Design and Development of Efficient Catalysts for Hydrogen Production

Ph.D. Thesis

by

MAHENDRA KUMAR AWASTHI



DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE SEPTEMBER 2021

Design and Development of Efficient Catalysts for Hydrogen Production

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

by MAHENDRA KUMAR AWASTHI



DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE SEPTEMBER 2021



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Design and Development of Efficient Catalyst for Hydrogen Production" in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT/SCHOOL OF CHEMISTRY, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from December and 2016 to September 2020 under the supervision of Dr. Sanjay Kumar Singh, Associate Professor, Discipline 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.

Mahendry KrAwasthi 06.09.2021

Signature of the student with date

(MAHENDRA KUMAR AWASTHI)

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

06.09.2021

Signature of Thesis Supervisor with date

(Dr. SANJAY KUMAR SINGH)

MAHENDRA KUMAR AWASTHI has successfully given his/her Ph.D. Oral Examination held on 25/02/2022.

25.02.2022

Signature of Thesis Supervisor with date

(Dr. SANJAY KUMAR SINGH)

Acknowledgements

A positive environment brings positivity in your life to achieve what you want to achieve. I want to express my gratitude to everyone who ever supported me throughout this journey of my life. I would like to take this opportunity to acknowledge all who prepared me for this achievement.

In the first place, I would like to express my sincere gratitude to **Dr. Sanjay Kumar Singh**, my respectable thesis supervisor, for his aspiring guidance, invaluably constructive feedback and sincere advice during my research work. I am also genuinely grateful to him for his unwavering support in shedding light on me with his insightful and enlightening views and discussions on my project and research-related issues. It was wonderful learning about integrity, competence and dedication, through my entire Ph.D. working with him. I am thankful to him for his suggestion and guidance for the all-time of my research work. I am thankful to him for providing his precious time and suggestions for my papers and thesis corrections. I feel a deep sense of respect for him and I surely can say that I could not have imagined having a better supervisor for my Ph.D. research.

I am also thankful to my **PSPC members, Dr. Biswarup Pathak**, and **Dr. Mrigendra Dubey**, for the considerate endorsement and their honest, cooperative response and queries solicited in this study. I am thankful to Convener, **DPGC** for all the immense help. I would like to acknowledge **Head**, **Discipline of Chemistry and Head**, **School of Basic Sciences, IIT Indore** for providing infrastructure and lab facilities.

I would like to express my special gratitude and thanks to **Prof. Nilesh Jain, (Officiating Director, Indian Institute of Technology Indore)** for providing me the opportunity to be a part of such a prestigious institute which is having 68th rank in times higher education ranking among young universities. I am grateful to him for providing all supports and best research facilities and a pleasant environment at Indian Institute of Technology Indore.

I would like to thank to all faculty members of the department of chemistry for their guidance and help during various activities in the Department of Chemistry, IIT Indore, I would like to thank all faculty members, Dr. Rajneesh Misra, Dr. Suman Mukhopadhyay, Dr. Apurba K. Das, Dr. Shaikh M. Mobin, Dr. Anjan Chakraborty, Dr. C. Venkatesh, Dr. Tridib K. Sarma, Dr. Tushar K. Mukherjee, Dr. Satya S. Bulusu, Dr. Amrendra K. Singh, Dr. Abhinav Raghuvanshi, Dr. Dipak Kumar Roy, Dr. Selvakumar Sermadurai, and Dr. Umesh A. Kshirsagar.

I am extremely grateful to **Dr. Abhinav Kumar** (University of Lucknow) for her generous advice, motivation, and encouragement in many ways throughout my M.Sc. and PhD.

I am also very much thankful to my institute, **IIT Indore** for providing the best infrastructure, and **SIC**, for all necessary instrumentation facilities. I would like to thank to **Ministry of Human Resource Development (MHRD)** (JRF) and **DST –INSPIRE**

(JRF and SRF grants) New Delhi for providing financial support for my Ph.D. research at IIT Indore.

I wish to thank the technical staff from Sophisticated Instrumentation Center (SIC), IIT Indore, Mr. Kinny Pandey, Mr. Ghanshyam Bhavsar, Ms. Sarita Batra, Mr. Manish Kushwaha, Ms. Vinita Kothari, Mr. Parthiban P K, Mr. Rameshwar Dauhare and Mr. Nitin Upadhyay for their timely technical support without which it would never have been possible to complete my work. I am also thankful to academic staff members Ms. Dibya, Mr. Sunny Namdev, Mr. Tapesh Parihar, Mr. Roshan Bhatia, Mr. Amber Dixit, and Ms. Rinky Kukreja for all their timely help. I would also like to thank Mrs. Anjali Bandiwadekar, Mr. Rajesh Kumar, Mr. Lala Ram Ahirwar and other library staff, Mr. Nitin Bhate, Mr. Prahalad, Deepak, Mr. Dayaram, Mr. Manoj Pal, and other technical and non-technical staff for their constant help, whenever required. I would also like to thank all the technical, non-technical staff of IIT Indore for all their direct/ indirect help and support.

I am also very much grateful to my former lab mates cum friends Dr. Rohit Kumar Rai, Dr. Deepika Tyagi, Dr. Kavita Gupta, Dr. Hemanta Deka and Dr. Ambikesh Dhar Dwivedi who supported me and guided me in every important aspect of research. I would like to give special thanks to Mr. Rohit for encouraging me in each difficulty related to my research work. I extend my acknowledgment to all my other labmates, Soumyadip Patra, Vinod Kumar Sahu, Ankit Kumar Chaurasiya, Bhanupriya Sharma, Vaishnavi Kulkarni, Sanjeev Kushwah and Tushar Kharde for their pleasant company. I cannot forget to acknowledge the most energetic and enthusiastic engineers of our lab Dr. Dharmendra Panchariya and Debashis Panda for their love and care for me like brothers. I wish to acknowledge past members (M.Sc. students) from our group, Ms. SK Nazmul Hasan Md Dostagir, Ms. Vanitha Readdy, Ms. Nirupama Sheet, and Ms. Chanchal Saini who did their master's project in our lab.

I would like to extend my sincere thanks to all my seniors, juniors and friends at IIT Indore, Mr. Praveen, Mr. Vishal, Mr. Abhinav, Mr. Vivek, Ms. Dibya, Dr. Kuber, Dr. Promod, Dr. Siddharth, Dr. Rohit, Mr. Saurabh, Mr. Sayan, Dr. Novina, Ms. Anupama, Dr. Ajeet, Dr. Sagnik, Mr. Soumitra and Dr. Priyanka.

I would like to express my sincere thanks to my loving families. I express my deep sense of gratitude to my parents **Mrs. Tarawati** and late **Mr. Radhey Shyam Awasthi** for the love and faith they kept in my dreams. My special thanks go to my all loving brothers, especially **Mr. Girijesh Kumar Awasthi** for all their constant help, love and support. I am also thankful to all my other family members and friends for supporting me at every stage of my life and support me for my dreams.

Words are short to express my deep sense of gratitude, but at the end of this journey, it is my great pleasure to thank them all who contributed in many ways to my success and made it an unforgettable experience for me.

Thank You!!!!!

Mahendra Kumar Awasthi



SYNOPSIS

Huge dependency on the limited resources of fossil fuels and adverse effects on the environment due to its consumption enforces the scientific society to search for sustainable and renewable energy sources to cater for the increasing global energy demand. Hydrogen is now a well-known clean source of energy. However, the production and storage of hydrogen using renewable resources are challenging due to the physical property of hydrogen. This thesis comprises the six chapter in which we discussed about the importance of hydrogen as well as the design and development of efficient catalytic systems for the production of hydrogen gas from various liquid organic hydrogen carriers (LOHCs) such as hydrazine, methanol, formaldehyde and other alcohols. The first chapter of this thesis is about the brief discussion and literature survey on the importance of hydrogen, its utility, storage and production. Further, subsequent chapters 2-5 describe the synthesis and development of catalytic systems for hydrogen production from several LOHCs under varying reaction conditions. The prime objective of the research work presented in this thesis is to develop a highly active and efficient catalytic system for hydrogen production from various liquid organic hydrogen carriers and to study the mechanistic pathways for hydrogen production using various instrumentation techniques. The last chapter concludes the important outcome of the research work present in this these, and briefly describes the outlook and future scope of the present research work.

The content of each chapter included in the thesis are briefly summarized here:

Chapter 1. An Overview on Hydrogen Production from Various Liquid Hydrogen Storage Materials: Role of the Catalyst

Chapter 1 describes the important highlights of hydrogen gas as a potential clean fuel, and its production using different liquid organic hydrogen carriers. This chapter also describes, in brief, the role of different homogeneous and heterogeneous catalysts for hydrogen production. The increasing content of greenhouse gases due to the excessive usage of fossils fuels has raised an alarming situation globally. Therefore, for a sustainable future, the search for an efficient renewable resource of energy is the need of the hour. Hydrogen can be the one key sources of energy as upon reacting in the fuel cell with oxygen it produces electricity along with the water as the sole byproduct. One of the major hurdles to use hydrogen as an energy source is the storage and handling of hydrogen due to few of its physical properties. Due to the lightweight of hydrogen, the natural occurrence of molecular hydrogen in the environment is too low, but it is present in abundance in various other forms. The hydrogen can be generated using different liquid organic hydrogen carriers (NH₂NH₂.H₂O, CH₃OH, HCHO, HCOOH, C₆H₅CH₂OH and other alcohols and amines) as the transportation of hydrogen in the form of these LOHCs is easier as compared to the gaseous hydrogen. This chapter describes, in brief, most of the literature available on hydrogen production from liquid organic hydrogen carriers. Further, the role of the catalyst is also elaborated for the process of hydrogen production from various LOHCs. Though several reports on the production of hydrogen using various metal based catalyst are available but still there are several major challenges associated with the purity of hydrogen produced, reaction temperature, and using the renewable energy sources needs to be addressed properly. In this regard, this thesis describes results on the design and developed several ruthenium based catalysts for hydrogen production from various liquid organic hydrogen carriers such as hydrazine, methanol, formaldehyde and other alcohols. Based on the identified research gaps in the available literature reports, the principal objectives of the present study are as below:

• To develop ruthenium catalyst for the activation of hydrazine monohydrate for hydrogen production.

• To design and develop molecular catalysts based on ruthenium complexes for alcohol dehydrogenation and to extensively investigate the mechanistic pathway.

• To develop the ruthenium complexes-based catalysts for hydrogen production from formaldehyde and to study the mechanistic pathway.

• To develop the ruthenium nanoparticle catalytic system for methanol dehydrogenation.

III

Chapter 2. Hydrogen Production from Hydrazine Hydrate over Ruthenium Catalyst

In this chapter, we have discussed the synthesis of ruthenium-arene complexes containing N-imine-substituted iminopyridine ligands $[(\eta^6-C_6H_6)Ru(\kappa^2-L1)Cl]+$ ([**Ru**]-3), $[(\eta^6-C_6H_6)Ru(\kappa^2-L2)Cl] + ([$ **Ru** $]-4), [(\eta^6-C_6H_6)Ru(\kappa^2-L3)Cl] + ([$ **Ru**]-5)synthesized by treating $[(\Box 6-C6H6)RuCl2]2$ (**[Ru]-1**) with the respective ligands (L1 = N-hydroxy-iminopyridine, L2 = N-methoxy-iminopyridine and L3 = N-isopropyl-iminopyridine). These complexes were further employed for the catalytic dehydrogenation of hydrazine in tetrahydrofuran and ethanol. The release of H2 and N2 gas during the catalytic reaction was confirmed by GC-TCD. Results inferred that the ligand played a crucial role in the process of hydrogen production from hydrazine, where the ruthenium-arene ([Ru]-1) complexes having L1 ligand outperformed over others, suggesting the plausible involvement of the hydroxyl group of L1 with hydrazine coordinated to ruthenium center. Further, the screening of different parameters inferred that the catalytic activity for hydrogen production from hydrazine depends on the reaction temperature (30 $^{\circ}C - 80 ^{\circ}C$), base (KO'Bu and KOH), and solvents used (THF, ethanol and water). Moreover, the studied complex **[Ru]-1** also shows good recyclability for the dehydrogenation of hydrazine (in THF) for six consecutive catalytic runs. For the mechanistic investigation of reaction, NMR and mass investigations were performed which revealed the formation of end-on Ru(II)-arene intermediate $[(\eta^{6}-C_{6}H_{6})Ru(\kappa^{2}-L1)(\kappa^{1}$ coordinated hydrazine NH₂NH₂)]+, where the coordination of hydrazine to Ru center and subsequent activation of hydrazine ($E_a = 13.98$ kcal mol⁻¹) are expected to be the key steps involved in achieving dehydrogenation of hydrazine. Hence, this chapter shows our results on hydrogen production from hydrazine using the homogeneous rutheniumarene catalyst where the role of the ligand is found to be crucial in facilitating the activation of hydrazine over the ruthenium center.



Chapter 3. Hydrogen Production from Aromatic Alcohols over Ruthenium Catalyst

In this chapter, we have discussed the synthesis of ruthenium complexes and their application for hydrogen production from alcohols. Catalytic acceptorless dehydrogenation of alcohols to produced acids is a promising route for the production of hydrogen gas, which enables the scientific community to explore alcohols as an appropriate liquid organic hydrogen carrier. Alcohol dehydrogenation process is an atom economic process by generating pure hydrogen gas (a potential clean fuel) along with the desired carboxylic acid (industrial importance). Herein, we synthesized pyridylamine ligated arene-Ru complexes [Ru]-6 - [Ru]-15 and employed then for the catalytic acceptorless dehydrogenation of primary alcohols to carboxylic acids in toluene with the qualitative release of H_2 gas. The gas generation monitored via water displacement method and characterized using GC-TCD as hydrogen. All the complexes [Ru]-6 - [Ru]-15 are well characterized using several spectro-analytical techniques such as ¹H NMR, ¹³C NMR and ESI-MS and also the structure of the complexes [Ru]-6, [Ru]-7 and [Ru]-10 are determined using single crystal X-ray crystallography. The substrate scope for carboxylic acids synthesis with hydrogen generation is also studied employing the studied protocol over a wide range of substrates (aliphatic alcohols, aromatic alcohols and hetero aromatics alcohols) to obtain the respective carboxylic acids in good yields (up to 86%). The arene-Ru catalysts [Ru]-6 also displayed superior catalytic performance to achieve a turnover of 1378 for the bulk reaction. In addition, detailed mass investigations also carried out to elucidate the mechanistic pathway by identifying several important catalytic

intermediates, including aldehyde and diol-coordinated Ru species, under catalytic and controlled reaction conditions.



Chapter 4. Hydrogen Production from Formaldehyde over Ruthenium Catalyst in Water

Formaldehyde is a liquid and has potential to be used as a promising liquid organic hydrogen carrier for hydrogen production. In this chapter, we demonstrated a selective production of hydrogen from formaldehyde and paraformaldehyde catalyzed by an in situ generated ruthenium-imidazole complex from [Ru]-2 complex and imidazole under mild reaction condition in water at 95 °C. Further, we also synthesized and characterized the ruthenium-imidazole complexes containing mono-imidazole ([Ru]-16), bis-imidazole ([Ru]-17) and tris-imidazole ([Ru]-18) coordinated ligand(s). The reaction performed with these purified imidazole-based ruthenium complexes exhibited a close agreement with the in situ generated ruthenium complexes. This catalytic system produced hydrogen gas under base-free conditions leading to a turnover number >12000 in <32 h, which is the second-largest TON reported to date. The higher conversion (>98%) with the release of >2.94equivalents of gas per mol of formaldehyde was achieved with the in situ generated ruthenium-imidazole complex for a diluted aqueous formaldehyde solution (1.5 mol L-1) at 95 °C. Furthermore, this catalytic system also showed appreciably good recyclability up to 8 cycles with good conversion of formaldehyde.



For the identification and characterization of catalytic intermediate species involved in the hydrogen production from formaldehyde, an extensive mass analysis of reaction aliquots is performed. Results inferred the presence of several rutheniumimidazole species along with the ruthenium hydride species during the catalytic reaction, postulated the involvement of such species in the conversion of formaldehyde to hydrogen gas. Further, the ruthenium hydride dimer species is also characterized using X-ray crystallography.

