## DEVELOPMENT OF CATALYSTS FOR TRANSFORMATION OF BIOMASS-DERIVED COMPOUNDS

M.Sc Thesis

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## DEPARTMENT OF CHEMISTRY

## INDIAN INSTITUTE OF TECHNOLOGY INDORE

May, 2022

## DEVELOPMENT OF CATALYSTS FOR TRANSFORMATION OF BIOMASS-DERIVED COMPOUNDS

### A THESIS

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

of

**Master of Science** 

by

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## INDIAN INSTITUTE OF TECHNOLOGY INDORE

May, 2022



## INDIAN INSTITUTE OF TECHNOLOGY INDORE CANDIDATES DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Development of Catalysts for Transformation of Biomass-derived Compounds" in the partial fulfillment of the requirements for the award of the degree of Master of Science and submitted in the Department of Chemistry, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2021 to May 2022 under the supervision of Dr. Sanjay Kumar Singh, Professor, Department of Chemistry, IIT Indore

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

Ankita Mondal Ankita Mondal

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

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Dedicated to my Parents .....

#### ACKNOWLEDGEMENT

First of all, I would like to thank my M.Sc. project supervisor, Prof. Sanjay Kumar Singh. It has been a pretty exciting and satisfying journey and I thank him for his constant encouragement and excellent guidance. It is said that the best teachers don't just give you answer, they help you to find it out. He has always encouraged independent thinking but also made sure that I don't get too much carried away. On various occasions he advised in various ways, but largely allowed me to explore the obscure area of heterogeneous catalyst. Things were tough at times and he ensured that I don't lose my motivation. It is a true privilege to have such a great advisor.

I would also like to thanks my PSPC members Dr. Tridib Kumar Sarma and Dr. Satya S. Bulusu for their suggestion during my project work.

I very much enjoyed the coursework during my M.Sc first year and learnt a lot. I would like to thank all the faculty members of department of Chemistry. I am very grateful to Dr. Biswarup Pathak (HoD, Department of Chemistry) and Dr. Tushar Kanti Mukherjee (DPGC convener, Department of Chemistry) for their support.

The Chemistry office staff members deserve special thanks. They are always ready to help and personally take care of any problem or task.

I would also like to thank SIC, IIT Indore for providing all the needed instrumentation facilities.

I would also like to thank DST-FIST NMR facility for the NMR facility.

I thank my present group members Ms. Bhanu Priya, Mr. Ankit Kumar, Mr. Sanjeev Kushwaha, Ms. Vaishnavi Kulkarni, Mr. Tushar Ashok Kharde, Ms. Jayashree Parthiban and Mr. Manoj Kumar Joshi for their constant support. They have enriched my understanding of chemistry through various questions in the group meeting and other discussion.

I would also like to thank two of my seniors Dr. Soumyadip Patra and Dr. Mahendra K. Awasthi for their suggestions and help.

I would also like to thank my brother Riku. We are quite close to each other and share a special bond. I must acknowledge the love and support of other family members.

One of my friends whom I am deeply indebted to is Souvik for his help, support and motivation at a stage when I really needed him.

I enjoyed the life at IIT very much and it would have been impossible without all of my friends, especially this acknowledgement will not be completed without thanking Shalini, Shruti, Sajal, Saroj and Sudarshan. I have learnt a lot from them, both in Chemistry and outside it.

Last but not the least, I would like to thank my parents for their love, support and faith they showed on me. They have been extremely encouraging and allowed me the maximal freedom. Sometimes it surprises me that despite being in an isolated village atmosphere they can thinks so high. My mother, especially, believes in a strong value for true education and possibly that helped us in our childhood to grow a natural love towards learning. Whatever I am today would have never been possible without them.

