.90}Pd_{0.10}$ alloy nanoparticles is important to achieve a selective and higher catalytic performance (Table 6.1, entry 7). It should be noted that the physical mixture of monometallic Ni and Pd nanoparticles (Ni/Pd = 9:1) exhibited only poor conversion (24%), which further revealed the crucial role of atomic level mixing of Ni and Pd in the observed higher catalytic performance of Ni_{0.90}Pd_{0.10} catalyst instead of mere presence of Ni and Pd (Table 6.1, entry 8). Further, the effect of Ni/Pd molar ratio in the catalytic hydrogenation of $\mathbf{1}$ was also examined using various bimetallic $Ni_{1-x}Pd_x$ (x = 0.25 to 0.75) nanoparticles under the optimized reaction conditions (Table 6.1 entries 9-11). The obtained results revealed the high catalytic performance in terms of turn over number (TON with respect to Pd content) of Ni_{0.90}Pd_{0.10} over other Ni₁. $_{x}Pd_{x}$ (x > 0.10) nanoparticles (Figure 6.4).



Figure 6.4. Influence of Ni/Pd molar ratio on the catalytic total hydrogenation of compound **1** to **1a** using H_2 gas at room temperature under aqueous reaction conditions.

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	о он <u></u> 1	_{1-x} Pd _x cata), H ₂ balloc	lyst on, rt 1a	H + HO 1b
Entry	Catalyst	t (h)	Conv. (%)	Sel. (%)
				(1a:1b)
1	Ni	12		
2	$Ni_{0.90}Pd_{0.10}$	6	66	>99:0
3	$Ni_{0.90}Pd_{0.10}$	12	>99	$>99 (79)^b:0$
4	Pd	6	>99	61:39
5 ^{<i>c</i>}		12		
6 ^{<i>d</i>}		12		
7^e	Pd	12	30	>99:0
8 ^{<i>f</i>}	Ni+Pd	12	24	>99:0
9	Ni _{0.75} Pd _{0.25}	6	82	>99:0
10	Ni _{0.50} Pd _{0.50}	6	88	>99:0
11	Ni _{0.25} Pd _{0.75}	6	98	>99:0

Table 6.1. Total hydrogenation of furfuryl alcohol: Reaction optimization.^{*a*}

^{*a*}Reaction conditions: compound **1** (1.0 mmol), catalyst (5 mol%), H₂ balloon, water (10.0 mL), rt = room temperature. ^{*b*}isolated yield. ^{*c*}without catalyst. ^{*d*}reaction with NaBH₄ (1 equiv.) in the absence of catalyst and H₂ gas. ^{*e*}0.5 mol% catalyst (equivalent to the amount of Pd in Ni_{0.90}Pd_{0.10}). ^{*f*}physical mixture of monometallic Ni and Pd nanoparticles (Ni/Pd = 9:1).

6.2.3. Catalytic total hydrogenation of furan derivatives. Efficacy of $Ni_{0.90}Pd_{0.10}$ catalyst was also evaluated for the catalytic hydrogenation of other furan derivatives. In this way, $Ni_{0.90}Pd_{0.10}$ catalyst exhibited remarkably high activity towards the room temperature hydrogenation of 3-furfuryl alcohol (**2**) to tetrahydro-3-furfuryl alcohol (**2a**) with >99% selectivity (76% isolated yield of **2a**) in 12 h under aqueous reaction conditions (Table 6.2, entry 1). Notably, a sluggish hydrogenation of 5-methyl-2-furfuryl alcohol (**3**) to 5-methyltetrahydro-2-furfuryl alcohol (**3a**) was observed, where 73% conversion is achieved in 12 h (Table 6.2, entry 2). However, increasing the time to 18 h resulted in the complete conversion of **3** with >99% selectivity for **3a** (82% isolated yield) (Table 6.2, entry 3).