Chapter 5. Low-temperature Hydrogen Production from Methanol over Ruthenium Catalyst in Water

In this chapter, we employed organometallic ruthenium complex (**[Ru]-1**) as a precursor in presence of several ligands for in situ generation of active ruthenium nanoparticles supported on carbon in the temperature range of 90 – 130 °C. Optimization of several reaction parameters such as temperature, base, additives and water content are performed to achieve the higher yield of hydrogen gas per mole of methanol and found that 49 mol H₂ per mol Ru per hour is produced from methanol-water mixture at 130 °C. The present catalyst is also active at 90 °C producing 4 mol H2 per mol of Ru per hour. The released gas is identified as hydrogen gas by GC-TCD. Furthermore, the present catalytic system exhibited appreciable long-term stability, where a total turnover number of 762 mol of H₂ per mol of Ru from methanol is achieved.



The chemical nature and morphology of the ruthenium nanoparticle catalyst reported herein is established by ICP analysis, powder X-ray diffraction, transmission electron microscopy, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy investigations and Hg(0) poison experiments. The experimental and spectroscopic investigations confirmed the presence of ruthenium catalyst with Ru in its zero-oxidation state. TEM imaging evidenced the formation of Ru nanoparticles with approximate particle size of 1.5 nm homogenously dispersed over the carbon support. Therefore, the present study demonstrated an efficient process for a low temperature (110 - 130 °C) hydrogen production from the inexpensive and biomass-derived methanol in water using ruthenium catalyst for application in onboard and off-board (stationery) hydrogen production.

Chapter 6. Summary and Future Scope

We developed several ruthenium based catalytic system for hydrogen production from various liquid hydrogen storage materials. First, we synthesized the halfsandwich ruthenium complexes for the catalytic hydrogen production from hydrazine monohydrate as hydrogen sources, and investigated the mechanistic pathway of the dehydrogenation process by identifying important reaction intermediate species using different spectroscopic techniques including ¹H NMR and ESI-MS spectrometry. Further, arene-ruthenium complexes having N,N–donor ligands were synthesized and characterized using the different characterization techniques including characterization of a few using the X-ray crystallography. These complexes were employed for the hydrogen production from alcohols, where valueadded acids were obtained as product. Furthermore, detailed mechanistic investigation was also performed to elucidate the role of the catalyst in the dehydrogenation pathway. Later on, we investigated imidazole based areneruthenium complexes for efficient hydrogen production from aqueous formaldehyde, where a high conversion of formaldehyde to hydrogen and CO_2 was achieved. The detailed mechanistic investigation revealed that crucial role of the imidazoleruthenium interaction and the identification of several important catalytic intermediate species by mass spectrometry helped us to establish the role of the catalyst and the dehydrogenation reaction pathway. Using arene-ruthenium complexes and a suitable ligand, ruthenium nanoparticles were synthesized in situ for efficient hydrogen production from methanol in water at low temperature (<120 $^{\circ}$ C). Advantageously, the hydrogen gas was produced from the developed process is with high conversion of methanol, where the produced hydrogen gas is free from CO₂ and other contamination. Moreover, the developed catalyst exhibited appreciably high long-term stability for hydrogen production from methanol in water. Therefore, through the work presented in this thesis, a range of rutheniumbased catalysts were explored for hydrogen production from several important liquid hydrogen storage materials including hydrazine, methanol, formaldehyde and other alcohols.

Hydrogen has gained center point of attraction considering it as a clean fuel for the society, and therefore extensive efforts are being made by the scientific community for the development of efficient and sustainable routes for hydrogen production from various liquid organic hydrogen carrier. In the recent past, extensive attention has been paid towards the use of homogeneous and heterogeneous catalysts to achieve efficient hydrogen production from liquid organic hydrogen carriers. Both the catalytic systems have their own advantages and disadvantages, but the application of heterogeneous catalysts for hydrogen production reactions has revolutionized the field in various aspects.

Despite rapid advancement in the field, the development of a robust catalytic system for hydrogen production is still in the top-most requirement of the scientific community. Moreover, efforts to develop homogeneous catalytic systems for more suitable for industrial-scale hydrogen production from various liquid organic carriers

IX

needs particular attention. Furthermore, the development of air-stable and less expensive non-noble metal catalysts also need particular attention to bring down the cost of the process. Further, detailed investigations can be performed to establish the structure-activity relationship at the molecular level for the designing catalysts for the several dehydrogenation reactions and a further improvement in the process can be done. Attempts can be made to isolate and completely characterize the identified reaction intermediates in the studied catalytic dehydrogenation processes in this thesis. These detailed results may further authenticate the possible reaction pathway for the dehydrogenation reaction over the synthesized catalysts, which will boost up the mechanistic understanding of benchmark catalytic transformations. Though attempts have been made in this thesis work to evaluate the catalyst performance at the bulk-scale production of hydrogen gas, development of a prototype and the process optimization can be performed to evaluate the industrial application of the developed processes.

Publications included in the thesis

1. Awasthi M. K., Tyagi D., Patra S., Rai R. K., Mobin S. M., Singh S. K. (2018), Ruthenium complexes for catalytic dehydrogenation of hydrazine and transfer hydrogenation reactions, *Chem. Asian J.*, 13, 1424-1431 (DOI: 10.1002/asia.201800315). (IF: 4.568)

2. Awasthi M. K., Singh S. K. (2019), Ruthenium Catalyzed Dehydrogenation of Alcohols and Mechanistic Study, *Inorg. Chem.*, 58, 14912-14923 (DOI: 10.1021/acs.inorgchem. 9b02691). (IF: 5.165)

3. Awasthi M. K., Singh S. K. (2021), Hydrogen Production From Formaldehyde Catalyzed by Ruthenium(II) Complex in Water, *Sustainable Energy Fuels*, 5, 549-555 (DOI: 10.1039/D0SE01330G). (IF: 6.367)

4. Awasthi M. K., Rai R. K., Behrens S., Singh S. K. (2021), Low-temperature hydrogen production from methanol over Ruthenium catalyst in water, *Catal. Sci. Technol.*, 11, 136-142 (DOI: 10.1039/D0CY01470B). (IF: 6.119)

Publications other than those included in the thesis

5. Patra S., Awasthi M. K., Rai R. K., Deka H., Mobin S. M., Singh S. K. (2019), Dehydrogenation of Formic Acid Catalyzed by Water-Soluble Ruthenium Complexes: X-ray Crystal Structure of a Diruthenium Complex, *Eur. J. Inorg. Chem.*, 1046-1053 (DOI: 10.1002/ejic.201801501). (IF: 2.524)

6. Dostagir SK N. H. MD, **Awasthi M. K.,** Kumar A., Gupta K., Behrens S., Shrotri A., Singh S. K. (2019), Selective Catalysis for Room-temperature Hydrogenation of Biomass-derived Compounds over Supported NiPd Catalysts in Water, *ACS Sustainable Chem. Eng.*, 7, 9352-9359 (DOI: 10.1021/acssuschemeng.9b00486). (IF: 8.198)

7. Deka H., Kumar A., Patra S., **Awasthi M. K.,** Singh S. K. (2020), Synthesis, structure and catalytic activity of manganese(II) complexes derived from bis(imidazole)methane-based ligands, *Dalton Trans.*, 49, 757-763 (DOI: 10.1039/C9DT03886H). (IF: 4.390)

8. Panda D., Patra S., Awasthi M. K., Singh S. K. (2020), Lab Cooked MOF for CO2 Capture: A Sustainable Solution to Waste Management, *J. Chem. Edu.*, 97, 1101-1108 (DOI: 10.1021/acs.jchemed.9b00337). (IF: 2.979)

Rai R. K., Awasthi M. K., Singh V. K., Barman S. R., Behrens S., Singh S. K. (2020), Aqueous Phase Semihydrogenation of Alkynes over Ni-Fe Bimetallic Catalysts, *Catal. Sci. Technol.*, 10, 4968-4980 (DOI: 10.1039/D0CY01153C). (IF: 6.119)

Conferences and workshops

1. Attended *RSC-IIT Indore Symposium in Chemical Science* organized by Indian Institute of Technology Indore & Royal Society of Chemistry, at Indian Institute of Technology Indore, January 2018.

2. Attended GIAN Course: "*Metal-Ligand Interplay in Advanced Coordination Chemistry*" (Course Instructor: **Prof. Pierre Braunstein**, CNRS-Université de Strasbourg, France) at IIT Indore, India, February 2018. 3. Dwivedi A. D., **Awasthi M. K.** and Singh S. K., "Ruthenium Catalyzed Ring Hydrogenation of (Hetero) Arenes in Water" Modern Trends in Inorganic Chemistry, Pune, December 2017.

4. Awasthi M. K., Kumar A., and Singh S. K., "Bimetallic Ni-Pd Alloy Nanoparticles: An Efficient Nanoparticle Catalyst for Upgradation of Biomass Derived Furans" In-house Chemistry Symposium, Indore (India), February 2019.

5. Attended Industry Academia Conclave on **Hydrogen and Fuel Cells** organized by DST at IISER Thiruvananthapuram on 27th -28th February 2020.

TABLE OF CONTENTS

1.	List of Figures	XVII
2.	List of Schemes	XXVI
3.	List of Tables	XXVIII
4.	Nomenclature	XXX
5.	Acronyms	XXXI
Chapter	1. An Overview on Hydrogen Production from Various Liquid H	Iydrogen
Storage	Materials: Role of the Catalyst	1-35
1.1	Introduction	1
1.2	Hydrogen storage and production	4
	1.2.1 Physical storage	5
	1.2.2 Chemical storage	5
1.3	Role of catalyst for the hydrogen production reaction	12
1.4	Research Gaps and Objectives of the Thesis	23
1.5	Organization of the Thesis	25
1.6	References	26
Chapter	2. Hydrogen Production from Hydrazine Hydrate over Ruthenium	Catalyst
		36-62
2.1	Introduction	36
2.2	Experimental section	38
	2.2.1 Materials	38
	2.2.2 Instrumentations	38
	2.2.3 Single-crystal X-ray diffraction Studies	39
	2.2.4 Catalytic dehydrogenation of hydrazine over ruthenium	39
	catalysts.	
	2.2.5 Mass spectral studies to identify the hydrazine-coordinated	39
	ruthenium species [Ru]-3A	
	2.2.6 NMR spectral studies to identify the hydrazine-	40
	coordinated ruthenium species [Ru]-3A	

	2.2.7 Recyclability experiments	40
2.3	Results and Discussion	40
	2.3.1 Synthesis and X-ray structure of ruthenium-arene	40
	complexes	
	2.3.2 Ruthenium catalyzed dehydrogenation of hydrazine	44
2.4	Conclusions	56
2.5	References	57
Chapter	3. Hydrogen Production from Aromatic Alcohols over Ruthenium	Catalyst
		63-123
3.1	Introduction	63
3.2	Experimental section	65
	3.2.1 Materials	65
	3.2.2 Instrumentation	65
	3.2.3 Single-crystal X-ray diffraction studies	66
	3.2.4 General Procedure for the catalytic alcohol	66
	dehydrogenation reaction over pyridylamine-based (η^6 -	
	arene)Ru(II) complexes	
	3.2.5 Dehydrogenation of benzaldehyde	67
	3.2.6 General procedure for the synthesis of $(\eta^6-C_6H_6)Ru(II)$	67
	complexes [Ru]-6 – [Ru]-10 and $(\eta^6$ -C ₁₀ H ₁₄)Ru(II) complexes	
	[Ru]-11 – [Ru]-15	
3.3	Results and Discussion	71
	3.3.1 Synthesis and characterization of arene-Ru complexes	71
	3.3.2 Catalytic dehydrogenation of alcohols to carboxylic acids	79
	3.3.3 Substrate screening	85
	3.3.4 Bulk reaction for the catalytic alcohol dehydrogenation	87
	reaction	
	3.3.5 Mechanism	89
3.4	Conclusions	96
3.5	References	120

Chapte	7 4. Hydrogen I Touuchon from Formalaenyae over Kainenium C	uuiysi in
Water		124-159
4.1	Introduction	124
4.2	Experimental section	126
	4.2.1 Materials	126
	4.2.2 Instrumentation	126
	4.2.3 Single-crystal X-ray diffraction studies	127
	4.2.4 General Procedure for the catalytic formaldehyde	127
	dehydrogenation reaction over in situ generated complexes	
	4.2.5 Procedure for the synthesis of (η6-C10H14)Ru(II)	128
	complexes [Ru]-17 – [Ru]-19	
	4.2.6 Mercury poisoning experiment	129
	4.2.7 Recyclability experiment	129
	4.2.8 TON and TOF calculation	129
4.3	Results and discussion	130
4.4	Conclusions	148
4.5	References	156
Chapte	r 5. Low-temperature Hydrogen Production from Methanol over R	uthenium
Catalys	t in Water	160-186
5.1	Introduction	160
5.2	Experimental section	162
	5.2.1 Materials	162
	5.2.2 Instrumentation	162
	5.2.3 Catalytic hydrogen production from methanol	163
	5.2.4 Catalytic hydrogen production from ethanol/ <i>n</i> -propanol	163
	5.2.5 Synthesis of ruthenium nanoparticles	163
	5.2.6 Long term stability and recyclability experiments	164
	5.2.7 Estimating the performance of Ru/L9 catalyst for	164
	hydrogen production from methanol for industrial application	
5.3	Results and discussion	165
5.4	Conclusions	180

5.5	References	181
Chapte	er 6. Summary and Future Scope	187-192
6.1	Summary	187
6.2	Future Scope	191

LIST OF FIGURES

Chapter 1. An (Overview on Hydrogen Production from Various Liquid Hyd	drogen	
Storage Materials: Role of the Catalyst		1-35	
Figure 1.1	Schematic representation of hydrogen storage, production		
	and application		
Figure 1.2	Overview of key hydrogen production and usage pathways		
Figure 1.3	Various available methods for the hydrogen storage system		
Figure 1.4	re 1.4 (a) 1-phenylethanol dehydrogenation with 2 (ortho-CH ₃)		
	and 3 (ortho-H). (b) 1-octylamine dehydrogenation with 2		
	(ortho- CH_3) and 3 (ortho- H)		
Figure 1.5	Reaction pathway for methanol dehydrogenation and best	18	
	performing Ru-pincer complex for the methanol		
	dehydrogenation process performed with 0.5 M KOH at 72		
	°C		
Chapter 2. Hydr	rogen Production from Hydrazine Hydrate over Ruthenium C	atalyst	
		36-62	
Figure 2.1	(a) Ruthenium-arene catalyzed dehydrogenation of	41	
	hydrazine and transfer hydrogenation of nitro substrate and		
	styrene, (b) X-ray crystal structure of complex [Ru]-4 with		
	30% ellipsoid probability. Counter ion (Cl ⁻) are omitted for		
	sake of clarity.		
Figure 2.2	GC-TCD analysis of gas produced for dehydrogenation of	45	
	Hydrazine monohydrate (1.0 mmol) using KO ^t Bu (0.020		
	mmol), cat. [Ru]-3 (2.5 mol %), THF-methanol (5.5 mL,		
	10:1 v/v) in Ar gas atmosphere at 80 °C		
Figure 2.3	Linear fitting of log [TOF(h ⁻¹)] vs 1/T for calculating	46	
	activation energy from the graph (value for activation		

Figure 2.4(a-b) Comparative catalytic efficacy (a) amount of gas48released vs time and (b) TOF (h⁻¹) for the dehydrogenation

energy $E_a = 13.98 \text{ kJ} \cdot \text{mol}^{-1}$)

of hydrazine monohydrate over ruthenium-arene catalysts. Reaction condition: hydrazine monohydrate (1.0 mmol) over various ruthenium catalysts (2.5 mol%) in the presence of KO^tBu (20 mol%) in THF-methanol (5.5 mL, 10:1 v/v) at 80 °C