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#### Abstract

National energy security and climate change are the primary reasons to find alternative renewable and reliable sources to fulfill energy demand. The consumption of petroleumbased chemicals is increasing the  $CO_2$  emission which affects the global climate. Our main aim is to look for similar products derived from renewable sources which can replace the fossil fuels. Despite of being an agricultural waste, biomass is an easily available source of renewable carbon, which does not compete with the food and can be used for producing fuels and chemicals. This thesis is focused on development of heterogeneous catalysts for the transformation of biomass-derived compounds into fuel and value-added chemicals. This thesis contains four chapters. The structure of my thesis work is as follows: The 1st chapter describes the general scenario of global dependency of fossil fuel and the effect of combustion of fossil fuel thereby focusing on the importance of alternative and renewable energy resources which can replace the fossil fuels. It also describes the background of metal based heterogeneous catalyst for the transformation of biomass derived components to value-added chemicals and fuel components. In the 2<sup>nd</sup> chapter, I have described the experimental procedures for catalyst synthesis and different catalytic reactions. In the 3<sup>rd</sup> chapter I have discussed about my experimental results. In the last chapter I have concluded my thesis with my major findings. Main goal of this thesis is to develop an active and efficient heterogeneous catalyst which is active under environment benign conditions.

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## ACRONYMS

CDCl <sub>3</sub>	Chloroform-d
<b>CO</b> <sub>2</sub>	Carbon dioxide
СТАВ	Cetyltrimethylammonium bromide
EDS	Energy Dispersive Spectroscopy
H <sub>2</sub>	Hydrogen
НТ	Hydrotalcite
НМТ	Hexa-methylentetramine
NMR	Nuclear Magnetic Resonance
NP'S	Nanoparticles
PXRD	Powder X-ray Diffraction
PAF	Porous Aromatic Framework
Ru	Ruthenium
RuCl <sub>3</sub> . xH <sub>2</sub> O	Ruthenium (III) chloride hydrate
SEM	Scanning Electron Microscopy
NaBH <sub>4</sub>	Sodium borohydride
TGA	Thermo-gravimetric Analysis
TMS	Tetramethylsilane

## NOMENCLATURE

Conv.	Conversion
°C	Degree Celsius
g	gram
h	Hour
λ	Lambda
mL	Milliliter
Min	Minutes
mmol	Millimole
MHz	Mega Hertz
P <sub>H2</sub>	Pressure of H <sub>2</sub> gas
RB	Round bottom
Ref.	Reference
Sel.	Selectivity
Τ	Temperature
t	Time

### **Chapter-1**

### Introduction

#### **1.1 General Introduction:**

Now a day, the energy demand is increasing globally with increase in the population, industrialization and civilization.<sup>1-4</sup> Since the world's primary sources for energy are fossil fuels, this growth raises important issues at environmental, economical and social levels. Petroleum is exploited at a much faster rate than its natural regeneration through the planet carbon cycle.<sup>2-8</sup> The price for crude oil, transportation fuels and petroleum-derived chemicals increases due to decreasing the amount of fossil fuel. Also the emission of greenhouse gases (GHG), such as carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ) and nitrous oxide ( $N_2O$ ) arising from the combustion of fossil fuels. Global warming and others issues can be mitigated by shifting from fossil fuels to renewable energy sources.<sup>9</sup> Renewable sources are solar energy, wind energy, geothermal energy, biomass energy etc. Out of this biomass occupies 70% of total renewable energy. Lignocellulosic biomass is one of the most abundant natural sources of carbon-rich materials for the generation of fuel and a variety of compounds with a wide range of uses, ranging from fuels, medications and value-added chemicals.<sup>10-12</sup> Among the various renewable resources, biomass is one of the most reliable sources because of its high abundance and low cost. The major components of lignocellulosic biomass are cellulose (40-50%), hemicellulose (25-30%) and lignin (10-25%).<sup>12-13</sup> Cellulose is composed of hexoses units held together via  $\beta$ -1,4-glycosidic bonds. The 2<sup>nd</sup> component of lignocellulosic biomass is hemi-cellulose which contains both pentoses and hexoses. Lignin is the most complex component of lignocellulosic biomass. Lignin is amorphous, threedimensional highly branched polyphenolic substance. Lignin is mainly composed of p-coumaryl alcohol, sinapyl alcohol and coniferyl alcohol units.