Entry	Substrate	t (h)	Product	Conv. (%)	Sel. (%)
1	о <u></u> ОН 2	12	офорности Составляется и составляется и составляется и составляется составляется и составляется составляется с 2а	>99	>99 (76%) ^b
2	О	12	ОН	73	>99
3	3	18	За	99	>99 (82%) ^b
	3		3a		

Table 6.2. Catalytic total hydrogenation of furan derivatives over Ni_{0.90}Pd_{0.10} catalyst.^{*a*}

^{*a*}Reaction conditions: substrate (1.0 mmol), catalyst (5 mol%), H_2 balloon, water (10.0 mL), room temperature. ^{*b*} isolated yield.

6.2.4. Catalytic total hydrogenation of furan/acetone aldol adducts. Envisioned by the above results, catalytic activity of Ni_{0.90}Pd_{0.10} nanoparticles was further explored for the room temperature hydrogenation of furan/acetone aldol adducts. Interestingly, an efficient conversion (>99%) of 4-(furan-2yl)but-3-en-2-one (4) was achieved in 6 h, with 35% selectivity for 4-(tetrahydrofuran-2-yl)but-3-en-2-one having only (**4a**) furan ring hydrogenated and 65% selectivity for 4-(tetrahydro-furan-2-yl)butan-2-one (4b) with both the furan ring and olefin bond hydrogenated (Table 6.3, entry 1; Figure 6.5). Further increasing the reaction duration to 12 h, the complete hydrogenated product 4c was also obtained in 50% selectivity along with 4b in 50% selectivity (Table 6.3, entry 2; Figure 6.5). Subsequently, complete selectivity (>99%) for the product 4c (with 89% isolated yield) was achieved in 24h (Table 6.3, entry 4; Figure 6.5).

Ni _{0.90} Pd _{0.10} H ₂ O , H ₂ balloon,		rt $4a$		
Entry	t (h)	Conv.(%)	Sel. (%)	
			(4a:4b:4c)	
1	6	>99	35:65:0	
2	12	>99	0:50:50	
3	16	>99	0:40:60	
4	24	>99	$0:0:>99(89\%)^b$	

Table 6.3. Catalytic hydrogenation of compound 4 over Ni_{0.90}Pd_{0.10}.^a

^{*a*}Reaction conditions: compound **4** (1.0 mmol), catalyst (5 mol%), H₂ balloon, water (10.0 mL), rt = room temperature. ^{*b*} isolated yield.



Figure 6.5. Time-dependent study for the catalytic hydrogenation of compound **4** over $Ni_{0.90}Pd_{0.10}$ catalyst.

Analogous to the compound **4**, Ni_{0.90}Pd_{0.10} catalyst was also displayed high catalytic activity towards the hydrogenation to another furfural/acetone aldol adducts, 1,5-(difuran-2-yl)penta-1,4-dien-3-one (**5**), under the optimized reaction conditions. Complete hydrogenation of furan ring along with the olefin and C=O bonds was achieved in 24 h, with >99% selectivity of the product **5c** (91% isolated yield) (Table 6.4, entry 1-3). The observed results

for the time-scaled hydrogenation studies of compound **4** and **5** infer that the $Ni_{0.90}Pd_{0.10}$ catalyst has high efficacy towards the hydrogenation of furan ring, followed by the hydrogenation of olefin over carbonyl group.

Ni_{0.90}Pd_{0.10} 5b 5a H₂O. H₂ balloon. rt он 5 5c Conv. (%) Sel. (%) Entry t (h) (5a:5b:5c) 1 6 >99 12:88:0 2 12 >99 8:58:34 $0:0:>99(91\%)^{b}$ 3 24 >99 ^aReaction conditions: compound 5 (1.0 mmol), catalyst (5 mol%), H₂ balloon, water (10.0 mL). ^bisolated yield.

Table 6.4. Catalytic hydrogenation of compound **5** over Ni_{0.90}Pd_{0.10}.^a

Similarly, Ni_{0.90}Pd_{0.10} catalyst also showed high efficiency for the complete hydrogenation of 3-furfural/acetone aldol adduct (compound **6**) and >99% selectivity with 89% isolated yield of the product **6c** was attained after 24 h under optimized reaction conditions (Figure 6.6). Among various furan/acetone aldol adducts, compound **7**, having methyl (-CH₃) at the 5th position of furan rings, exhibited the hydrogenation of only branch C=C bonds to **7d** in 24 h, and complete furan ring hydrogenation could not be achieve (Figure 6.6). The observed lower catalytic hydrogenation of compound **7** was presumably because of the poor adsorption of furan ring of compound **7** or its hydrogenated product (**7d**) on the surface of Ni_{0.90}Pd_{0.10} catalyst due to the hindrance of methyl groups.