- Figure 2.5 Recyclability experiments for the catalytic dehydrogenation 49 of hydrazine monohydrate over [Ru]-3 catalyst. Reaction condition: hydrazine monohydrate (1.0 mmol) over various ruthenium catalysts (2.5 mol%) in the presence of KO^tBu (20 mol%) in THF-methanol (5.5 mL, 10:1 v/v) at 80 °C
- Figure 2.6 ¹H NMR and mass spectral experiments evidenced the 50 formation of a hydrazine coordinated Ru-species [Ru]-3A during the treatment of [Ru]-3 complex with an excess of N₂H₄·H₂O in D₂O
- Figure 2.7 Mass spectral analysis for the hydrazine coordinated 51 ruthenium species, [Ru]-3A, [Ru]-4A and [Ru]-5A, obtained by the addition of hydrazine to an aqueous solution of the corresponding complexes [Ru]-3, [Ru]-4 and [Ru]-5, respectively
- Figure 2.8 Mass spectral experiments showing the generation of a 52 hydrazine coordinated ruthenium species ([Ru]-3A), which upon addition of a dilute solution of HCl regenerated the original ruthenium precursor ([Ru]-3)
- Figure 2.9 Variable temperature ¹H NMR spectral experiments 53 evidenced the formation of a hydrazine coordinated Ruspecies during the treatment of [Ru]-3 complex with an excess of N₂H₄·H₂O in D₂O [Reaction condition: [Ru]-3 (0.010 g) in D₂O (500 μL) and hydrazine monohydrate (12.5 μL)]
- Figure 2.10Mass analysis (at $30 \ ^{\circ}C 60 \ ^{\circ}C$) evidenced the formation of54a hydrazine coordinated Ru-species [Ru]-3A during the

treatment of **[Ru]-3** complex with an excess of N₂H₄·H₂O in H₂O. Along with the hydrazine coordinated ruthenium species (**[Ru]-3A** m/z 333.0), a water coordinated species $[([(\eta^6-C_6H_6)Ru(\kappa^2-L)(OH_2)]^+)]$ at m/z 319.0 was also observed. All the observed mass spectra of various species identified were matching well with corresponding simulated patterns

Chapter 3. Hydrogen Production from Aromatic Alcohols over Ruthenium Catalyst 63-123

- Figure 3.1 X-ray crystal structures of the complex (a) [Ru]-6, (b) [Ru]-74
 7 and (c) [Ru]-10 with 30% ellipsoid probability. Counter anions are omitted for the sake of clarity
- Figure 3.2 GC-TCD (using Argon as carrier gas) of (a) H₂ gas (Pure 81 sample) (b) evolved gas from the reaction mixture. Reaction condition: 1a (1 mmol), catalyst (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 110 °C
- Figure 3.3 Hydrogen gas generation profile for benzyl alcohol 82 dehydrogenation to benzoic acid over [Ru]-6 and [Ru]-7 catalysts. Reaction condition: 1a (1 mmol), catalyst (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 110 °C
- Figure 3.4(a) Dehydrogenation of benzyl alcohol (1a) over [Ru]-684catalyst at various temperatures. (b) Arrhenius plot of TOFvalues. Reaction condition: 1a (1 mmol), catalyst (2 mol%),KOH (1.1 equiv.), toluene (2 mL)
- **Figure 3.5** ¹H NMR spectra after the reaction of benzyl alcohol in 84 absence of base
- Figure 3.6 Hydrogen generation profile for gram scale 88 dehydrogenation of benzyl alcohol (1a) to benzoic acid (1b) over [Ru]-6 catalyst. Reaction conditions: 1a (10 mmol), [Ru]-6 (0.2 mol%), KOH (1.1 equiv.), toluene (10 mL), 9 h, 110 °C

Figure 3.7	(a) ESI-MS analysis in water, [Ru]-6, KOH (b) ESI-MS	89
	analysis in water, [Ru]-6, KOH, p-methylbenzaldehyde	
Figure 3.8	ESI-MS analysis of the reaction mixture after heating at 110	90
	°C in catalytic reaction condition using the [Ru]-8 (2 mol%),	
	KOH (1.1 equiv.), benzyl alcohol (1 mmol), toluene (2 mL)	
	in 30 min and 1 h	
Figure 3.9	ESI-MS analysis of the reaction aliquot for benzyl alcohol	90
	dehydrogenation after heating at 110 °C for 1 h under	
	controlled reaction condition using the catalyst [Ru]-8 (0.1	
	mmol), benzyl alcohol (0.3 mmol) and KOH (0.3 mmol) in	
	toluene (2 mL)	
Figure 3.10	¹ H NMR of the reaction aliquot (diluted with methanol-d ₄)	91
	for benzyl alcohol dehydrogenation after heating at 110 $^{\circ}\mathrm{C}$	
	for 1 h under controlled reaction condition using the catalyst	
	[Ru]-8 (0.1 mmol), benzyl alcohol (0.3 mmol) and KOH	
	(0.3 mmol) in toluene (2 mL)	
Figure 3.11	(a) ESI-MS analysis in water before heating, [Ru]-8, KOH,	92
	p-methylbenzaldehyde (b) ESI-MS analysis in water after	
	heating, [Ru]-8, KOH, p-methylbenzaldehyde, gentle	
	heating (85 °C)	
Figure 3.12	Hydrogen generation from benzaldehyde to benzoic acid	94
	using [Ru]-6 catalyst. Reaction conditions: benzaldehyde (1	
	mmol), catalyst (2 mol%), KOH (1.1 equiv.), toluene (2	
	mL), 1 h, 110 °C	
Figure 3.13	¹ H NMR spectra after the reaction of benzaldehyde	94
Figure 3.14	Hydrogen generation from p-methyl benzaldehyde to	95
	benzoic acid using [Ru]-6 catalyst. Reaction condition: p-	
	methyl benzaldehyde (1 mmol), [\mathbf{Ru}]-6 (2 mol%), KOH (1.1	
	equiv.), toluene (2 mL), 1 h, 110 °C	
Chanter A Hud	Irogen Production from Formaldehyde over Ruthenium Cataly	ct in

Chapter 4. Hydrogen Production from Formaldehyde over Ruthenium Catalyst in Water 124-159

- Figure 4.1 GC- TCD of (a) H₂ gas (Pure sample) (b) CO₂ gas (Pure 131 sample) and (c-f) gas evolved from aqueous formaldehyde at different time interval of the catalytic reaction. (Reaction condition: aq. formaldehyde (13.55 mmol, 1.07 mL), catalyst [Ru]-2 (13 µmol) and ligand L14 (26 µmol) at 95 °C) (Analyses performed using Argon as carrier gas)
- Figure 4.2 Initial time course for hydrogen production from aqueous 132 formaldehyde. (Reaction condition: aq. formaldehyde (13.55 mol L⁻¹, 1.07 mL), catalyst [Ru]-2 (13 μmol) and ligand L14 (26 μmol) at 95 °C)
- Figure 4.3 (a) Time course for hydrogen production from aqueous 134 formaldehyde (13.55 mol L⁻¹, 1.07 mL) over catalyst [Ru]-2 (13 μmol) in the presence of 1, 2 and 3 equiv. of ligand L14 at 95 °C and (b) The H₂/CO₂ ratios in the produced gas mixture from aqueous formaldehyde
- Figure 4.4 (a) The H₂/CO₂ ratios in the produced gas mixture and (b) 135
 ¹H NMR yield of HCOOH during the catalytic dehydrogenation of aqueous formaldehyde in the initial 1 h of the reaction. (Reaction condition: aq. formaldehyde (13.55 mol L⁻¹, 1.07 mL), catalyst [Ru]-2 (13 µmol) and ligand L14 (26 µmol), at 95 °C. HCOOH yield was determined using dioxane as an internal standard)
- Figure 4.5 Time course for hydrogen production from formic acid (a) 136 13.55 mol L⁻¹, 1.07 mL and (b) 1.5 mol L⁻¹, 1.07 mL over catalyst [Ru]-2 (13 μmol) in the presence of ligand L14 (26 μmol) at 95 °C
- Figure 4.6(a) Ruthenium-imidazole (L14/Ru ratio of 1) species, (b)137methanediol coordinated ruthenium-imidazole (L14/Ru
ratio of 1), (c) ruthenium-bis-imidazole (L14/Ru ratio of 2),
and (d) ruthenium-tris-imidazole (L14/Ru ratio of 3)
coordinated species observed during mass studies

XXI

- Figure 4.7 (a) X-ray crystal structures of the complex [Ru]-14 (with 138 30% ellipsoid probability and counter anion PF₆⁻ is omitted for the sake of clarity) and (b) ESI-MS of the complex [Ru]-16
- **Figure 4.8** X-ray crystal structure of the complex **[Ru]-18** with 30% 139 ellipsoid probability (Counter anions are omitted for the sake of clarity)
- Figure 4.9 Time course for hydrogen production from aqueous 140 formaldehyde (13.55 mol L⁻¹, 1.07 mL) in the presence of catalyst [Ru]-2 (13 μmol) (with ligand L14), [Ru]-17 (26 μmol) and [Ru]-16 (26 μmol)
- Figure 4.10 (a) Temperature dependent hydrogen production from 142 aqueous formaldehyde and (b) the corresponding Arrhenius plot of initial TOF values (initial 10 min). (Reaction condition: aq. formaldehyde (13.55 mol L⁻¹, 1.07 mL), catalyst [Ru]-2 (13 μmol) and ligand L14 (26 μmol) at 95 °C
- Figure 4.11 Mercury poisoning test for the catalytic reaction for 143 hydrogen production from aqueous formaldehyde (13.55 mol L⁻¹, 1.07 mL) over the catalyst [Ru]-2 (13 μmol) in the presence of ligand L14 (26 μmol) at 95 °C (with/without added Hg).
- Figure 4.12 Hydrogen production from varying concentration of 143 aqueous formaldehyde (1.1–13.55 mol L⁻¹) over the catalyst
 [Ru]-2 (13 μmol) and ligand L14 (26 μmol) at 95 °C.
- Figure 4.13 Time course plot for hydrogen production from aqueous 144 formaldehyde. (Reaction condition: aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst [Ru]-2 (13 μmol) and ligands L9, L11 and L14 (26 μmol) at 95 °C)
- Figure 4.14 (a) The H_2/CO_2 ratios in the produced gas mixture and (b) 145 ¹H NMR yield of HCOOH during the catalytic

dehydrogenation of aqueous formaldehyde in the initial 1 h of the reaction. (Reaction condition: aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst [**Ru**]-2 (13 μ mol) and ligand **L14** (26 μ mol), at 95 °C. HCOOH yield was determined using dioxane as an internal standard)

- Figure 4.15 Hydrogen production from a paraformaldehyde-water 146 solution (inset shows the GC traces for the evolved gas in initial 5 min). (Reaction conditions: paraformaldehyde-water (1.5 mol L⁻¹, 40 mL), catalyst [Ru]-2 (2.5 μmol) and ligand L14 (5 μmol) at 95 °C)
- Figure 4.16 Long term stability and recyclability experiment for 147 catalytic hydrogen production from aq. formaldehyde over the catalyst [Ru]-2 in the presence of ligand L14. (Reaction condition: aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst [Ru]-2 (13 μmol) and ligand L14 (26 μmol) at 95 °C, 1.5 mmol of formaldehyde added in each cycle)
- Figure 4.17 Long term stability and recyclability experiment for 147 hydrogen production from aqueous formaldehyde over complex [Ru]-2. (Reaction condition: aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst [Ru]-2 (13 μmol) at 95 °C; 1.5 mmol of formaldehyde added in each cycle)
- Figure 4.18 TOF comparison graph for hydrogen production from 148 aqueous formaldehyde over [Ru]-2/L14 and [Ru]-2. (Reaction condition: aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst [Ru]-2 (13 μmol) and ligands L14 (26 μmol) at 95 °C)

Chapter 5. Low-temperature Hydrogen Production from Methanol over Ruthenium Catalyst in Water 160-186

Figure 5.1TEM images of ruthenium nanoparticles obtained from165[Ru]-1 in the absence of the ligand

- Figure 5.2 Effect of (a) ligand L9 and (b) methanol to water molar ratio 166 on the Ru/L9 catalyzed hydrogen production from methanol at 110 °C. (Reaction condition: methanol (16.08 mmol), Ru catalyst (0.625 mol%, n([Ru]-1)/n(L9) 1:2), KOH (1.2 equiv.) and methanol to water molar ratio (1:1), argon, ^amethanol to water molar ratio is 2:1, and ^b[Ru]-2 precursor is used)
- Figure 5.3Hydrogen production from NaOMe over Ru/L9 catalyst.169Reaction condition: NaOMe (16.08 mmol), Ru/L9 catalyst(0.625 mol%, n([Ru]-1)/n(L9) = 1:2), water (1 equiv.), 110°C, Argon
- Figure 5.4 Kinetic isotope effect (KIE) experiments for hydrogen 169 production from methanol over Ru/L9 catalyst. Reaction condition: CH₃OH/CD₃OD (16.08 mmol), Ru/L9 catalyst (0.625 mol%, n([Ru]-1)/n(L9) = 1:2), KOH (1.2 equiv.), H₂O/D₂O (1 equiv.), 110 °C, Argon
- **Figure 5.5** ¹³C NMR spectra of the reaction mixture obtained after the 170 reaction performed using the recovered catalyst. Reaction condition: methanol (16.08 mmol), spent **Ru/L9** catalyst, KOH (1.2 equiv.), water (1 equiv.), 110 °C, Argon
- **Figure 5.6** (a) Temperature dependent hydrogen production from 171 aqueous methanol, and (b) the corresponding Arrhenius plot of initial TOF values (initial 10 min). Reaction condition: methanol (16.08 mmol), Ru/L1 catalyst (0.625 mol%, n([Ru]-1)/n(L9) = 1:2), KOH (1.2 equiv.), water (1 equiv.), 110 °C – 130 °C, Argon
- Figure 5.7 Effect of ligands (L9, L17 L19) on the ruthenium 172 catalyzed hydrogen production from methanol. Reaction condition: methanol (16.08 mmol), Ru/Ligand catalyst (0.625 mol%, n([Ru]-1)/n(Ligand) = 1:2), KOH (1.2 equiv.), water (1 equiv.), 3 h, 110 °C, Argon.
- Figure 5.8Long term stability and recyclability experiment for Ru/L9174catalyzed production of H2 from methanol at 130 °C
- Figure 5.9 Hydrogen production using different alcohols (methanol, 175 ethanol and n-propanol) over Ru/L9 catalyst. Reaction condition: alcohol (16.08 mmol), Ru/L9 catalyst (0.625 mol%, n([Ru]-1)/n(L9) = 1:2), KOH (1.2 equiv.), water (1 equiv.), 110 °C, Argon
- Figure 5.10 XPS spectra corresponding to (a) Ru 3p_{3/2} (b) Ru 3d_{5/2} and 176
 (c) N 1s core for ruthenium catalyst obtained in the absence of ligand L9
- Figure 5.11 (a) TEM image (inset particle size distribution), (b) EDS 177 point analysis, and (c) HAADF image and the corresponding (d) EDS line scan analyses for Ru/L9 catalyst
- Figure 5.12XPS spectra corresponding to the (a) Ru 3p_{3/2} (b) Ru 3d_{5/2}179and (c) N 1s core levels of Ru/L9 catalyst