The energy content of different biomass constituents increases with increasing the H:C ratio and decreases with increasing oxygen content. Among the three constituents, lignin has higher H:C ratio so it is the most promising candidate for fuel components. Lignin cannot be used directly because of its complex polymeric structure. So firstly, depolymerization of lignin is required. After the depolymerization, different monomeric unit mainly phenolic and other aromatic products are obtained. The hydrogenation of these phenolic compounds is dragging more attention due to wide applications of hydrogenated products as solvents, fuel and polymer precursors.



Figure 1: Catalytic transformation of biomass derived lignin component.

For hydrogenation of these phenolic compounds various noble metal (Ru, Rh, Pt, Pd) and non-noble metal catalysts (Ni) have been used.<sup>1-19</sup> In most of the cases, the reactions were

performed at higher temperature and higher pressure of  $H_2$  gas was used along with the use of expensive noble metals and additives. Also, in some cases the reaction yield is low with poor selectivity for total hydrogenated product.

So herein, we have synthesized and characterized Ru nanoparticle catalyst by chemical reduction method using sodium borohydride and performed the hydrogenation reaction of various phenolic compounds using hydrogen balloon at room temperature in water.

### **1.2 Literature Review:**

## Table 1: Hydrogenation of different lignin components

Substrate	Catalyst	Solvent	Product	Т	P <sub>H2</sub>	t	Conv.	Yield	Ref.
				(°C)	(bar)	( <b>h</b> )	(%)	(%)	
Phenol	Pd/y-Al <sub>2</sub> O <sub>3</sub>	Water	Cyclohexanol	80	20	12	100	100	12
Phenol	Pt-PAF-30	Water	Cyclohexanol	80	30	4	77	75	13
Phenol	Pt-PAF-30	Iso-propanol	Cyclohexanol	80	30	4	98	87	13
Phenol	Ru-PAF-30	Water	Cyclohexanol	80	30	4	100	100	13
Phenol	Ru-PAF-30	Iso-propanol	Cyclohexanol	80	30	4	64	58	13
Eugenol	NiRu-HT	Iso-propanol	4- propylcyclohex anol	150	25	6	100	83.8	14
Phenol	Rh-HMT	Water	Cyclohexanol	30	5	6	100	100	15
Diphenyl methane	Rh-HMT	Water	Dicyclohexylm ethane	80	15	24	100	98	15
Benzyl phenyl ether	Rh-HMT	Water	(cyclohexylmet hoxy)cyclohex ane	100	15	24	98	45	15
Diphenyl ether	Rh-HMT	Water	Oxydicyclohex ane	80	15	24	100	82	15
Phenol	RuO <sub>2</sub> - MCM-41	Water	Cyclohexanol	100	10	24	100	100	16
Guaiacol	Ru-TiO <sub>2</sub>	Water	Cyclohexanol	160	15	1.5	100	78.1	17

Substrate	Catalyst	Solvent	Product	Т	P <sub>H2</sub>	t	Conv.	Yield	Ref.
				(°C)	(bar)	( <b>h</b> )	(%)	(%)	
Guaiacol	Ru-SiO <sub>2</sub>	Water	Cyclohexanol	160	15	1.5	100	75.2	17
Guaiacol	Ru-	Water	Cyclohexanol	160	15	1.5	100	76.9	17
	TiO <sub>2</sub> @SiO <sub>2</sub>								
Phenol	Ni/SiO <sub>2</sub>	Decalin	Cyclohexanol	120	20	2	99.9	99.9	18
Diphenyl	Ru/Nb <sub>2</sub> O <sub>5</sub>	Isopropa	Oxydicyclohexa	30	30	2	100	72.2	19
ether		nol	ne						