Impressively, methodology with $Ni_{0.90}Pd_{0.10}$ catalyst was further employed for a gram-scale hydrogenation of compound **5** (1.0703 g), where complete conversion with 78% isolated yield (0.8892 g) of the product **5c** was achieved in 72 h at room temperature (Figure 6.6).



Figure 6.6. Catalytic hydrogenation of furan/acetone aldol adducts. *Gram-scale catalytic hydrogenation of compound **5**.

6.2.5. Leaching and poisoning experiments. To further examine the nature of Ni_{0.90}Pd_{0.10} catalyst, heterogeneous or homogeneous, leaching and catalyst poising experiments (Hg and CS_2) [52, 53] were carried out. For leaching experiment, the hydrogenation of compound 1 was performed over $Ni_{0.90}Pd_{0.10}$ under the optimized reaction conditions. After 6 h, catalyst was recovered by centrifugation (6000 rpm for 10 min) and the obtained supernatant was divided into two parts. The one part was analyzed using ¹H NMR spectroscopy (66% conversion) while the other part was continued for another 6 h under the optimized reaction conditions (Figure 6.7). ¹H NMR analysis of the second part exhibited no remarkable increment in the conversion of compound **1**, which depicted the heterogeneous nature of $Ni_{0.90}Pd_{0.10}$ during the catalytic hydrogenation reaction (Figure 6.7). Additionally, catalyst poisoning experiments were performed with Hg and CS₂ exhibited a noteworthy quenching in the catalytic activity of Ni_{0.90}Pd_{0.10} catalyst, which also reinforced to the heterogeneity of catalytic hydrogenation reaction (Figure 6.7). Moreover, ICP-AES analysis of reaction mixture revealed no significant leaching of Ni and Pd metals from the catalyst and the Ni/Pd ratio remained constant before and after the catalytic reaction.



Figure 6.7. (1) Catalytic hydrogenation of furfuryl alcohol (compound 1) over $Ni_{0.90}Pd_{0.10}$ at room temperature in 12 h under the optimized reaction conditions. (2a-2b) Leaching experiments: catalytic hydrogenation of compound **1** over (2a) $Ni_{0.90}Pd_{0.10}$ at room temperature in 6 h; and subsequently (2b) catalyst was recovered from reaction mixture by centrifugation and reaction was continued for another 6 h at room temperature (without catalyst). (3) Hg poisoning experiment. (4) CS₂ poisoning experiment.

6.2.6. Stability and recyclability of Ni_{0.90}Pd_{0.10} nanoparticle catalyst. Furthermore, the highly active Ni_{0.90}Pd_{0.10} catalyst also displayed high stability in water as well as under employed reaction conditions. The recyclability experiments for Ni_{0.90}Pd_{0.10} nanoparticle catalyst was carried out for the catalytic hydrogenation of compound **1** to **1a** under the optimized reaction conditions for the 5 consecutive catalytic runs without any significant loss in the conversion and selectivity to the product **1a** (Figure 6.8). Notably, PXRD analysis of recovered catalyst showed identical patterns as of fresh Ni_{0.90}Pd_{0.10} nanoparticles (Figure 6.9). Moreover, SEM-EDS and elemental mapping of the used particles also revealed the presence of both Ni and Pd in 9:1 ratio (Figure 6.10).



Figure 6.8. Recyclability of $Ni_{0.90}Pd_{0.10}$ alloy catalyst for total hydrogenation of compound **1** to **1a**.



Figure 6.9. Powder X-ray diffraction pattern of fresh and used $Ni_{0.90}Pd_{0.10}$ alloy nanoparticles.



Figure 6.10. (a-c) SEM image and corresponding elemental mapping showing Ni (green) and Pd (red) for fresh Ni_{0.90}Pd_{0.10} nanoparticles. (d-

f) SEM image and corresponding elemental mapping showing Ni (green) and Pd (red) for used Ni_{0.90}Pd_{0.10} nanoparticles.