LIST OF SCHEMES

Chapter 1. An (Overview on Hydrogen Production from Various Liquid Hydrogen Production from Various Liquid Hydrogen Production	drogen	
Storage Materia	ls: Role of the Catalyst	1-35	
Scheme 1.1	(a) Proposed Noyori Type cooperative pathways for	13	
	acceptorless dehydrogenation of alcohols, in a Gas-Phase		
	context (b) Structure of complex used for the study.		
Scheme 1.2	Base Induced dehydrogenation of Ruthenium hydrazine	14	
	complex		
Scheme 1.3	Hydrogen production pathways for hydrogen production	15	
	from amine		
Scheme 1.4	Proposed catalytic cycle for the hydrogen production from	17	
	amines		
Scheme 1.5	Proposed catalyst activation and catalytic cycle for low-19		
	temperature methanol reforming catalysed by 2c, made in		
	situ from 2a. The phosphorus iPr substituents have been		
	omitted for clarity. ‡ denotes transition state; solvent-H		
	indicates a molecule of solvent involved in hydrogen bonding		
Scheme 1.6	Catalyst for the dehydrogenation of alcohols to acid along	20	
	with generation of hydrogen under basic condition		
Scheme 1.7	Reaction pathway for the hydrogen production from the	20	
	alcohols using the ruthenium catalyst 5 under aqueous basic		
	condition		
Scheme 1.8	Ruthenium catalyst for aldehyde water shift reaction	22	
Chapter 2. Hydr	ogen Production from Hydrazine Hydrate over Ruthenium C	atalyst	
		36-62	
Scheme 2.1	Various hydrazine coordinated metal complexes – a key step	37	
	to the activation of hydrazine		
Scheme 2.2	Plausible reaction pathway for the dehydrogenation of	56	
	hydrazine over the studied ruthenium catalysts		

Chapter 3. Hydrogen Production from Aromatic Alcohols over Ruthenium Catalyst

		63-123	
Scheme 3.1	Literature reported active catalysts for the dehydrogenation	63	
	of alcohol to carboxylic acid		
Scheme 3.2	Synthesis of complexes [Ru]-6 – [Ru]-15	72	
Scheme 3.3	A proposed mechanistic pathway for the dehydrogenation of		
	alcohol		
Chapter 4. Hydrogen Production from Formaldehyde over Ruthenium Catalyst in			
Water	124	4-159	
Scheme 4.1	Literature known homogeneous catalysts for hydrogen	125	
	production from formaldehyde		
Scheme 4.2	Comparative TON for the catalytic hydrogen production	132	
	from aqueous formaldehyde (13.55 mmol, 1.07 mL) over		
	catalyst [Ru]-2 (13 μ mol) in the presence of ligands (L9-L16,		
	26 μmol) at 95 °C		
Sahama 12	A plausible nothway for debudrogenetion of equation	1/1	

Scheme 4.3 A plausible pathway for dehydrogenation of aqueous 141 formaldehyde over [Ru]-17

LIST OF TABLES

Chapter 1. An	n Overview on Hydrogen Production from Various Liquid Hy	drogen
Storage Mater	rials: Role of the Catalyst	1-35
Table 1.1	Comparison table for the different wt% of liquid hydrogen	3
	storage system	
Chapter 2. Hy	drogen Production from Hydrazine Hydrate over Ruthenium C	Catalyst
		36-62
Table 2.1	Crystal refinement data for complexes [Ru]-4	41
Table 2.2	Bond lengths [Å] for [Ru]-4	42
Table 2.3	Bond angles [deg] for [Ru]-4	42
Table 2.4	Optimization of the reaction condition for the catalytic	47
	dehydrogenation of hydrazine over [Ru]-3 catalyst	
Chapter 3. Hy	drogen Production from Aromatic Alcohols over Ruthenium C	Catalyst
		63-123
Table 3.1	Crystal structure refinement data for [Ru]-6, [Ru]-7, and	75
	[Ru]-10	
Table 3.2	Important bond parameters of the complexes [Ru]-6, [Ru]-	76
	7, and [Ru]-10	
Table 3.3	Selected bond lengths for complexes [Ru]-6, [Ru]-7 and	76
	[Ru]-10	
Table 3.4	Selected bond Angles for complexes [Ru]-6, [Ru]-7 and	78
	[Ru]-10	
Table 3.5	Screening of the catalyst [Ru]-6 – [Ru]-10 for benzyl	80
	alcohol dehydrogenation	
Table 3.6	Screening of the catalyst for benzyl alcohol	80
	dehydrogenation	
Table 3.7	Screening of the base for benzyl alcohol dehydrogenation	83
Table 3.8	Substrate scope for alcohol dehydrogenation using [Ru]-6	86
	catalyst	

Table 3.9	Screening of catalyst amount in benzyl alcohol	
	dehydrogenation	
Chapter 4. H	lydrogen Production from Formaldehyde over Ruthenium Ca	talyst in
Water		124-159
Table 4.1	Optimization of reaction parameters for hydrogen	133
	production from formaldehyde in water catalyzed by [Ru]-	
	2	
Table 4.2	Hydrogen production from varying concentration of	144
	formaldehyde	
Table 4.3	Hydrogen production from formaldehyde in water: Effect	145
	of ligands	
Chapter 5. Le	ow-temperature Hydrogen Production from Methanol over ru	thenium
Catalyst in W	'ater	160-186
Table 5.1	Screening of catalyst to producing hydrogen from	167
	methanol	
Table 5.2	Effect of base concentration on catalytic hydrogen	168
	production from methanol over Ru/L9 catalyst	
Table 5.3	Effect of base on catalytic hydrogen production from	168
	methanol over Ru/L9 catalyst	

NOMENCLATURE

А	Alpha
В	Beta
Λ	Gamma
Å	Angstrom
Λ	Wavelength
Μ	Micro
Σ	Sigma
П	Pi
η	Eta
Δ	Delta
K	Kappa
J	Coupling constant
Hz	Hertz
MHz	Mega hertz
Κ	Kelvin
D	Density
V	Volume
mM	Milli Molar
Mm	Micro Molar
Cm	Centimeter
0	Degree
°C	Degree centigrade
mL	Milliliter
μL	Microliter
a. u.	Arbitrary Unit
Min	Minute
mL	Milliliter
Mm	Millimeter

ACRONYMS

Arene-Ru(II)	Arene ruthenium (II) complexes
[Ru]-1	$[(\eta^6-p-\text{cymene})\text{RuCl}_2]_2]$
[Ru]-2	$[(\eta^6-\text{benzene})\text{RuCl}_2]_2]$
[Ru]-3	$[(\eta^6$ -benzene)Ru(N-hydroxy-iminopyridine)Cl] ⁺
[Ru]-4	$[(\eta^6$ -benzene)Ru(N-methoxy-iminopyridine)Cl] ⁺
[Ru]-5	$[(\eta^6$ -benzene)Ru(N-isopropyl-iminopyridine)Cl] ⁺
[Ru]-6	$[(\eta^6-C_6H_6)RuCl(\kappa^2-(N,N)-2-(aminomethyl)-pyridine)]PF_6$
[Ru]-7	$[(\eta^6-C_6H_6)RuCl(\kappa^2-(N,N)-N-(pyridin-2-ylmethyl)propan-2-amine)]PF_6$
[Ru]-8	[$(\eta^6-C_6H_6)RuCl(\kappa^2-(N,N)-N-(pyridin-2-ylmethyl)propan-1-amine)]PF_6$
[Ru]-9	$[(\eta^6-C_6H_6)RuCl(\kappa^2-(N,N)-N-(pyridin-2-ylmethyl)butan-1-amine)]PF_6$
[Ru]-10	$[(\eta 6-C_6H_6)RuCl(\kappa^2-(N,N)-3-methyl-N-(pyridin-2-$
	ylmethyl)butan-1-amine)]PF ₆
[Ru]-11	$[(\eta^6-C_{10}H_{14})RuCl(\kappa^2-(N,N)-2-(aminomethyl)-pyridine)]PF_6$
[Ru]-12	$[(\eta^{6}-C_{10}H_{14})RuCl(\kappa^{2}-(N,N)-N-(pyridin-2-ylmethyl)propan-2-amine)]PF_{6}$
[Ru]-13	$[(\eta^6-C_{10}H_{14})RuCl(\kappa^2-(N,N)-N-(pyridin-2-ylmethyl)propan-1-amine)]PF_6$
[Ru]-14	$[(\eta^6-C_{10}H_{14})RuCl(\kappa^2-(N,N)-N-(pyridin-2-ylmethyl)butan-1-amine)]PF_6$
[Ru]-15	$[(\eta^6-C_{10}H_{14})RuCl(\kappa^2-(N,N)-3-methyl-N-(pyridin-2-$
	ylmethyl)butan-1-amine)] PF ₆
[Ru]-16	$[\{(\eta^{6}-C_{10}H_{14})Ru\}_{2}(\mu-H)(\mu-HCO_{2})(\mu-Cl)]^{+}$
[Ru]-17	$[(\eta^6-C_{10}H_{14})Ru(imidazole)Cl_2]$
[Ru]-18	$[(\eta^6-C_{10}H_{14})Ru(imidazole)_2Cl]Cl$
[Ru]-19	$[(\eta^6-C_{10}H_{14})Ru(imidazole)_3]Cl_2$
L1	N-hydroxy-iminopyridine

L2	N-methoxy-iminopyridine
L3	N-isopropyl-iminopyridine
L4	2-(aminomethyl)-pyridine
L5	N-(pyridin-2-ylmethyl)propan-2-amine
L6	N-(pyridin-2-ylmethyl)propan-1-amine
L7	N-(pyridin-2-ylmethyl)butan-1-amine
L8	3-methyl-N-(pyridin-2-ylmethyl)butan-1-amine
L9	N-hydroxy pyridine
L10	N-amino pyridine
L11	Aniline
L12	4-methyl aniline
L13	4-chloro aniline
L14	Imidazole
L15	2-methyl imidazole
L16	2-methyl, 4-ethyl imidazole
L17	2-methoxy pyridine
L18	Pyridine
L19	Phenol
DFT	Density Functional Theory
NMR	Nuclear Magnetic Resonance
UV-vis	UV-visible Spectroscopy
ESI-MS	Electrospray Ionization- Mass Spectrometry
GC-MS	Gas Chromatography-Mass Spectrometry
TGA	Thermogravimetric Analysis
TLC	Thin Layer Chromatography
SCXRD	Single crystal X-ray Diffraction
GOF	Goodness of fit
CDCl ₃	Chloroform-d
D ₂ O	Deuterium oxide
DMSO- d_6	Dimethylsulphoxide-d ₆
Ar	Argon

O ₂	Oxygen
H_2	Dihydrogen
N_2	Nitrogen
0	ortho
Μ	meta
Р	para
NHC	N-heterocyclic carbine
PCy ₃	Tricyclohexylphosphine
PPh ₃	Triphenylphosphine
S	Singlet
D	Doublet
Т	Triplet
Q	Quartet
m	Multiplet
Br	Broad
Ppm	Parts per million
r.t.	Room temperature
Temp	Temperature
TMS	Trimethylsilane
TON	Turnover number
TTN	Total turnover number
TOF	Turnover frequency
Abs	Absorption
calc.	Calculated
cat.	Catalyst
cm ³	Cubic centimeter
Су	Cyclohexane
Et	Ethyl
Me	Methyl
ⁱ Pr	iso-propyl
Ph	Phenyl

XXXIII

equiv.	Equivalents
Gm	Gram
Н	Hour
EtOH	Ethanol
MeOH	Methanol
DCM	Dichloromethane
CH ₃ CN	Acetonitrile
Et ₂ O	Diethyl ether
Atm	Atmospheres (pressure)

XXXV

Chapter 1

An Overview on Hydrogen Production from Various Liquid Hydrogen Storage Materials: Role of the Catalyst

1.1. Introduction

Hydrogen is a simple but highly flammable molecule with having no odour and taste. Hydrogen gas was firstly produced by reacting the metal with acid in the 16th century, further Henry Cavendish in the 17th century was the first to recognize hydrogen gas as a discrete substance, and discovered that upon burning hydrogen gas with air produced water. Later, Antoine Lavoisier reproduced the Cavendish experiment, and named this gas "hydrogen", which is a Greek word that means "water-former".^[1] Hydrogen is the alternative for cleaner energy production, as the only by-product produced was water when combined with oxygen in the fuel cell.^[2] The world's first hydrogen-powered internal combustion engine was claimed to be invented by French-Swiss inventor Isaac de Rivaz in 1804.^[3] Depleting fossil fuels resources and deteriorating environmental issues triggered the world's attention to the search for new alternative fuels to fossil fuels that should be renewable, sustainable and most importantly environment friendly. In this regard, 'Hydrogen gas' is identified as a potential clean fuel for both stationary and mobile applications, as it has a very high energy density of approx. 120 MJ/kg, almost thrice to that of gasoline.^[4] Though hydrogen is the third most abundant element on earth, but mostly exits as various chemical forms, and its presence as hydrogen gas is extremely rare in the earth's atmosphere (1 ppm by volume).^[5] Therefore, using hydrogen as a fuel may help in controlling the environmental pollution problem with zero emission of any harmful substance, but the production, storage and transportation of hydrogen gas has several challenges and safety issues due to the chemical and physical properties of hydrogen gas.^[6] Therefore, it is the need of the hour to develop a new and efficient process for the storage and transportation of hydrogen. Now a day's upto 96% of hydrogen gas is being produced from non-renewable sources with major contributors being coal gas (48%) and oil (30%) steam reforming, and water gas shift reaction (18%). On the other hand, hydrogen production by a more sustainable way from the electrolysis

of water contributing only 4% of the total hydrogen gas production. ^[6b] Therefore to develop new sustainable and renewable energy sources for the production of hydrogen gas free from CO₂ and other contamination gases is the prime need of society.



Figure 1.1. Schematic representation of hydrogen storage, production and application.

Though efforts are being made to store hydrogen gas in tanks under high pressure (300 bar) and/or as a liquid under cryogenic conditions (-252.87 °C and 1.013 bar), the low volumetric energy density of hydrogen gas (70.8 kg/m³) and potential safety issues has made its storage and transport a critical challenge.^[6a] In addition the porous structures and metal hydrides have also been explored to store and transport hydrogen gas.^[6a] However storing hydrogen in chemical bonds in a suitable liquid hydrogen storage material has also received considerable global attention. These liquid hydrogen storage materials can release hydrogen gas in the presence of a suitable catalyst and in most of the cases the hydrogen storage materials can be recovered back via hydrogenation.^[77] In this regard, hydrazine hydrate (7.9 wt% H₂), formic acid (4.3 wt% H₂), formaldehyde (8.4 wt% H₂) and methanol (8 – 12.5 wt% H₂) and other alcohols have been identified as efficient liquid hydrogen carriers.^[7,8] Such as methanol which is considered an efficient hydrogen generation source (12.5 wt%), can be produced from biomass/food waste and by hydrogenation of CO₂.^[7]

S. No.	Liquid hydrogen carriers	Reaction equation	wt%
1.	$N_2H_4.H_2O$	$N_2H_4.H_2O \longrightarrow N_2 + 2H_2 + H_2O$	7.9
2.	CH ₃ OH	(a) CH ₃ OH \rightarrow HCHO +H ₂	6.25
		(b) $CH_3OH + H_2O \rightarrow HCOOH + 2H_2$	8
		(c) $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$	12.5
3.	НСНО	$HCHO + H_2O \longrightarrow CO_2 + 2H_2$	8.4
4.	НСООН	HCOOH \longrightarrow CO ₂ + H ₂	4.3
5.	ArCH ₂ OH	ArCH ₂ OH \rightarrow ArCOOH + 2H ₂	-
		$Ar = C_6H_5$, other alcohols	

Table 1.1. Comparison table for the different wt% of liquid hydrogen storage system

Further, most of these liquid hydrogen storage materials have an appreciably high gravimetric density of hydrogen, are inexpensive, ready-to-use and can be obtained from renewable resources. Advantageously being liquid at room temperature makes these liquids as a viable candidate for hydrogen storage materials which is compatible with the existing infrastructure for dispensing fossil fuels. Similarly, methanol, formic acid, and formaldehyde have a considerably high content of hydrogen and emerging a promising liquid hydrogen storage material.^[7,8] In addition, using higher alcohols, hydrogen gas can be produced along with the industrially valuable side products, for instance using benzyl alcohol for hydrogen production, producing benzoic acid as the side product which is of industrial importance in the food industry. Further, the storage and importance of hydrogen gas are briefly discussed in the following sections.