Li et al.<sup>2</sup> reported hydrogenation of phenolic derivatives using Pt supported on carbonnanotubes at 50 °C and 0.5 MPa H<sub>2</sub> pressure. They achieved 97.3% conversion of phenol in 30 min and selectivity for cyclohexanone and cyclohexanol is 77.5 and 22.5% respectively while using DCM-water as solvent. Zhou et al.<sup>3</sup> reported Pd catalyst supported on Cheteropoly acid for hydrogenation of phenol selectively at 80  $^{\circ}$ C and 1 MPa H<sub>2</sub> pressure. They got complete conversion of phenol in 3 h and selectivity for cyclohexanone is 93.6%. In presence of acidic supports the Pd shows higher efficiency in hydrogenation reactions. In the similar direction, Hu et al. reported a  $Pd/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for hydrogenation of different lignin derivatives at 80 °C and 20 bar H<sub>2</sub> pressure.<sup>12</sup> In case of phenol they achieved complete conversion in 12 h and got cyclohexanol in 100% yield. They explored hydrogenation of different substrates like guaiacol using same catalyst but they got only 47.4% conversion and yield was also very low in this case. Kulikov et al. investigated Ru and Pt metal supported on aromatic framework as a catalyst for the hydrogenation of phenolic monomers at 80°C and 30 atm pressure and also, they checked the effect of different solvents on the catalytic hydrogenation reaction.<sup>13</sup> Ru gave complete conversion in water but in isopropanol only 64% conversion of phenol was observed. But different behavior was observed in case of Pt where in water only 77% conversion was observed and use of isopropanol resulted in 98% conversion of phenol. These results imply that the mechanism of hydrogenation of these phenolic monomers was different. In case of Ru, the water molecule dissociated on the surface of nanoparticles due to high oxygen affinity of

ruthenium. In order to make catalyst more cost effective, Sakthivel et al. reported bimetallic NiRu catalyst for the hydrogenation of lignin monomers at 150 °C and 25 bar H<sub>2</sub> pressure and they got complete conversion of eugenol with 83.8% yield of 4-propyl cyclohexanol.<sup>14</sup> They used non-noble Ni metal to increase the catalytic activities of Ru. Later, Dyson et al. reported Rh nanoparticles supported on N-doped carbon based, hexamethyl tetramine for the hydrogenation of lignin components.<sup>15</sup> They carried out the reaction at 30 °C temperature and 5 bar H<sub>2</sub> pressure. The disadvantage of this catalyst was that if substrate contains two or more electron donating group the hydrogenation process gets hindered. Also, hydrogenolysis products were formed along with total hydrogenated products. So, this catalyst was not selective for the hydrogenation of lignin components.

Literature has revealed that various non-noble and noble metal catalysts have been used for the hydrogenation of lignin components. Also, in some cases we saw use of bimetallic catalysts.<sup>14</sup> Because in the presence of a second metal the catalytic activity is enhanced. The acidic supports also help in catalytic hydrogenation reaction. The noble metals are more active than the non-noble metals for such kind of reactions. Ru acts as a good catalyst for the hydrogenation of aromatic ring selectively and also Ru is the cheaper than other noble metals. In most of the cases the reaction was carried out at a higher temperature and higher-pressure conditions, which is not very environment friendly.

#### **1.3 Challenges in Hydrogenation of Lignin Components:**

Hydrogenation is considered to be a crucial step for the synthesis of bio-fuels from the biomass-derived components. But this process is very challenging as harsher reaction conditions like higher temperature and higher H<sub>2</sub> pressure are required. Also use of high cost noble metals is very common.



Figure 2: Challenges in hydrogenation of lignin-derived compounds

Therefore, an efficient catalytic system which is active under mild and environment benign conditions is highly desirable.

#### **1.4 Objectives of the Project:**

Depletion of fossil fuel resources made us to look for renewable resource as an alternate option to fulfill the growing energy demands. In this regard, the bio-derived short chain chemicals are transformed into various useful fuel grade components which are a more prominent route to decrease the worldwide reliance on fossil assets. Thus, lignocellulosic biomass (most naturally plentiful low-cost carbon-source) can serve as best alternative to substitute non-renewable fossil assets. This conversion of bio-derived compounds to various chemicals has been the subject of exceptional examination endeavors for the last few decades.

This project aims the preparation of novel, active and stable heterogeneous catalyst for the conversion of bio-derived lignin components into highly value added chemicals and fuel grade components.