Hence, the efficient catalytic activity, stability and recyclability of the studied bimetallic $Ni_{0.90}Pd_{0.10}$ catalyst for the hydrogenation of biomass-derived furans and furan/acetone aldol adducts in H₂ atmosphere at room temperature under aqueous conditions make the methodology significantly important as most of the earlier reported studies are with noble metal catalysts using high pressure of H₂ gas and high reaction temperature.

6.2.7. Catalytic reaction pathway for the hydrogenation of furans. The high catalytic performance and reusability of explored bimetallic Ni/Pd alloy nanoparticles towards hydrogenation was established due to effective synergistic interaction between Ni and Pd metals. It is reported in literature that Pd nanoparticles based catalysts have high affinity for the adsorption and hydrogenation of C=C bond in comparison to C=O bond [54-57]. Furthermore, studies suggested that electropositive sites on the catalyst facilitate the adsorption and activation of C=O bond through the lone pair of electron present on carbonyl oxygen atom [57]. In this context, Ni-based catalysts have exhibited high efficiency for C=O bond hydrogenation over C=C bond, where the hydrogenation of C=O bond was assisted by the presence of a small fraction of Ni²⁺ in Ni nanoparticles based catalyst, while Ni(0) facilitated the adsorption of atomic hydrogen [58]. Further, our earlier reported DFT calculation suggested an electronic charge transfer from Ni (having lower ionization potential than Pd) to Pd in the bimetallic Ni/Pd alloy nanoparticles which resulted to an electron rich Pd center and partial positive charge on Ni center [42,59]. Hence, the observed efficient hydrogenation reaction over bimetallic Ni_{0.90}Pd_{0.10} nanoparticles as compared to monometallic nanoparticles and the physical mixture of Ni and Pd nanoparticles, was attributed to the homogenous alloy composition of the studied Ni_{0.90}Pd_{0.10} nanoparticles, where the Ni to Pd electronic charge transfer made Ni sites slightly positive which facilitated the adsorption of C=O bond on the catalyst surface, while electron rich Pd center promoted efficient adsorption of C=C bonds/furan ring and the activation of H₂ gas.

6.3. Conclusions

To summarize, we demonstrated a feasible and highly efficient room temperature total hydrogenation of biomass-derived furans and furan/acetone aldol adducts over Ni-Pd alloy nanoparticles catalyst under mild and environmental benign reaction conditions. Our findings established Ni_{0.90}Pd_{0.10} nanoparticles catalyst as the most efficient among the range of Ni-Pd with varied Ni/Pd ratios used for this reaction, and various other reports available in literature. We achieved hydrogenation of furan ring along with the active C=O and olefin bonds to produce long carbon chain (C8–C15) tetrahydrofuran products. The procedure could also be scaled up to transform gram-scale furan/acetone aldol adducts and showed remarkable recyclability. We believe this work will give insights into the development to other high-performing low-cost catalyst and catalytic methodologies for remarkable activity under mild reaction conditions.

6.4. Experimental section

6.4.1. General procedure for the synthesis of $Ni_{1,x}Pd_x$ (x = 0.10 to 0.75) **nanoparticles.** Bimetallic Ni_{1-x}Pd_x (x = 0.10 to 0.75) alloy nanoparticles are synthesized following our earlier reported process for the co-reduction Ni²⁺ and Pd²⁺ salts using NaBH₄ in the presence of polyvinylpyrrolidone (PVP), as a stabilizer, in water at room temperature [41, 42]. Briefly for the synthesis of bimetallic Ni_{0.90}Pd_{0.10}, an aqueous solution of NaBH₄ (0.0125 g in 5 mL water) was added dropwise to a 5.0 mL 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) at room temperature. The resultant mixture was sonicated for 10 min to obtain a black suspension of bimetallic Ni-Pd nanoparticles. In the similar way, other bimetallic Ni-Pd alloy nanoparticles, with different Ni/Pd molar ratios, as well as monometallic Ni and Pd nanoparticles were also synthesized using their suitable metal salts in specific molar ratios. Moreover, a physical mixture of Ni+Pd nanoparticles was prepared by the mixing of separately synthesized monometallic Ni and Pd nanoparticles in 9:1 molar ratio. For catalytic reactions, freshly prepared nanoparticles were properly washed with distilled water and re-dispersed in 10 mL distilled water.