The current energy system which highly depends upon the use of non-renewable resources is now needed to be replaced by renewable energy resources.^[9] Hydrogen can be produced using many ways such as using electrical, thermal and photochemical energy, and it also presents as in chemical form in large amount, further it can be generated through renewable energy sources.^[10] In addition, the use of hydrogen in fuel cell produces water as the only byproduct, which is green and has no adverse effect on the environment. The major application of hydrogen as an energy carrier is to use it in the fuel cell to generate electricity to power the buildings and as well as vehicles.^[10] Further, hydrogen is also an important component in ammonia synthesis and in fertilizer

industries. Similarly, the CO_2 which is the major component for the greenhouse effect can be reduced using hydrogen to methanol, which is also an efficient pathway to mitigate CO_2 from the atmosphere by transforming it to methanol. The overview of hydrogen utilization is shown in Figure 1.2.



Figure 1.2. Overview of key hydrogen production and usage pathways. Reproduced from Ref. 10b with permission from the Royal Society of Chemistry.

1.2. Hydrogen storage and production

Notably, the safe storage and transportation of hydrogen gas are typically difficult due to its various physical and chemical properties.^[6] Storage and transport of hydrogen gas in cylinder/tanks under high pressure (300 bar) or as liquid hydrogen (-252.87 °C) is not safe.^[11] Hence it is highly desirable to search for suitable carriers for hydrogen to safely store and transport the hydrogen and to effectively dispense the hydrogen gas on site. Compared to hydrogen gas, storing hydrogen in various liquid hydrogen carriers, where hydrogen is chemically bonded, which contains appreciably high gravimetric/volumetric content of hydrogen is more appropriate and suitable, as being liquid at room temperature these liquid hydrogen carriers can be easily and safely stored and transported without any significant challenges.^[7,8] The various available physical and



chemical storage based hydrogen storage systems are briefly described below.

Figure 1.3. Various available methods for hydrogen storage.

1.2.1. Physical storage

Hydrogen can be stored as compressed hydrogen gas (35-70 MPa, room temperature),^[12] liquid hydrogen $(0.1-1 \text{ MPa}, \text{ approx. } -253 \text{ °C})^{[11]}$, Cryo-adsorption on high-surface-area materials (0.2-0.5 MPa, approx. $-193 \text{ °C})^{[6]}$ and over different adsorbents such as zeolites, carbon materials, MOFs (metal organic framework) and so on.^[13] Currently, compressed gaseous hydrogen and liquid hydrogen are the most developed technology for fuel-cell-powered cars, transportation of hydrogen and so on.^[6] However, the physical and chemical property of hydrogen makes the storage of hydrogen difficult in high pressurized cylinders and also the liquification of hydrogen is a highly energy-intensive process. Though physisorption of hydrogen in porous materials such as MOF, zeolites and carbon-based materials displayed promising development and advancement, these systems still have suffered from low hydrogen wt%.

1.2.2. Chemical Storage

Although physical storage of hydrogen has several advantages and disadvantages, the chemical storage of hydrogen is more efficient as it can storage high content hydrogen

and hydrogen can be released efficiently. In chemical storage methods, hydrogen can be stored in various chemicals such as hydride, amine borane adducts, amides/imides and in form of liquid organic hydrogen carriers.^[6] For instance, chemical storage of hydrogen in methanol, water and other liquid hydrogen organic carriers, which are stable at room temperature, has its own advantages of easy and safe storage and transportation of hydrogen gas. Hydrocarbons are also a good source of hydrogen gas, where hydrogen can be produced by gasification, reforming, and other processes at high temperature.^[6] Few of the chemical storage of hydrogen storage materials are briefly described in the following sections.

1.2.2.1. Metal hydride

There are various metal hydrides available for the storage of hydrogen such as NaBH₄, NaH, LiBH₄ and other metal hydrides.^[14] The basic requirement for considering a metal hydride as a hydrogen storage system is to have a redox potential below that of the H⁺/H₂ system at the corresponding pH, which upon reaction with water produce hydrogen along with metal hydroxide or oxide as side products. Metal hydrides have several advantages such as favourable oxidation of metal hydrides to release hydrogen gas, and the high hydrogen storage capacity such as LiBH₄ with H₂O can release 8.4 wt% of hydrogen gas. However, the major challenge for the metal hydride storage systems is the energy-intensive and cumbersome process for the regeneration of metal hydride from metal hydroxides.

1.2.2.2. Amine borane adduct

The amine borane adducts are also extensively investigated for hydrogen generation.^[15] They contain a high wt% of hydrogen, such as H₃N·BH₃ has 19.6 wt% of hydrogen which can be partially decomposed at 130 °C in a multistep decomposition process.^[16] The major challenge in fully utilizing ammonia borane adducts as the hydrogen reservoir is the highly energy-intensive and challenging regeneration of ammonia borane from borate.

1.2.2.3. Inorganic Amides/Imides

Amides/Imides systems are shown to be promising hydrogen materials. Amides can efficiently generate hydrogen and can be used as hydrogen storage materials.^[17] In 2002, Chen and co-worker rediscovered that LiNH₂/Li₃N shows the hydrogen storage property.^[18] For the hydrogen production using LiNH₂ needs a high temperature (420 °C) for the complete generation of hydrogen. This system has major limitations due to the thermodynamically favorable side reaction for ammonia generation from pure amides at high temperature, as compared to the desired hydrogen production pathway.

1.2.2.4. Hydrocarbons (fossil fuels)

The industrial hydrogen production process involves the steam reforming of hydrocarbons (such as methane steam reforming, eq. 1.1). Hydrocarbons can generate hydrogen and carbon-based chemicals when heated at high temperature (700–1000 °C) under pressure (3-25 bar).^[19] Methane gas contains 25 wt% of hydrogen, in the case of methane reforming or natural gas reforming hydrogen production, occurred following the below pathways: firstly the steam methane reforming reaction takes place to produce carbon monoxide and three equivalents of hydrogen along with a slight impurity of CO₂. Further, carbon monoxide via water- gas shift reaction (eq. 1.2) produces CO₂ and two equivalents of hydrogen. Though the steam methane reforming technology has been very well explored and is a stablished process for industrial-scale hydrogen production, the need of high temperature and high production cost are few of the drawbacks of this process.^[20]

Steam-methane reforming reaction

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
 $\Delta H = 206 \text{ kJ mol}^{-1}$ (eq. 1.1)

Water-gas shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41 \text{ kJ mol}^{-1}$$
 (eq. 1.2)

One of the major hurdles for the production of hydrogen via the steam reforming process is the very stable nature of methane, which makes the activation of methane molecules difficult. Due to this, the process needs a high temperature and pressure to activate the methane molecule. There are various metal catalyst has been explored for the methane reforming, but the application of noble metals (Ru or Rh) based catalyst which shows good activity and stability is limited.^[21] However, non-noble metal catalysts such as commercially available Ni/Al₂O₃ catalyst suffered from easy deactivation due to sintering and coke formation. In addition, the generation of carbon dioxide along with hydrogen gas also increases the cost of the process.^[22]

1.2.2.5. Ammonia-based Liquid Hydrogen Carriers and Liquid organic hydrogen carriers

Unlike metal hydride and other inorganic hydrogen storage materials, a wide range of liquid hydrogen carriers based on ammonia-based (e.g., ammonia and hydrazine) and liquid organic hydrogen carriers (LOHCs, e.g., CH₃OH, HCOOH, formaldehyde and others) are also been extensively explored as a potential candidate for hydrogen storage, transport and delivery. Liquid hydrogen carriers have the potential to store hydrogen under ambient conditions and to produce hydrogen at room temperature in presence of a suitable catalyst. Being liquid, these liquid hydrogen carriers can be easily and safely transported and delivered using the current infrastructure of dispensing petroleum products. Further, these liquid hydrogen carriers contain a sufficiently high content of hydrogen (volumetric and gravimetric), and most importantly many of the liquid hydrogen carriers can efficiently regenerate through the catalytic hydrogenation and dehydrogenation cycles. For instance, hydrogenation and dehydrogenation of cyclic hydrocarbons, benzene/cyclohexane (7.1 wt%) and naphthalene/decalin (7.2 wt%), which also have reasonably high volumetric H_2 storage capacity. Therefore, for a sustainable hydrogen storage system, the liquid hydrogen carriers should have the property to produce hydrogen gas in presence of the catalyst and further, the dehydrogenated liquid hydrogen carriers can be regenerated upon hydrogenation to their original form.^[23] Currently, valuable chemicals such as CH₃OH, HCOOH, HCHO and NH₃ and being extensively explored as potential liquid hydrogen storage materials. Notably, these hydrogen storage materials can be produced by the hydrogenation of CO₂ and N₂. Therefore, it is worth exploring these liquid hydrogen carriers for hydrogen production, storage and transportation.

Liquid hydrogen carriers have several advantages for hydrogen production over the other hydrogen storage materials, as from the liquid hydrogen carriers, hydrogen can be produced under mild reaction conditions. The most conventional way for hydrogen production using these liquid hydrogen carriers is reforming at a higher temperature. Industrially the hydrogen production via the reforming of hydrocarbon (methane reforming) is being operated at a very high temperature (700 °C – 1000 °C) and pressure (3-25 bar).^[19] Similarly, methanol-reforming also occurred at a high temperature (>200 °C) and pressure (>25 bar).^[24] However, methanol has several advantages as it can be produced from biomass (food waste) and also via hydrogenation of carbon dioxide, which is important in view of the sustainability of these processes.^[25] The below section briefly described the hydrogen production process from various liquid hydrogen carriers.

1.2.2.5.1. Ammonia and hydrazine

Ammonia contains 17.65 wt% of hydrogen and has vapor pressure 9.2 bar at room temperature, so can be liquefied at mild conditions. Further, the decomposition of ammonia produces hydrogen and nitrogen only, showing no greenhouse gas emissions (eq. 1.3).

 $NH_3 \rightarrow 1/2N_2(g) + 3/2H_2(g)$ $\Delta H = +46 \text{ kJ mol}^{-1}$ (eq. 1.3)

The production of hydrogen from ammonia is an endothermic process and needs a high temperature.^[26,27] Depending upon the catalysts used the hydrogen production from ammonia needs >650-700 °C temperature. Various heterogeneous metals catalysts including Fe, Ni, Pt, Ru, Ir, Pd, Rh, Ni/Pt, Ni/Ru, Pd/Pt/Ru/La, and alloys of Fe with other metal oxides including Ce, Al, Si, Sr, and Zr are investigated for ammonia decomposition to hydrogen.^[27] Notably, ammonia can be reversibly produced from nitrogen and hydrogen, therefore ammonia can efficiently store and transport hydrogen. Along with ammonia, hydrazine is also well explored for low-temperature hydrogen production using various heterogeneous catalytic systems. Hydrazine in presence of a catalyst can produce two equivalents of hydrogen and one equivalent of nitrogen (eq. 1.4), leading to carbon-free hydrogen production, while the partial decomposition of hydrazine produces

ammonia and nitrogen gas (eq. 1.5).^[28] Though anhydrous hydrazine contains 12.5 wt% of hydrogen but is mutagenic, highly toxic, and unstable. On the other hand, monohydrate hydrazine is safe as compared to anhydrous and it also contains a high H₂ content of 8 wt%.^[28]

$$N_2H_4 \rightarrow N_2(g) + 2H_2(g) \Delta H = -95.5 \text{ kJ mol}^{-1}$$
 (eq. 1.4)

$$3N_2H_4 \rightarrow N_2(g) + 4NH_3(g) \Delta H = -157 \text{ kJ mol}^{-1}$$
 (eq. 1.5)

Both equations 1.4 and 1.5, inferred that both the processes are exothermic and the decomposition of hydrazine to ammonia is thermodynamically more favorable. The main advantage of hydrazine as a hydrogen source is that its carbon-free energy source, liquid at room temperature and that hydrogen can be produced from hydrazine at room temperature.^[28] Moreover, the complete conversion of hydrazine to hydrogen resulted in the generation of nitrogen as the only byproduct which does not have any adverse effect on the environment. Though hydrogen production over heterogeneous catalysts is well explored, reports for hydrogen production from hydrazine using homogeneous catalyst are still less.^[29] However, hydrazine coordinated complexes of Fe, W, Mo, Ir, Ru and others are extensively explored due to important intermediates in several reactions of global importance including nitrogen to ammonia reduction, and therefore these results may act as the pathfinder for exploring homogeneous catalysts for hydrogen production from hydrazine.^[29,30]

1.2.2.5.2. Liquid Organic Hydrogen Carriers (LOHCs)

As stated above for methane steam reforming reaction the hydrogen production takes place at higher temperature (700 °C – 1000 °C) and pressure (3-25 bar), while the processes such as methanol steam reforming required relatively low temperature (200 °C – 350 °C), and 25 bar pressure.^[24] For steam reforming of methanol, a wide range of catalysts such as CuO/ZnO/Al₂O₃, Pd/CeO₂–ZrO₂, Pt₃Ni and Ni–Fe–Mg alloys have been extensively explored, but most of these catalysts require a temperature more than 200 °C. Though recently few of the catalysts such as Pt/MoC catalyst have been explored which can operate at a temperature below 200 °C, but still the operating temperature (150–190 °C) is high and the catalyst is of an expensive Pt metal. Apart from

heterogeneous catalysts, several homogenous catalysts based on Ru, Ir, Fe, and Mn metal complexes have also been explored for hydrogen production from methanol at a lower temperature (< 100 °C). Further, the higher primary alcohols are also a good candidate for hydrogen production as with the production of hydrogen the carboxylic acid is produced which is also the industrially important product.^[20,31,32] Furthermore, the alcohol dehydrogenation to acids is an atom economical reaction and so it is considered as a sustainable and green pathway for hydrogen production. These alcohols such as methanol, ethanol and others are liquid at room temperature and can be stored at room temperature, and hence can be easily stored and transported which is also an important requirement for a liquid hydrogen carrier.^[31] Further other alcohols such as benzyl alcohol produce two equivalents of hydrogen and benzoic acid as a byproduct.^[32] Various Ir-, Rh-, and Ru-based homogenous catalysts have also been explored for hydrogen production from these aromatic alcohols in water and organic solvents under highly basic conditions.

In the case of methanol, the hydrogen production process is endothermic in nature, where three equivalents of hydrogen are produced from methanol-water in a two-step process (i) methanol to formic acid with two equivalents of hydrogen (eq. 1.6), and (ii) formic acid transformed to one equivalent of hydrogen with one equivalent of CO_2 (eq. 1.7).^[31]

$$CH_3OH + H_2O \rightarrow HCOOH + 2H_2 \quad \Delta H = 53.3 \text{ kJ mol}^{-1}$$
 (eq. 1.6)

$$\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \qquad \Delta \text{H} = -14.5 \text{ kJ mol}^{-1}$$
 (eq. 1.7)

Moreover, various intermediates formed during the hydrogen production from methanol such as formaldehyde and formic acid are also important liquid hydrogen carriers. Formaldehyde contains 8 wt% of hydrogen and can be efficiently dehydrogenated using a metal-based catalyst at low temperature.^[33] The favourable thermodynamics showing the reaction is exothermic for hydrogen production from formaldehyde-water dehydrogenation.

$$CH_2O + H_2O \rightarrow 2H_2 + CO_2$$
 $\Delta H = -35.8 \text{ kJ mol}^{-1}$ (eq. 1.8)

Typically in water, formaldehyde exists in the form of a stable methanediol, and in the presence of a suitable catalyst produces hydrogen and carbon dioxide. Recently various Ru and Ir metal-based homogeneous complexes were explored for the low temperature

(<100 °C) hydrogen production from formaldehyde water solution.^[34] Very recently, (η^{6} - C_6Me_6 Ru(II)-diamine complexes for H₂ production from aqueous formaldehyde under the base free condition at 95 °C were investigated by Himeda et al.. Their finding shows that paraformaldehyde produced a total turnover number of 24000 over the catalyst [$(\eta^6$ - C_6Me_6)Ru(κ^2 -bipyridyl-2,2'-diamine)OH₂]SO₄ at 95 °C in water. ^[34b] Except these homogeneous metal catalysts, some heterogeneous metal-based catalysts especially Cu, Ag, Au, Pd, Pt, and Zn explored near or at room temperature dehydrogenation of formaldehyde. ^[33] Similarly, formic acid (4.3 wt% H₂) was also extensively explored for hydrogen production at low temperature as compared to methanol. Equation 1.7 shows that formic acid decomposition is an endothermic process and produce one equivalent of hydrogen along with CO₂. Various noble and non-noble metal-based homogeneous catalysts have been explored for hydrogen production from the formic acid solution.^[35] Our group also developed a range of ruthenium-based homogeneous metal complexes for hydrogen production from formic acid in water.^[36] Except these the formic acid can be regenerated via hydrogenation of carbon dioxide which makes it a viable candidate for hydrogen storage source (LOHC).