### **Chapter-2**

### **Experimental section**

#### 2.1 Materials and Instrumentation:

All chemicals and metal salts were purchased from Alfa-Aesar, Sigma-Aldrich and Spectrochem which were used without any further purification. <sup>1</sup>H NMR were recorded in deuterated solvent (CDCl<sub>3</sub>) using Bruker Avance 400 and Bruker Ascend 500. Chemical shifts were referenced to the internal solvent resonances and reported relative to TMS. Powder X-ray diffraction (P-XRD) measurements were performed using Rigaku Smart Lab, Automated Multipurpose X-ray diffractometer at 40 KV and 30 mA (Cu<sub> $\alpha$ </sub>  $\lambda$  = 1.5418 A). SEM was performed using JSM-7610FPlus.

#### 2.2 Synthesis of Ru catalyst:

50 mg CTAB was added to 5 mL aqueous solution of  $RuCl_{3.xH_2O}$  (0.0104 g). To which aqueous solution of NaBH<sub>4</sub> (25 mg in 5 mL H<sub>2</sub>O) was added dropwise under sonication. The contenst of the flask were sonicated for 10 minutes at room temperature to obtain black suspension of Ru nanoparticles, which are then collected by centrifugation and washed with distilled water several times, dried under vacuum and then used for catalytic reactions.

# 2.3 Hydrogenation of Lignin components over Ru catalyst at room temperature:

For the hydrogenation reactions, the substrate (1 mmol) was taken in a 50 mL RB. Then an aqueous suspension of 5 mol% Ru nanoparticles in 10 mL water was added to it. The reaction vessel was equipped with  $H_2$  balloon and stirred for desired time at room temperature. After the completion of reaction, catalyst was recovered by centrifugation and product was extracted using dicholoromethane (5x10 mL). Organic layer was dried using rotatory evaporator. Conversion and selectivity were calculated from <sup>1</sup>H NMR using benzaldehyde as an internal standard.

### **Chapter-3**

### **Results and discussion**

#### **3.1 Characterization of the catalyst:**

We have synthesized Ru nanoparticles and catalyst was characterized by PXRD and SEM. Powder X-ray diffractogram of Ru np's shows  $2\theta$  value at  $43^{\circ}$  which corresponds to (101) plane of hexagonal closed packed Ru nanoparticles (Figure 3). PXRD spectrum showing the broad peaks indicating amorphous nature and small size of Ru np's.



Figure 3: PXRD spectrum of Ru catalyst

FE-SEM was carried out to know about the morphology of catalyst. SEM image and corresponding EDS spectra confirming the presence of Ru (Figure 4).



Figure 4: SEM image and corresponding EDS spectra of Ru catalyst

We have also performed the thermo-gravimetric analysis of Ru catalyst to check the stability of the catalyst.



Figure 5: Thermogravimetrc Analysis (TGA) of fresh Ru catalyst

Above figure concluded that first 17% weight loss below 100 °C was due to the moisture adsorbed on the catalyst surface. Then there was no major weight loss. So this figure (Figure 5) inferred that catalyst is stable up to higher temperature.

#### **3.2 Optimization of the catalytic hydrogenation reaction condition:**

We have chosen diphenylmethane as a model substrate to optimize the reaction conditions because of its simplest structure. First we have performed the reaction without catalyst only in presence of  $H_2$  balloon (Table 2, entry 1) and observed that no conversion of diphenylmethane was observed which shows that catalyst plays a crucial role in carrying out the hydrogenation reaction. Then we used Ru nanoparticles as a catalyst (5 mol%) for the hydrogenation of **1** in water using hydrogen balloon for 12 h and we observed 98% conversion of **1** with the selectivity of 86 and 14% for **1a** and **1b** respectively (Table 2, entry 2). Reaction performed in the absence of hydrogen balloon resulted in no conversion at all signifying that hydrogen balloon is required for the catalytic reaction (Table 2, entry 3). In order to achieve the complete conversion we performed the reaction for 18 and 24 h and achieved the complete conversion in both the cases but the complete selectivity towards **1a** could not be achieved in 18 h (Table 2, entries 4-5). These results inferred that in order to achieve high selectivity for total hydrogenated product we require Ru catalyst and  $H_2$  balloon as a hydrogen source.