6.4.2. Synthesis of compound 4. For the synthesis of compound **4**, 10.0 mmol of furfural and 10.0 mmol of K_2CO_3 were added to 10.0 mL solution of acetone and ethanol (2:3 v/v). Reaction mixture was stirred in an oil bath for 1 h at 50 °C. Afterwards, all volatiles were removed under reduced pressure. To the obtained residue, 10.0 mL distilled water was added and extracted using ethyl acetate (10 x 10.0 mL). The combined organic layers were collected, dried over anhydrous Na₂SO₄, filter off and all the volatiles were removed under reduced pressure. Purification of the obtained compound **4** was carried out with column chromatography using a mixture of ethyl acetate and dichloromethane (2:8 v/v). Identity of the compound **4** was confirmed by ¹H NMR, ¹³C NMR and HRMS.

6.4.3. Synthesis of compound 5. Compound **5** was synthesized using 10.0 mmol of furfural and 0.5 equivalents of acetone with 10.0 mmol of K_2CO_3 in 10.0 mL of ethanol. Reaction mixture was stirred at 50 °C in an oil bath for 36 h. Extraction and purification of compound **5** was performed as for compound **4** and the purified compound **5** was analyzed using ¹H NMR, ¹³C NMR and HRMS.

6.4.4. Synthesis of compound 6 and 7. Analogous to compound 5, compound6 and 7 were also synthesized using 3-furfural and 5-MF, respectively.

6.4.5. General procedure for the catalytic room temperature hydrogenation of furans and furan/acetone aldol adducts. Catalytic hydrogenation of furans and furan/acetone aldol adducts was carried out in a 50.0 mL round bottom reaction flask. Typically for hydrogenation reaction, 1.0 mmol of furan or furan/acetone aldol adduct was added to 10.0 mL aqueous suspension of 5.0 mol% Ni-Pd nanoparticle catalyst, and reaction mixture was stirred at room temperature equipped with a H_2 balloon for a desired reaction time. Reaction progress was monitored by thin layer chromatography (TLC). After completion of the reaction, the reaction mixture was centrifuged at 6000 rpm for 10 min to recover the catalyst and the obtained solution was extracted using ethyl acetate (5 x 10.0 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filter off and all the volatiles were removed under reduced pressure. Identity of the isolated products was confirmed by ¹H NMR, ¹³C NMR and HRMS. Conversion and selectivities of the obtained products were confirmed by ¹H NMR. To recycle,

centrifuged nanoparticles catalyst was washed with ethanol (1 x 2.0 mL) and distilled water (2 x 2.0 mL), and then re-dispersed in 10 mL distilled water for the subsequent catalytic runs.

6.4.6. Gram-scale hydrogenation of compound 5. For the gram-scale hydrogenation of compound **5**, a 100 mL round bottom flask was charged with 1.0703 g (5.0 mmol) of compound **5** and freshly prepared $Ni_{0.90}Pd_{0.10}$ catalyst (5 mol%) dispersed in 50 mL water. The whole mixture was stirred at room temperature in H₂ atmosphere (H₂ balloon) for 72 h. After the completion, catalyst was recovered from the reaction mixture by centrifugation at 6000 rpm for 10 min. The obtained reaction mixture was extracted using ethyl acetate (20 x 10.0 mL) and the combined organic layers were dried over anhydrous Na₂SO₄, filtered off followed by the removal of all the volatiles under reduced pressure. The obtained product was analysed by NMR and HRMS.

6.4.7. Hg poisoning experiment: To authenticate the heterogeneity of bimetallic Ni_{0.90}Pd_{0.10} alloy nanoparticle catalyst during the hydrogenation reaction, 10.0 mL aqueous suspension of 5.0 mol% of Ni_{0.90}Pd_{0.10} was vigorously stirred with an excess of Hg at room temperature. After 2 h, compound **1** (1.0 mmol) was added to the suspension and further stirred for 12 h in H₂ atmosphere under the optimized reaction conditions.