1.3. Role of catalyst for the hydrogen production reaction

Catalysts have a wide range of possible applications in the synthesis of several key industrial products. Wilkinson's catalyst RhCl(PPh₃)₃ [chloridotris(triphenylphosphane)rhodium(I)], is known to be a very active homogeneous metal catalyst for the hydrogenation of olefins using molecular hydrogen to produce alkanes.^[37] Other catalysts, such as Schrock and Grubbs, were the first to demonstrate the air-sensitive metallo-carbene complex for olefin metathesis, for which Chauvin, Grubbs, and Schrock were awarded the Nobel Prize in 2005.^[38] Noyori, Ikariya and colleagues developed very efficient and novel catalytic systems for the enantioselective and transfer hydrogenation of aromatic ketones in 1995.^[39] So all these examples presented the importance of catalyst for the production of industry-oriented value-added chemicals.

Catalysts played a pivotal role in bond activation, and hence tune the selectivity and productivity of the reaction. For instance, the activation of bonds for hydrogen gas release from alcohols and amines requires a large amount of energy. The Δ H (+130.7 kJ mol⁻¹) for methanol dehydrogenation process clearly indicating that the activation of bonds for

hydrogen production is an energy-intensive process.^[40] When the catalyst is introduced into the reaction, it interacts with the substrate and generates several intermediates and transition states, lowers the reaction's Gibbs free energy and allowing the hydrogen to be produced at milder reaction conditions. CO2/methanol can undergo reversible hydrogenation/ dehydrogenation, which makes methanol a potential hydrogen carrier and several catalysts for both hydrogenation of CO₂ to methanol and dehydrogenation of methanol to CO₂ have been extensively explored.^[40] For example, Beller and co-workers reported highly efficient and active catalyst [RuH(CO)Cl(HN(C₂H₄PⁱPr₂)₂)] for hydrogen production from methanol. Moreover, several other metals complexes based on Fe, Ru, Ir, and Mn having R_2N amido donors in a chelating ligand framework have also been studied for the methanol dehydrogenation reaction.^[41] The outer-sphere Noyori-type mechanism is proposed for most of the alcohol dehydrogenation catalysts, with proton transfer to the amido ligand and hydride transfer to the metal in the MeOH activation steps. Furthermore, the amine ligand donor's cooperative action with the metal hydride produced above results in hydride-proton coupling, which resulted in H₂ generation and the regeneration of the active amido catalyst (Scheme 1.1).^[41]



Scheme 1.1. (a) Proposed Noyori Type cooperative pathways for acceptorless dehydrogenation of alcohols, in a Gas-Phase context (b) Structure of complex used for the study. Reprinted with permission from ACS Catalysis, 8, 6908–6913. Copyright 2018 American Chemical Society. Further permission related to the material excerpted should be directed to the ACS.

Recently alcohols and amines gain much attention as promising candidates for the production of hydrogen along with the generation of value-added chemicals. With special reference to hydrazine, there are many reports available on the hydrazine coordinated metal complexes in literature but the activation of hydrazine to produced hydrogen is not explicitly explored. However, the metal-hydrazine complexes are considered to be the key component in the activation of N-H bonds in the hydrazine molecules. Chirik *et. al.* reported the coordination induced bond weakness in ammonia, water and hydrazine coordinated molybdenum complexes.^[42] After that Field *et al.* reported the base induced dehydrogenation of ruthenium hydrazine complex.^[43] Scheme 1.2 shows that at first Ruhydrazine moiety gets deprotonated in presence of a base and produced the end-on coordinated diazene species, which further form the nitrogen coordinated species with hydrogen generation or alternatively nitrogen is produced with the generation of metal-di-hydride species.^[43]



Scheme 1.2. Base-induced dehydrogenation of ruthenium-hydrazine complex. Reprinted with permission from Inorg. Chem., 52, 1570-1583. Copyright 2013 American Chemical Society.

It is evident that the tetradentate phosphine ligand in the above-mentioned ruthenium complex exhibited a unique coordination-decoordination behaviour and hence facilitated the base induced activation of hydrazine molecule to produce the diazene coordinated ruthenium complex with the generation of nitrogen and hydrogen. Moreover, the ruthenium center in the said complex also played an important role during the dehydrogenation of ruthenium-hydrazine complexes, wherein the transfer of electrons to the ruthenium from the hydrazine N-N bond form the end-on ruthenium diazene complex, which can further be transformed to produce the hydrogen and nitrogen gases. Analogously, the catalytic dehydrogenation of other amines, such as benzylamine and other aromatic and aliphatic amines also produce pure hydrogen along with imines and nitriles as byproducts.^[44] The benzylamine can produce two equivalents of hydrogen upon double dehydrogenation via cross-coupling to produce imine with one equivalent of hydrogen.^[44,45,46]



Scheme 1.3. Hydrogen production pathways for hydrogen production from amine. Reprinted with permission from ACS Catal., 6, 4799–4813. Copyright 2016 American Chemical Society.

Recently various Ru-based catalysts have been explored for amine dehydrogenation.^[44,45] For instance, Szymczak *et al.* also explored the mechanism of amine dehydrogenation to nitrile over N,N,N-amide-ruthenium(II) hydride complex (Scheme 1.3).^[46] Their results inferred that the catalyst having ortho-methyl group attached to pyridine moiety of the ligand plays a crucial role in the double dehydrogenation of amine to nitrile. They also explored the alcohol dehydrogenation reaction over the same catalyst and found that ortho-CH₃ group decreases the rate of reaction of the dehydrogenation process.^[46] Based

on the experimental and computational studies, they proposed that the ortho- CH_3 group plays both steric and electronic effects on the metal center to facilitate the amine dehydrogenation reaction (Figure 1.4).



a. Alcohol dehydrogenation: ortho-CH3 groups decrease rate

b. Amine dehydrogenation: ortho-CH₃ groups are required



Figure 1.4. (a) 1-phenylethanol dehydrogenation with 2 (ortho-CH₃) and 3 (ortho-H). (b) 1-octylamine dehydrogenation with 2 (ortho-CH₃) and 3 (ortho-H). Reprinted with permission from ACS Catal., 6, 4799–4813. Copyright 2016 American Chemical Society.

On the basis of experimental and computational results, an inner-sphere catalytic cycle was proposed for hydrogen production from primary amines (Scheme 1.4). The mechanism shows the effect of the ligand attached to the metal center for the selective production of nitrile and hydrogen from amines.



Scheme 1.4. Proposed catalytic cycle for the hydrogen production from amines. Reprinted with permission from ACS Catal., 6, 4799–4813. Copyright 2016 American Chemical Society.

Furthermore, ruthenium complexes having nitrogen-based ligand shows good catalytic activity for hydrogen production from methanol and other alcohols. Methanol dehydrogenation is a three-step reaction for the complete conversion of methanol to hydrogen gas. In the first step, methanol is dehydrogenated to formaldehyde and produce one equivalent of hydrogen gas. In the second step, the formaldehyde molecule in presence of water produced the diol, which dehydrogenated to produce one equivalent of hydrogen and CO_2 .^[31a]

Beller *et. al.* reported the ruthenium pincer catalyst for the low-temperature dehydrogenation of aqueous methanol under basic condition, wherein the catalytic activity was dependent on the ligand structure (Figure 1.5).^[31a] Initial results inferred that in 0.5M NaOH solution the complex **4** exhibited higher activity with TOF of 124 h⁻¹ as compared to **5** with TOF of 45 h⁻¹. However, their studies showed that using 8M KOH

solution, complex **5** (*i*Pr substitution) exhibited higher catalytic activity for methanol dehydrogenation due to lower solubility of complex 4 in water.



Figure 1.5. Reaction pathway for methanol dehydrogenation and best performing Rupincer complex for the methanol dehydrogenation process performed with 0.5 M KOH at 72 °C. Reproduced from Nature, 495, 85–89 with permission from Copyright © 2013, Nature Publishing Group.

Further, the purposed catalytic cycle (Scheme 1.5) involves the following steps: initially, the ligand gets deprotonated in presence of a base to produce nitrogen deprotonated ruthenium species. Further, this nitrogen deprotonated ruthenium species which is the active molecular species dehydrogenated methanol to hydrogen and formaldehyde via an outer-sphere concerted process. Furthermore, the hydroxide attacks on formaldehyde and produce the gem-diol(ate) stabilized by the solvent cage of protic methanol and water. The second molecule of hydrogen is also released via the outer sphere dehydrogenation of gem-diol to produced formate. At this stage, the catalyst either release the formate and

restart the cycle or decompose the formate to generate the third molecule of hydrogen along with CO₂.



Scheme 1.5. Proposed catalyst activation and catalytic cycle for low-temperature methanol reforming catalysed by ruthenium complex. The phosphorus iPr substituents have been omitted for clarity. ‡ denotes transition state; solvent-H indicates a molecule of solvent involved in hydrogen bonding. Reproduced from Nature, 495, 85–89 with permission from Copyright © 2013, Nature Publishing Group.

This concerted mechanism shows the base and ligand plays an important role in the hydrogen production from methanol. Similarly, the other groups also reported the methanol dehydrogenation using ruthenium-based complexes with other nitrogen and

phosphorus-based donor atom ligands. On the other hand, dehydrogenation of higher alcohols (such as benzyl alcohol and others) was also reported over other ruthenium catalysts having pincer or carbene ligands to produce the hydrogen along with the industrially important side products such as benzoic acid used for the preservative in the food industry.^[48]



Scheme 1.6. Catalyst for the dehydrogenation of alcohols to acid along with generation of hydrogen under basic condition. Reproduced from Nat. Chem., 5, 122–125 with permission from Copyright © 2013, Nature Publishing Group.

Recently Milstein *et. al.* reported the three ruthenium-based complexes having pincer ligand for benzyl alcohol dehydrogenation to benzoic acid and hydrogen in aqueous basic condition (Scheme 1.6).^[49] Studies inferred that the pre-catalyst 5 is transformed to species 6 in basic condition. The newly generated species is considered to be the active species for the hydrogen production from alcohols. They proposed a plausible mechanism for the hydrogen production from catalyst 5 in an aqueous basic condition to understand the role of catalyst (metal and the ligand) in alcohol dehydrogenation reaction (Scheme 1.7).



Scheme 1.7. Reaction pathway for the hydrogen production from the alcohols using the ruthenium catalyst 5 under aqueous basic condition. Reproduced from Nat. Chem., 5, 122–125 with permission from Copyright © 2013, Nature Publishing Group.

Initially, the methylene arm of the pyridyl group in complex 5 undergoes deprotonation to form the catalytic active species 6 with the dearomatized pyridyl group in presence of a base. Further, this unsaturated de-aromatized species reacted with the water molecule to produce the hydroxy coordinated aromatized species, which in presence of alcohols transformed to the alcohol coordinated species with the release of the water molecule. The alcohol coordinated species undergoes de-aromatization of ligand to produce the hydrogen and alcohol coordinated de-aromatized system which is further involved in the β -hydride elimination to produce the aldehyde coordinated hydride species. The aldehyde reacted with water to form the diol coordinated ruthenium hydride species, which further dehydrogenated via β -hydride elimination to produce carboxylate and regenerated the catalytic active species. It is evident that the reported catalytic system exhibited a strong relationship of the ligand and metal to facilitate the efficient production of hydrogen gas from alcohols.

Apart from alcohols, formaldehyde can also be explored for hydrogen production over a suitable catalyst. In this regard, Goldberg *et. al.* recently reported the (*para*-cymene)Ruthenium precatalysts for the hydrogen production from acetaldehyde and other aldehydes *via* aldehyde water shift reaction in water at 105 °C.^[50]



Scheme 1.8. Ruthenium catalyst for aldehyde water shift reaction. Reprinted with permission from ACS Catal., 6, 6302 -6305. Copyright 2016 American Chemical Society.

Results evidenced the crucial role of the ligand in tuning the catalytic activity, where the highest conversion was achieved with Ru(PDA) catalyst. Analogous, (hexamethylbenzene)Ru catalysts were also explored for the aldehyde-water shift reaction, where the catalytic activity was also found to be influenced by the arene ligand coordinated with the ruthenium center. ^[51]

Formaldehyde dehydrogenation was also studied over ruthenium complexes with N,N-donor ligands.^[52] Studies revealed that such catalytic systems are also active for the hydrogen production from alcohols, aldehyde, amines and hydrazine.

Moreover, several heterogeneous catalysts have also been explored for hydrogen production reactions, where they offer advantage over the homogeneous catalysts in easy recovery and recyclability of the catalyst but also have some disadvantages such as reaction takes place at higher temperature in case of alcohols. For instance, hydrogen production from hydrazine at near ambient condition is well explored by Xu et. al. over various metal (Fe, Co, Ni, Cu, Ru, Rh, Ir, Pt and Pd) nanoparticles,^[53] whereas in the case of alcohols the heterogeneous catalyst needs higher temperature to activate it. Such as in the case of methanol dehydrogenations, the reaction could efficiently work at the higher temperature over 200 °C and pressure using different metal-based catalysts such as CuO/ZnO/Al₂O₃,^[54] Pd/CeO₂–ZrO₂,^[55] Pt₃Ni,^[56] and Ni–Fe–Mg^[57] alloys. On the other hand, industrially viable heterogeneous catalysts for low-temperature hydrogen production are rarely explored, until recently when the Pt/MoC catalyst was explored for hydrogen production from methanol, but this catalyst only worked effectively at higher temperature (150–190 °C) and is composed of an expensive Pt catalyst.^[58]

1.4. Research Gaps and Objectives of the Thesis

Extensive research has been done to explore a sustainable and renewable energy source, wherein hydrogen is being produced as a clean energy source. It is to be noted that upon utilization it only produces water as a byproduct with a large amount of energy on combining with oxygen in the fuel cell. However, the physical and chemical property of hydrogen makes difficult to handle and store the hydrogen. Based on the literature, we found some open questions for hydrogen production from various liquid hydrogen storage sources.

- For hydrazine dehydrogenation, most of the literature reports are based on heterogeneous catalysts, while homogeneous metal complexes-based catalysts are not extensively explored for hydrazine dehydrogenation
- Though the complexation of hydrazine with metal complexes are studied well, insitu identification of important intermediates and the detailed investigation of the mechanistic pathway for hydrogen production from hydrazine over homogeneous catalysts need to be explored.
- The acceptorless dehydrogenation of alcohols was explored using the various homogeneous complexes, but the activity of the studied complexes needs to be improved. Particularly, the reaction needs to be performed and designed to produce hydrogen gas with high turnover at low temperature and with green solvents under additive-free conditions.

- Though few recent reports using ruthenium-based complexes for hydrogen production from formaldehyde has been explored at a temperature <100 °C, efforts need to be made to develop more robust catalysts for hydrogen production from formaldehyde at low temperature/ room temperature in water. Further, detailed mechanistic investigations to study the role of the catalyst in hydrogen production from formaldehyde is also required.
- Apart from higher alcohols, methanol also contains a high weight percentage of hydrogen. However, the production of hydrogen from methanol is being performed at a high-temperature reforming process (>200 °C), which suffers from several drawbacks including contamination of hydrogen produced. Therefore, considering the importance of this process, efforts need to be made for the selective production of hydrogen gas from methanol at low temperature using a suitable catalyst.