 Table 2: Hydrogenation of compound 1: Reaction optimization<sup>a</sup>



Entry	Catalyst	Time (h)	Conversion	Selectivity (%)	
			(%)	(1a:1b)	
1 <sup>b</sup>	-	24	-	-	
2	Ru	12	98	86: 14	
<b>3</b> <sup>c</sup>	Ru	24	-	-	
4	Ru	18	99	94: 6	
5	Ru	24	>99	>99: 0	
<sup><i>a</i></sup> Reaction condition: Compound 1 (1.0 mmol), Catalyst (5 mol%), H <sub>2</sub> balloon, water (10.0					
mL), rt: room temperature, <sup>b</sup> without catalyst, <sup>c</sup> absence of H <sub>2</sub> balloon					

### 3.3 Substrate Scope:

After optimizing the reaction conditions for hydrogenation of diphenylmethane, we extended the scope of our catalyst for different substrate.

#### Table 3: Substrate Scope<sup>a</sup>

Entry	Substrate	Product	Conv.	Yield
			(%)	(%)
1 <sup><i>b</i></sup>	OH 2	OH J 2a	>99	48
2	OH 3	OH J 3a	>99	68
3		4a	>99	40
4	5 5	5a	>99	<10
5	OMe 6	6a	>99	<10
6	OH 7	OH 7a	35	11

<sup>*a*</sup>Reaction condition: substrate (1 mmol), Ru catalyst (5 mol%),  $H_2O$  (10.0 mL),  $H_2$  balloon, rt: room temperature, 24 h, <sup>*b*</sup>reaction time: 12 h.

From the table 3 we can see that in almost all the cases we got complete conversion (Table 3, entries 1-5). In case of Phenol we got complete conversion and yield was 48% (Table 3, entry 1). In case of cinnamyl alcohol the yield was 68% and complete conversion was occurred (Table 3, entry 2). Benzyl phenyl ether gives complete conversion and the yield was 40% (Table 3, entry 3). In case of diphenyl ether and anisole complete conversion was occurred but the yield was <10% in both the cases (Table 3, entries 4-5). This happens because in these two cases the hydrogenolysis of C-O bond occur leading to low yield of total hydrogenated product. Benzyl alcohol is not completely converted into hydrogenated product under the same reaction conditions (Table 3, entry 6). This might be due to the methylene group being present in different plane as that of the phenyl ring of benzyl alcohol thus making it difficult for the phenyl ring to be adsorbed on catalyst surface.

### **Chapter-4**

### Conclusions

We have hydrogenated a few monomer compounds of lignin at room temperature. We have achieved good conversions in most of the cases. We have performed the reactions under environment benign conditions using water as a solvent and hydrogen balloon. We have characterized our catalyst by PXRD, SEM-EDS and TGA analysis. Furthermore, the process involves the use of heterogeneous catalyst which is easy to separate and reuse. So, we found an efficient way to hydrogenate the lignin-derived compounds which are essential for the synthesis of different value-added chemicals and fuel components.

## **APPENDIX-A**



Figure 6: <sup>1</sup>H NMR spectrum of 1a



Figure 7: <sup>13</sup>C NMR spectrum of **1a** 



Figure 8: <sup>1</sup>H NMR spectrum of 2a



Figure 9: <sup>1</sup>H NMR spectrum of 3a



Figure 10: <sup>1</sup>H NMR spectrum of 4a with Internal Standard (Benzaldehyde)



Figure 11: <sup>1</sup>H NMR spectrum of compound **5a** with internal standard (Benzaldehyde)



Figure 12: <sup>1</sup>H NMR spectrum of compound 6a with internal Standard (Benzaldehyde)



Figure 13: <sup>1</sup>H NMR spectrum of compound 7a with internal standard (benzaldehyde)

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