6.4.8. CS₂ **poisoning experiment:** Analogous to Hg poisoning experiment, 10.0 mL aqueous suspension of 5.0 mol% Ni_{0.90}Pd_{0.10} was stirred with 1 equiv. of CS₂ (0.05 mmol) for 2 h, and then compound **1** (1.0 mmol) was added to the suspension. The suspension was further stirred for 12 h in H₂ atmosphere under the optimized reaction conditions.

6.4.9. Spectral data for the furan/acetone aldol adducts



Compound 4: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 2.33 (s, 3H), 6.49 (m, 1H), 6.64 (d, 1H, *J* = 16 Hz), 6.68 (d, 1H, *J* = 4 Hz), 7.30 (d, 1H, *J* = 16 Hz), 7.50 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 27.75, 112.47, 115.59,

124.20, 129.37, 144.95, 150.80, 197.80. HRMS (ESI) m/z: calculated 159.0417 [$C_8H_8O_2 + Na$], found 159.0363 [$C_8H_8O_2 + Na$].



Compound 5: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 6.48 (m, 2H), 6.68 (d, 2H, , J = 4 Hz), 6.92 (d, 2H, J = 12 Hz), 7.49 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 112.59, 115.86, 123.13, 129.18, 144.89, 151.47, 188.06. HRMS (ESI) m/z: calculated 237.0522 [C₁₃H₁₀O₃ + Na], found 237.0539 [C₁₃H₁₀O₃ + Na].



Compound 6: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 6.66 (m, 2H), 6.77 (d, 2H, J = 16 Hz), 7.46 (s, 2H), 7.64 (d, 2H, J = 16 Hz), 7.72 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 107.37, 123.07, 125.26, 133.08, 144.45, 145.23, 188.55. HRMS (ESI) m/z: calculated 237.0522 [C₁₃H₁₀O₃ + Na], found 237.0528 [C₁₃H₁₀O₃ + Na].



Compound 7: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 2.47 (s, 6H), 6.21 (m, 2H), 6.68 (m, 2H), 6.96 (m, 2H), 7.53 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 13.90, 109.21, 117.56, 121.76, 128.97, 150.19, 155.67, 188.14. HRMS (ESI) m/z: calculated 265.0835 [C₁₅H₁₄O₃ + Na], found 265.0838 [C₁₅H₁₄O₃ + Na].

6.4.10. Spectral data of products obtained by catalytic hydrogenation of bio-derived furans and furan/acetone aldol adducts

Compound 1a: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.62 (m, 1H), 1.89 (m, 3H), 2.45 (b, 1H), 3.49 (m, 1H), 3.66 (m, 1H), 3.77 (m, 1H), 3.85 (m, 1H), 4.00 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 25.89, 27.05, 64.76, 68.15, 79.46. HRMS (ESI) m/z: calculated 125.0573 [C₅H₁₀O₂ + Na], found 125.0578 [C₅H₁₀O₂ + Na].

2a

Compound 2a: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.55-1.63 (m, 1H), 1.94-2.02 (m, 1H), 2.39-2.46 (m, 1H), 2.60 (b, 1H), 3.48-3.61 (m, 3H), 3.67-3.73 (m, 1H), 3.78-3.85 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 28.61, 41.39, 64.61, 67.75, 70.56. HRMS (ESI) m/z: calculated 125.0573 [C₅H₁₀O₂ + Na], found 125.0582 [C₅H₁₀O₂ + Na].



Compound 3a: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.22 (d, 3H, J = 8 Hz), 1.37-1.46 (m, 1H), 1.64-1.73 (m, 2H), 1.82-2.00 (m, 1H), 2.59 (b, 1H), 3.44-3.48 (m, 1H), 3.62-3.66 (m, 1H), 3.93-4.01 (m, 2H). HRMS (ESI) m/z: calculated 139.0730 [C₆H₁₂O₂ + Na], found 139.0732 [C₆H₁₂O₂ + Na].