The work compiled in this thesis is mainly focused on the development of active catalysts for the dehydrogenation reactions to produce the hydrogen from the chemicals, which can be stored at room temperature and also liquid at room temperature. In this regard and on the basis of research gaps, we have developed the homogeneous as well as heterogeneous catalyst for the dehydrogenation of hydrazine, methanol, formaldehyde and benzyl alcohol at low temperature. Therefore, the principal objectives of the present study are:

- To develop ruthenium catalyst for the activation of hydrazine monohydrate for hydrogen production.
- To design and develop molecular catalysts based on ruthenium complexes for alcohol dehydrogenation and to extensively investigate the mechanistic pathway.
- To develop the ruthenium complexes-based catalysts for hydrogen production from formaldehyde and to study the mechanistic pathway.
- To develop the ruthenium nanoparticle catalytic system for methanol dehydrogenation.
1.5. Organization of the Thesis

In *Chapter 1* relevant literature survey on hydrogen storage, production and application along with the role of catalyst have been described.

Chapter 2 describes the catalytic activity of arene-Ru(II) complexes for the dehydrogenation of hydrazine to produce hydrogen and nitrogen, and the identification of the reaction intermediate species involved in the dehydrogenation pathway.

In *Chapter 3*, the synthesis and characterization of a series of pyridylamine ligated arene-Ru(II) complexes and their application for the catalytic dehydrogenation of aliphatic, aromatic and (hetero)aromatic alcohols are discussed. Further, the role of different ligands in tuning the catalytic activity and in the reaction pathway of the catalytic reaction is also investigated.

In *Chapter 4*, hydrogen production from formaldehyde-water solution over the imidazole-based ruthenium complexes is discussed in detail. Moreover, extensive mechanistic investigations have been performed to establish the reaction pathway by identifying various crucial reaction intermediate species.

Chapter 5 demonstrates the utilization of arene-ruthenium(II) as a precursor for the in situ synthesis of ruthenium nanoparticles, and the synthesized catalysts were explored for hydrogen production from methanol under the basic condition at low temperature.

Chapter 6 presents a brief summary of the present thesis, including the findings, limitations and future scope of the work.

1.6. References

- Grochala, W. (2015), First there was hydrogen, *Nat. Chem.*, 7, 264 (DOI: 10.1038/nchem.2186).
- Staffell I., Scamman D., Abad A. V., Balcombe P., Dodds P. E., Ekins P., Shah N., Ward K. R. (2019), The role of hydrogen and fuel cells in the global energy system, *Energy Environ. Sci.*, 12, 463-491 (DOI: 10.1039/C8EE01157E).
- 3. https://www.wipo.int/wipo_magazine/en/2009/02/article_0009.html.
- Schlapbach L., Züttel A. (2001), *Nature*, Hydrogen-storage materials for mobile applications, 414, 353–358 (DOI: 10.1038/35104634).
- (a) Bockris J. O'M. (1972), A Hydrogen Economy, *Science*, 176, 1323 (DOI: 10.1126/science.176.4041.1323); (b) Armaroli N., Balzani V. (2011), The Hydrogen Issue, *ChemSusChem*, 4, 21-36 (DOI: 10.1002/cssc.201000182); (c) Singh S. K., Xu Q. (2013), Nanocatalysts for hydrogen generation from hydrazine, *Catal. Sci. Technol.*, 3, 1889-1900 (DOI: 10.1039/C3CY00101F).
- 6. (a) Eberle U., Felderhoff M., Schuth F. (2009), Chemical and Physical Solutions for Hydrogen Storage, *Angew. Chem., Int. Ed.*, 48, 6608–6630 (DOI: 10.1002/anie.200806293); (b) Arregi A., Amutio M., Lopez G., Bilbao J., Olazar M. (2018), Evaluation of thermochemical routes for hydrogen production from biomass: A review, *Energy Convers. Manage.*, 165, 696–719 (DOI: 10.1016/j.enconman.2018.03.089).
- G. A. Olah, A. Goeppert, G. K. Sury Prakash, Beyond Oil and Gas: The Methanol Economy, Wiley-VCH, Weinheim, 2006.
- (a) Sartbaeva A., Kuznetsov V. L., Wells S. A., Edwards P. P. (2008), Hydrogen nexus in a sustainable energy future, *Energy Environ. Sci.*, 1, 79–85 (DOI: 10.1039/B810104N); (b) Jiang H. L., Singh S. K., Yan J. M., Zhang X. B., Xu Q. (2010), Liquid-phase chemical hydrogen storage: catalytic hydrogen generation under ambient conditions, *ChemSusChem*, **3**, 541–549 (10.1002/cssc.201000023); (c) Singh A. K., Singh S., Kumar A. (2016), Hydrogen energy future with formic acid: a renewable chemical hydrogen storage system, *Catal. Sci. Technol.*, 6, 12-40 (DOI: 10.1039/C5CY01276G); (d) Mellmann D., Sponholz P., Junge H., Beller M. (2016), Formic acid as a hydrogen

storage material – development of homogeneous catalysts for selective hydrogen release, *Chem. Soc. Rev.*, 45, 3954-3988 (DOI: 10.1039/C5CS00618J); (e) Sordakis K., Tang C. H., Vogt L. K., Junge H., Dyson P. J., Beller M., Laurenczy G. (2018), Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols, *Chem. Rev.*, 118, 372–433 (DOI: 10.1021/acs.chemrev.7b00182).

- International Renewable Energy Agency, Renewable Power Generation Costs in 2017, http://www.irena.org/publications/2018/Jan/Renewable-power-generationcosts-in-2017, Abu Dhabi, 2018.
- (a) Schiebahn S., Grube T., Robinius M., Tietze V., Kumar B., Stolten D. (2015), Power to gas: Technological overview, systems analysis and economic assessment for a case study in Germany. *Int. J. Hydrog. Energy*, 40, 4285–4294 (DOI: 10.1016/j.ijhydene.2015.01.123); (b) Quarton C. J., Tlili O., Welder L., Mansilla C., Blanco H., Heinrichs H., Leaver J., Samsatli N. J., Lucchese P., Robinius M., Samsatli S. (2020), The curious case of the conflicting roles of hydrogen in global energy scenarios, *Sustain. Energy Fuels*, 4, 80-95 (DOI: 10.1039/c9se00833k).
- Wolf J. (2010), Liquid hydrogen technology for vehicles. Handbook of Fuel Cells (DOI: 10.1002/9780470974001.f302008).
- Irani R. S. (2002), Hydrogen Storage: High-Pressure Gas Containment. *MRS Bulletin*, 27(09), 680–682 (DOI:10.1557/mrs2002.221).
- Thomas K. M. (2007), Hydrogen adsorption and storage on porous materials. *Catalysis Today*, 120, 389–398 (DOI:10.1016/j.cattod.2006.09.015); (b) Panella B., Hirscher M., Roth S. (2005), Hydrogen adsorption in different carbon nanostructures, *Carbon*, 43, 2209–2214 (DOI:10.1016/j.carbon.2005.03.037);
 (c) Nijkamp M. G., Raaymakers J. E. M. J., van Dillen A. J., de Jong K. P. (2001), Hydrogen storage using physisorption – materials demands, *Appl. Phys. A*, 72, 619–623 (DOI:10.1007/s003390100847); (d) Kuppler R. J., Timmons D. J., Fang Q.-R., Li J.-R., Makal T. A., Young M. D., Yuan D., Zhao D., Zhuang W., Zhou, H.-C. (2009), Potential applications of metal-organic frameworks, *Coord. Chem. Rev.*, 253, 3042–3066 (DOI:10.1016/j.ccr.2009.05.019).

- Schüth F., Bogdanović B., Felderhoff M. (2004), Light metal hydrides and complex hydrides for hydrogen storage, *Chem. Commun.*, 20, 2249–2258 (DOI: 10.1039/b406522k).
- 15. (a) Marder T. B. (2007), Will We Soon Be Fueling our Automobiles with Ammonia–Borane?, Angew. Chem., Int. Ed., 46, 8116–8118 (DOI:10.1002/anie.200703150); (b) Stephens F. H., Pons V., Tom Baker R. (2007), Ammonia–borane: the hydrogen source par excellence?, Dalton Trans., 2613–2626 (DOI: 10.1039/b703053c).
- Baitalow F., Bauman, J., Wolf G., Jaenicke-Rößler K., Leitner G. (2002), Thermal decomposition of B–N–H compounds investigated by using combined thermoanalytical methods, *Thermochim. Acta*, 391, 159–168 (DOI: 10.1016/s0040-6031(02)00173-9).
- 17. F. W. Dafert, R. Miklauz, (1910), *Monatsh Chem.*, 31, 981–996 (DOI: 10.1007/BF01518423).
- 18. Chen P., Xiong Z., Luo J., Lin J., Tan K. L. (2002), Interaction of hydrogen with metal nitrides and imides, *Nature*, 420, 302–304, (DOI:10.1038/nature01210).
- Chen L., Qi Z., Zhang S., Su J., Somorjai G. A. (2020), Catalytic Hydrogen Production from Methane: A Review on Recent Progress and Prospect, *Catalysts*, 10, 858 (DOI: 10.3390/catal10080858).
- Le Valley T. L., Richard A. R., Fan M. (2014), The progress in water gas shift and steam reforming hydrogen production technologies—A review, *Int. J. Hydrogen Energy*, 39, 16983–17000 (DOI: 10.1016/j.ijhydene.2014.08.041).
- 21. (a) Zhang L., Roling L. T., Wang X., Vara M., Chi M., Liu J., Choi S. I., Park J., Herron J. A., Xie Z., M. Mavrikakis, Y. Xia, Platinum-based nanocages with subnanometer-thick walls and well-defined, controllable facets (2015), *Science*, 349, 412–416 (DOI: 10.1126/science.aab0801); (b) Chen L. N., Li H. Q., Yan M. W., Yuan C. F., Zhan W. W., Jiang Y. Q., Xie Z. X., Kuang Q., Zheng L. S., Ternary Alloys Encapsulated within Different MOFs via a Self-Sacrificing Template Process: A Potential Platform for the Investigation of Size-Selective Catalytic Performances (2017), *Small*, 13, 1700683 (DOI: 10.1002/smll.201700683); (c) Qiao B., Wang A., Yang X., Allard L.F., Jiang Z.,

Cui Y., Liu J., Li J., Zhang T. (2011), Single-atom catalysis of CO oxidation using Pt1/FeOx, *Nat. Chem.*, 3, 634–641 (DOI: 10.1038/nchem.1095).

- (a) Meloni E., Martino M., Palma, V. (2020), A Short Review on Ni Based Catalysts and Related Engineering Issues for Methane Steam Reforming, *Catalysts*, 10, 352 (DOI: 10.3390/catal10030352); (b) Sun P., Young B., Elgowainy A., Lu Z., Wang M., Morelli B., Hawkins T. (2019), Criteria Air Pollutants and Greenhouse Gas Emissions from Hydrogen Production in US Steam Methane Reforming Facilities, *Environ. Sci. Technol.*, 53, 7103–7113 (DOI: 10.1021/acs.est.8b06197).
- 23. (a) Okada Y., Sasaki E., Watanabe E., Hyodo S., Nishijima H. (2006), Development of dehydrogenation catalyst for hydrogen generation in organic chemical hydride method, *Int. J. Hydrog. Energy*, 31, 1348–1356 (DOI: 10.1016/j.ijhydene.2005.11.014); (b) Yolcular S., Olgun Ö. (2007), Liquid Organic Hydrides for Hydrogen Storage, *Energy Sources A: Recovery, Util. Environ. Eff.*, 30, 309–315 (DOI: 10.1080/15567030600824841).
- Palo D. R., Dagle R. A., Holladay J. D. (2007), Methanol Steam Reforming for Hydrogen Production, *Chem. Rev.*, 107, 3992–4021 (DOI: 10.1021/cr050198b).
- (a) Cheng W. H., Kung H. H. (1994), Methanol production and use, Kung H. H and Cheng W.-H., Marcel Dekker, New York, (ISBN: 0824792238); (b) Dina I. U., Shaharunb M. S., Alotaibia M. A., Alharthia A. I., Naeem A. (2019), Recent developments on heterogeneous catalytic CO₂ reduction to methanol, *J. CO₂ Util.*, 34, 20–33 (DOI: 10.1016/j.jcou.2019.05.036).
- Ojelade O. A., Zaman S. F. (2020), Ammonia decomposition for hydrogen production: a thermodynamic study, *Chem. Pap.*, 57-65 (DOI:10.1007/s11696-020-01278-z).
- Yin S. F., Xu B. Q., Zhou X. P., Au C. T. (2004), A mini-review on ammonia decomposition catalysts for on-site generation of hydrogen for fuel cell applications, *Appl. Catal. A: Gen.*, 277, 1–9 (DOI: 10.1016/j.apcata.2004.09.020).
- Singh A. K., Yadav M., Aranishi K., Xu Q. (2012), Temperature-induced selectivity enhancement in hydrogen generation from Rh–Ni nanoparticle-catalyzed decomposition of hydrous hydrazine, *Int. J. Hydrogen Energy*, 37, 18915-18919 (DOI: 10.1016/j.ijhydene.2012.09.104).

- 29. (a) Barney B. M., Lukoyanov D., Yang T.-C., Dean D. R., Hoffman B. M., Seefeldt L. C. (2006), A methyldiazene (HN=N-CH3)-derived species bound to the nitrogenase active-site FeMo cofactor: Implications for mechanism, *Proc. Natl. Acad. Sci. USA.*, 103, 17113 (DOI: 10.1073/pnas.0602130103); (b) Barney B. M., Lee H.-I., Santos P. C. D., Hoffman B. M., Dean D. R., Seefeldt L. C. (2006), Breaking the N₂ triple bond: insights into the nitrogenase mechanism, *Dalton Trans.*, 2277-2284 (DOI: 10.1039/B517633F).
- Awasthi M. K., Tyagi D., Patra S., Rai R. K., Mobin S. M., Singh S. K. (2018), Ruthenium complexes for catalytic dehydrogenation of hydrazine and transfer hydrogenation reactions, *Chem. Asian J.*, 13, 1424-1431 (DOI: 10.1002/asia.201800315).
- 31. (a) Nielsen M., Alberico E., Baumann W., Drexler H.-J., Junge H., Gladiali S., Beller M. (2013), Low-temperature aqueous-phase methanol dehydrogenation to hydrogen and carbon dioxide, Nature, 495, 85–89 (DOI: 10.1038/nature11891). (b) Hu P., Diskin-Posner Y., Ben-David Y., Milstein D. (2014), Reusable Homogeneous Catalytic System for Hydrogen Production from Methanol and Water, ACS Catal., 4, 2649–2652 (DOI: 10.1021/cs500937f). (c) Bielinski E. A., Forster M., Zhang Y., Bernskoetter W. H., Hazari N., Holthausen M. C. (2015), Base-Free Methanol Dehydrogenation Using a Pincer-Supported Iron Compound and Lewis Acid Co-catalyst, ACS Catal., 5, 2404-2415 (DOI: 10.1021/acscatal.5b00137).
- Hu P., Milstein D. (2019), Conversion of Alcohols to Carboxylates Using Water and Base with H₂ Liberation, *Top. Organometal. Chem.*, 63, 175-192 (DOI: 10.1007/3418_2018_20).
- Trincado M., Grützmacher H., Prechtl M. H. G., CO₂-based hydrogen storage Hydrogen generation from formaldehyde/water, *Phys. Sci. Rev.*, 2018, 3, 20170013 (DOI: 10.1515/psr-2017-0013).
- (a) Fujita K. -I., Kawahara R., Aikawa T., Yamaguchi R. (2015), Hydrogen Production from a Methanol–Water Solution Catalyzed by an Anionic Iridium Complex Bearing a Functional Bipyridonate Ligand under Weakly Basic Conditions, Angew. Chem., Int. Ed., 54, 9057–9060 (DOI:

10.1002/anie.201502194); (b) Wang L., Ertem M. Z., Kanega R., Murata K., Szalda D. J., Muckerman J. T., Fujita E., Himeda Y. (2018), Additive-Free Ruthenium-Catalyzed Hydrogen Production from Aqueous Formaldehyde with High Efficiency and Selectivity, *ACS Catal.*, 8, 8600–8605 (DOI: 10.1021/acscatal.8b02088).