Compound 4c: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.16 (d, 3H, J = 4 Hz), 1.40-1.62 (m, 5H), 1.80-2.00 (m, 3H), 3.67-3.88 (m, 4H). HRMS (ESI) m/z: calculated 167.1043 [C₈H₁₆O₂ + Na], found 167.1046 [C₈H₁₆O₂ + Na].



Compound 5c: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.40-2.00 (m, 16H), 3.61-3.88 (m, 7H). HRMS (ESI) m/z: calculated 251.1618 [C₁₃H₂₄O₃ + Na], found 251.1619 [C₁₃H₂₄O₃ + Na].



Compound 6c: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.40-1.53 (m, 9H), 1.74 (m, 2H), 2.03 (m, 2H), 2.16 (m, 2H), 3.33 (t, 2H), 3.57 (b, 1H), 3.75 (m, 2H), 3.83-3.89 (m, 4H). HRMS (ESI) m/z: calculated 251.1618 [C₁₃H₂₄O₃ + Na], found 251.1630 [C₁₃H₂₄O₃ + Na].



7d

Compound 7d: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 2.23 (s, 6H), 2.74 (t, 4H), 2.86 (t, 4H), 5.82 (s, 4H). HRMS (ESI) m/z: calculated 269.1148 [C₁₅H₁₈O₃ + Na], found 269.1187 [C₁₅H₁₈O₃ + Na].

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Chapter 7: Conclusions and Future scopes

7.1. Conclusion

Production of different value-added chemicals and fuel components from naturally abundant biomass and its derived compounds is one of the most appealing alternatives to minimize global dependence on the fossil resources. The different projects included in this thesis highlight our efforts towards the development of highly active homogeneous and heterogeneous metal catalysts for the catalytic upgradation of biomass-derived furan under simple and environmental benign reaction conditions.

In this thesis, we have demonstrated the effect of different ligands on the catalytic activity of arene-ruthenium complexes (homogeneous catalyst) in the transformation of biomass-derived furans. Furthermore, the exploration of different bimetallic alloy nanoparticles based heterogeneous catalysts revealed that the synergistic interaction between two metals may play a crucial role in the high as well as selective catalytic performance as compare to corresponding monometallic nanoparticles. Moreover, strong synergistic interaction between two metals may also lead to high stability through the charge transfer from one to another metal.

In chapter 3, arene-ruthenium(II) complexes were developed and successfully explored for the catalytic transformation of biomass-derived furans to different open ring value-added chemicals using formic acid as a hydrogen source under moderate reaction conditions. The usage of formic acid resulted to the efficient catalytic transfer hydrogenation and assisted the acid catalyzed hydrolytic ring opening of furans. The study further inferred an important role of N-H moiety and a labile chloro ligand during the transfer hydrogenation. The chloro ligand followed to an easy substitution and provided a site to coordinate formate ion. Furthermore, The N-H moiety (8aminoquinoline ligand) form hydrogen bond to bring the furfural in the close vicinity of the ruthenium center as well as transfer a H⁺ ion to the formyl group to facilitate the formic acid driven transfer hydrogenation of furfural to furfuryl alcohol, a crucial reaction intermediate. The high aqueous solubility and stability of the studied ruthenium catalyst offered high recyclability of the catalyst even being a homogeneous catalyst. Therefore, the study inferred that very high temperature and H₂ gas (difficult to handle and explosive in nature) are not necessarily require to upgrade biomass-derived furans.

In chapter 4, we explored various bimetallic Ni_{1-x}Pd_x ($0.1 \le x \le 0.75$) alloy nanoparticles catalysts for the aerial oxidation of biomass-derived furans to their corresponding carboxylic acid using air as an oxidizing agent under aqueous reaction conditions. The high catalytic performance displayed by bimetallic Ni_{0.90}Pd_{0.10} (as compare to Ni-Pd nanoparticles having high Pd content as well monometallic Ni and Pd nanoparticles) was accounted to the strong synergistic interaction between Ni and Pd metals which manifested to electronic charge transfer from Ni to Pd centre. The study also suggested that atomic level mixing of two metals was crucial to achieve an efficient transformation instead of mere presence of Ni and Pd. Furthermore, synergistic interaction between two metals in bimetallic alloy nanoparticles was also led to high stability (no significant leaching of Ni and Pd) and excellent recyclability for the studied Ni_{0.90}Pd_{0.10} alloy nano-catalysts.

In chapter 5, bimetallic M-Pd (M = Ni, Co, Cu) alloy nanoparticles were synthesized and supported on *in situ* generated Mg(OH)₂ nanoflakes. Among various explored catalysts, Ni_{0.90}Pd_{0.10}/Mg(OH)₂ outperformed for the aerial oxidation of 5-HMF without addition of an external base. In addition to synergistic interaction between Ni and Pd, using Mg(OH)₂ (a basic support) in Ni_{1-x}Pd_x/Mg(OH)₂ catalysts could be advantageous and resulted to high catalytic performance for the oxidation of 5-HMF to FDCA. Comparative study with different supports having acid or amphoteric nature (SiO₂, Al₂O₃ and ZnO) further inferred that using Mg(OH)₂ as a support not only facilitate the oxidation reaction, but also avoid the use of a base additive. Interestingly, synergistic interaction between two metals as well as cooperative effect of support in Ni_{0.90}Pd_{0.10}/Mg(OH)₂ also facilitated to achieve the gram scale transformation of 5-HMF to FDCA. Furthermore, the synthesized FDCA could efficiently transform to a series of furan diesters (precursors of biomassbased polymers and different value-added chemicals).

Beside oxidative upgrdation of biomass-derived furans, **in chapter 6**, we explored a facile and highly efficient total hydrogenation of biomass-derived furans and furan/acetone aldol adducts over bimetallic Ni-Pd alloy nanoparticles catalyst under mild and environmental benign reaction conditions. The study further supports that the synergistic interaction between two metals may lead to high and selective catalytic activity of bimetallic alloy

nanoparticles as we observed monometallic nanoparticles were either inactive (Ni nanoparticles), less active (physical mixture of Ni and Pd monometallic nanoparticles) or less selective to desired total hydrogenated product (Pd nanoparticles). The synergistic interaction, due to electronic charge transfer from Ni to Pd, might result to electron rich sites (Pd) and electron deficient sites (Ni) which could facilitate the interaction of different functional groups (furan rings, olefins, and carbonyl group) with the surface of catalyst. Furthermore, synergistic interaction further promoted the stability as well as reusability of Ni_{0.90}Pd_{0.10} alloy nanoparticles and could be employed for the gram-scale transformation of furan/acetone aldol adduct.

7.2. Future scope

Catalytic upgradation of biomass-derived furans is one of facile ways for the selective production of various fine chemicals. In this direction, homogeneous catalysts can be efficiently explored for the synthesis of desired compounds by the structural modifications in ligands which we also observed in our study. Notably, nano-catalysts have also appraised as an important class for the transformation of different biomass-derived feedstocks to highquality chemicals with the several advantages such as high stability and easy recovery from the reaction mixture. Moreover, the smaller size associated with nano-catalysts leads to the high surface area and high exposer of the active site to the convenience of reactant-catalyst interaction which can be analogous to the homogeneous catalytic system. Hence, development of simple, cost-effective and highly active homogeneous catalysts as well as heterogeneous nano-catalysts (based on metal or non-metal) can facilitate the development of efficient methodologies for the production of fuel components and different value-added chemicals from the biomass-derived compounds.

We believe that the account of studies included in this thesis may give more insight to development new methodologies and catalysts to upgrade biomass-derived compounds and other transformations for commercial applications such as (1) design and development of the cost-effective and highly-active catalysts (2) development of multifunctional catalysts to promote the interaction with different substrates which may facilitate to convert multiple steps reaction to one-pot reaction and may lead to avoid separation as well as purification of intermediate compounds (3) establishment of simple, easy and low-cost methodologies for the large-scale production of catalysts and different high-quality chemicals for industrial applications (4) Apart from usage of noble metals, development of non-noble metal based catalysts for the upgradation of biomass-derived compounds to achieve sustainable methodologies. Appendix A



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