- Guan, C., Pan, Y., Zhang, T., Ajitha, M. J., Huang, K.-W. (2020), An update on Formic Acid Dehydrogenation by Homogeneous Catalysis, *Chem. Asian J.*, 15, 937-946 (doi:10.1002/asia.201901676).
- Patra S., Singh S. K. (2020), Hydrogen Production from Formic Acid and Formaldehyde over Ruthenium Catalysts in Water, *Inorg. Chem.*, 59, 4234–4243 (DOI: 10.1021/acs.inorgchem.9b02882).
- 37. Birch A. J., Walker K. A. M. (1966), Aspects of catalytic hydrogenation with a soluble catalyst, *J. Chem. Soc. C*, 1894–1896 (DOI: 10.1039/J39660001894).
- (a) Schrock R. R., Murdzek J. S., Bazan G. C., Robbins J., DiMare M., O'Regan 38. M. (1990), Synthesis of molybdenum imido alkylidene complexes and some reactions involving acyclic olefins, J. Am. Chem. Soc., 112, 3875-3886 (DOI: 10.1021/ja00166a023); (b) Grubbs, R. H. (2003), Handbook of Metathesis, Wiley-VCH, Weinheim, Germany, 1-3, (ISBN: 978-3-527-30616-9); (c) Schwab P., France M. B., Ziller J. W., Grubbs R. H. (1995), A Series of Well-Defined Metathesis Catalysts–Synthesis of [RuCl2(=CHR')(PR3)2] and its Reactions, Angew. Chem., Int. Ed., 34, 2039–2041 (DOI: 10.1002/anie.199520391); (d) Schwab P., Grubbs R. H., Ziller J. W. (1996), Synthesis and Applications of RuCl2(CHR')(PR3)2: The Influence of the Alkylidene Moiety on Metathesis Activity, J. Am. Chem. Soc., 118, 100–110 (DOI: 10.1021/ja952676d); (e) Scholl M., Ding S., Lee C. W, Grubbs R. H. (1999), Synthesis and Activity of a New Generation of Ruthenium-Based Olefin Metathesis Catalysts Coordinated with 1,3-Dimesityl-4,5-dihydroimidazol-2-ylidene Ligands, Org. Lett., 1, 953–956 (DOI: 10.1021/ol990909q); (f) Pappenfus T. M., Hermanson D. L., Ekerholm D. P., Lilliquist S. L. Mekoli M. L. (2007), Synthesis and Catalytic Activity of Ruthenium-Indenylidene Complexes for Olefin Metathesis, J. Chem. Educ., 84, 1998-2000 (DOI: 10.1021/ed084p1998).

- 39. (a) Noyori R., Hashiguchi S. (1997), Asymmetric Transfer Hydrogenation Catalyzed by Chiral Ruthenium Complexes, Acc. Chem. Res., 30, 97–102 (DOI: 10.1021/ar9502341); (b) Ohkuma T., Ooka H., Hashiguchi S., IkariyaT., Noyori R. (1995), Practical Enantioselective Hydrogenation of Aromatic Ketones, J. Am. Chem. Soc., 117, 2675–2676 (DOI: 10.1021/ja00114a043); (c) Hashiguchi S., Fujii A., Takehara J., Ikariya T., Noyori R. (1995), Asymmetric Transfer Hydrogenation of Aromatic Ketones Catalyzed by Chiral Ruthenium(II) Complexes, J. Am. Chem. Soc., 117, 7562–7563 (DOI: 10.1021/ja00133a037); (d) Fujii A., Hashiguchi S., Uematsu N., Ikariya T., Noyori R. (1996), Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation of Ketones Using a Formic Acid–Triethylamine Mixture, J. Am. Chem. Soc., 118, 2521–2522 (DOI: 10.1021/ja9541261); (e) Uematsu N., Fujii A., Hashiguchi S., Ikariya T., Noyori R. (1996), Asymmetric Transfer Hydrogenation of Imines, J. Am. Chem. Soc., 118, 4916-4917 (DOI: 10.1021/ja960364k); (f) Takehara J., Hashiguchi S., Fujii A., Inoue S., Ikariya T., Noyori R. (1996), Amino alcohol effects on the ruthenium(II)-catalysed asymmetric transfer hydrogenation of ketones in propan-2-ol, Chem. Commun., 233-234 (DOI: 10.1039/CC9960000233).
- Alberico E., Nielsen M. (2015), Towards a methanol economy based on homogeneous catalysis: methanol to H₂ and CO₂ to methanol, *Chem. Commun.*, 51, 6714–6725 (DOI: 10.1039/C4CC09471A).
- Sinha V., Govindarajan N., de Bruin B., Meijer E. J. (2018), How Solvent Affects C–H Activation and Hydrogen Production Pathways in Homogeneous Ru-Catalyzed Methanol Dehydrogenation Reactions, ACS Catalysis, 8, 6908–6913 (DOI: 10.1021/acscatal.8b01177).
- Bezdek M. J., Guo S., Chirik P. J. (2016), Coordination-induced weakening of ammonia, water, and hydrazine X–H bonds in a molybdenum complex, *Science*, 354, 730-733 (DOI: 10.1126/science.aag0246).
- Field L. D., Li H. L., Dalgarno S. J., McIntosh R. D., (2013), Base-Induced Dehydrogenation of Ruthenium Hydrazine Complexes, *Inorg. Chem.*, 52, 1570-1583 (DOI: 10.1021/ic302449n).

- Tseng K.-N. T., Rizzi A. M., Szymczak N. K. (2013), Oxidant-Free Conversion of Primary Amines to Nitriles, *J. Am. Chem. Soc.*, 135, 16352-16355 (DOI: 10.1021/ja409223a).
- 45. (a) Ventura-Espinosa D., Marza-Beltran A., Mata J. A. (2016), Catalytic Hydrogen Production by Ruthenium Complexes from the Conversion of Primary Amines to Nitriles: Potential Application as a Liquid Organic Hydrogen Carrier, *Chem. Eur. J*, 22, 17758-17766 (DOI: 10.1002/chem.201603423). (b) Dutta I., Yadav S., Sarbajna A., De S., Holscher M., Leitner W., Bera J. K. (2018), Double Dehydrogenation of Primary Amines to Nitriles by a Ruthenium Complex Featuring Pyrazole Functionality, *J. Am. Chem. Soc.*, 140, 8662-8666 (DOI: 10.1021/jacs.8b05009).
- Hale L. V. A., Malakar T., Tseng K.-N. T., Zimmerman P. M., Paul A., Szymczak, N. K. (2016), The Mechanism of Acceptorless Amine Double Dehydrogenation by N,N,N-Amide Ruthenium(II) Hydrides: A Combined Experimental and Computational Study, ACS Catal., 6, 4799–4813 (DOI: 10.1021/acscatal.6b01465).
- 47. Tseng K.-N. T., Kampf J. W., Szymczak N. K. (2015), Mechanism of *N*,*N*,*N*-Amide Ruthenium(II) Hydride Mediated Acceptorless Alcohol Dehydrogenation: Inner-Sphere β-H Elimination versus Outer-Sphere Bifunctional Metal–Ligand Cooperativity, *ACS Catal.*, 5, 5468-5485 (DOI: 10.1021/acscatal.5b00952).
- (a) Choi J., Heim L. E., Ahrens M., Prechtl M. H. G. (2014), Selective Conversion of Alcohols in Water to Carboxylic Acids by in situ Generated Ruthenium Trans Dihydrido Carbonyl PNP Complexes, *Dalton Trans.*, 43, 17248–17254 (DOI: 10.1039/C4DT01634C); (b) Malineni J., Keul H., Möller M. (2015), A Green and Sustainable Phosphine-Free NHC-Ruthenium Catalyst for Selective Oxidation of Alcohols to Carboxylic Acids in Water, *Dalton Trans.*, 44, 17409–17414 (DOI: 10.1039/C5DT01358E).
- Balaraman E., Khaskin E., Leitus G., Milstein D. (2013), Catalytic Transformation of Alcohols to Carboxylic Acid Salts and H₂ Using Water as the Oxygen Atom Source, *Nat. Chem.*, 5, 122–125 (DOI: 10.1038/nchem.1536).
- Brewster T. P., Goldberg J. M., Tran J. C., Heinekey D. M., Goldberg K. I. (2016), High Catalytic Efficiency Combined with High Selectivity for the Aldehyde–Water

Shift Reaction using (*para*-cymene)Ruthenium Precatalysts, *ACS Catal.*, 6, 6302 - 6305 (DOI: 10.1021/acscatal.6b02130).

- Phearman A. S., Moore J. M., Bhagwandin D. D., Goldberg J. M., Heinekey D. M., Goldberg K. I. (2021), (Hexamethylbenzene)Ru catalysts for the Aldehyde-Water Shift reaction, *Green Chem.*, 23, 1609-1615 (DOI: 10.1039/D0GC03809A).
- (a) Heim L. E., Schlorer N. E., Choi J.-H., Prechtl M. H. G., (2014), Selective and 52. mild hydrogen production using water and formaldehyde, Nat. Commun., 5, 3621 (DOI: 10.1038/ncomms4621); (b) Suenobu T., Isaka Y., Shibata S., Fukuzumi S. (2015), Catalytic hydrogen production from paraformaldehyde and water using an organoiridium complex, Chem. Commun., 51, 1670-1672 (DOI: 10.1039/C4CC06581F); (c) Trincado M., Sinha V., Rodriguez-Lugo R. E., Pribanic B., Bruin B. D., Grutzmacher, H. (2017), Homogeneously catalysed conversion of aqueous formaldehyde to H₂ and carbonate, Nat. Commun., 8, 14990 (DOI: 10.1038/ncomms14990); (d) Wang L., Ertem M. Z., Kanega R., Murata K., Szalda D. J., Muckerman J. T., Fujita E., Himeda Y. (2018), Highly Efficient and Selective Methanol Production from Paraformaldehyde and Water at Room Temperature, ACS Catal., 8, 5233–5239 (DOI: 10.1021/acscatal.8b00321).
- Singh S. K., Zhang X. B., Xu Q. (2009), Room-Temperature Hydrogen Generation from Hydrous Hydrazine for Chemical Hydrogen Storage, *J. Am. Chem. Soc.*, 131, 9894-9895 (DOI: 10.1021/ja903869y).
- Lee J. K., Ko J. B., Kim D. H. (2004), Methanol steam reforming over Cu/ZnO/Al₂O₃ catalyst: kinetics and effectiveness factor, *Appl. Catal. A Gen.*, 278, 25–35 (DOI: 10.1016/j.apcata.2004.09.022).
- Zhao M., Zhang H., Li X., Chen Y. (2014), Co-modified Pd/CeO₂-ZrO₂ catalysts for methanol decomposition, *J. Energ. Chem.*, 23, 755–760 (DOI: 10.1016/S2095-4956(14)60209-6).
- Du P., Wu P., Cai C. (2017), Mechanism of Methanol Decomposition on the Pt₃Ni(111) Surface: DFT Study, *J. Phys. Chem. C*, 121, 9348–9360 (DOI: 10.1021/acs.jpcc.7b01114).

- Mitani H., Xu Y., Hirano T., Demura M., Tamura R. (2017), Catalytic properties of Ni-Fe-Mg alloy nanoparticle catalysts for methanol decomposition, *Catal. Today*, 281, 669–676 (DOI: 10.1016/j.cattod.2016.10.036).
- Lin L., Zhou W., Gao R., Yao S., Zhang X., Xu W., Zheng S., Jiang Z., Yu Q., Li Y.-W., Shi C., Wen X.-D., Ma D. (2017), Low-temperature hydrogen production from water and methanol using Pt/α-MoC catalysts, *Nature*, 544, 80-83 (DOI: 10.1038/nature21672).

Chapter 2

Hydrogen Production from Hydrazine Hydrate over Ruthenium Catalyst

2.1. Introduction

Hydrazine coordinated transition metal complexes have been receiving huge scientific attention because of the involvement of metal-hydrazine species as important intermediates in several reactions of global importance including nitrogen to ammonia reduction.^[1-2] Therefore, such hydrazine coordinated complexes based on Fe, W, Mo, Ir, Ru and others have been extensively explored for diverse applications.^[1-27] For instance, Tyler et al. X-ray crystallographically characterized a Fe-hydrazine complexes cis- $[Fe(DMeOPrPE)_2(\eta^2-N_2H_4)][BPh_4]_2 \{DMeOPrPE=1,2-bis[bis(methoxypropyl)phosphin$ o]ethane} having η^2 -coordinated hydrazine, which further undergoes disproportionation to ammonia in the presence of acid.^[9] On the other hand, upon base-promoted deprotonation, such $Fe-\eta^2-N_2H_4$ complexes afforded Fe-diazene (Fe- $\eta^2-N_2H_2$) complexes, which converted back to Fe-hydrazine complex by treatment with a mild acid.^[10-14] Ikariya et al. reported Fe complexes containing proton responsive pyrazole pincer ligand, which also facilitated disproportionation of N₂H₄ into nitrogen via a intermediate.^[15] diazene Ir-based hydrazine complexes $[IrCl_2(RNHNH_2){P(OEt)_3}(AsPh_3)_2]^+$ (R = H, Me, Ph), synthesized by treating [IrCl₂H{P(OEt)₃}(AsPh₃)₂] with triflic acid followed by an excess of hydrazine, also undergoes oxidation in the presence of Pd(OAc)₂ to form Ir-diazene and Ir-hydride complexes.^[16] Very recently, Albertin *et al.* reported Ir-hydrazine complex $[(\eta^5 C_5Me_5$ [r{P(OR)₃}(N₂H₄)]⁺ which also exhibited Pb(OAc)₄ assisted oxidation to Irdiazene complex.^[17] Seino and Mizobe *et al.* also reported a $(\eta^5-C_5Me_5)$ Ir coordinated bis-hydrazine cluster $[{(\eta^5-C_5Me_5)Ir}_4(\mu_3-S)_2(\mu_2-H)_2(N_2H_4)_2]^{2+}$ having two hydrazine molecules coordinated to a single $(\eta^5-C_5Me_5)$ Ir molecules connected through the bridging sulphur of the Ir₃ cluster.^[18] Analogously, several Ru-hydrazine complexes were also reported, which upon oxidation may form corresponding diazene species,^[19a-e] such as, Ru-hydrazine $[RuH(N_2H_4)L_4]^+$ and Ru-bis-hydrazine complexes $[Ru(N_2H_4)_2L_4]^{2+}$ (L= P(OEt)₃, PPh(OEt)₂, P(OMe)₃ resulted in the formation of Ru-diazene complexes upon

treatment of Pb(OAc)₄ in DCM at -80 °C.^[20] Similarly, hydrazine coordinated Ru-arene and analogous Os-arene complexes $[(\eta^6-p\text{-}cymene)M\{PPh(OEt)_2\}Cl(\kappa^1-N_2H_4)]^+$ (M = Ru and Os) were also reported to be transformed into corresponding diazene complexes upon treatment with Pb(OAc)₄ at -30 °C.^[21] In similar fashion, Os-hydrazine complex $[Os(PPh_3)_2\{P(OMe)_3\}(CO)Cl(N_2H_4)]^+$ was also reported to be synthesized by direct treatment of N₂H₄ with $[OsHCl(CO)(PPh_3)_2\{P(OMe)_3\}]$ in the presence of triflic acid, which can be further oxidized to form corresponding Os-diazene complex.^[22] Interesting to note, that these important intermediates, including those containing N₂H₄ and N₂H₂ coordinated Fe complexes provided substantial mechanistic insights on the role of these species in several reactions, such as dehydrogenation reactions.



Scheme 2.1. Various hydrazine coordinated metal complexes – a key step to the activation of hydrazine.

In accordance with the above and several other precedent reports on the formation of metal-hydride complex upon treatment of metal-diazene complex with a base, clearly evidenced a possible pathway for the dehydrogenation of hydrazine.^[23-26] For instance, Chirik *et al.* demonstrated the dehydrogenation of hydrazine upon coordination of hydrazine with molybdenum-terpyridine-phosphine in $[(^{Ph}Tpy)(PPh_2Me)_2Mo(\kappa^2-N_2H_4)]$

complex.^[26] Field *et al.* also investigated the base-induced dehydrogenation of hydrazine *via* a '*coordination induced activation pathway*' over Ru-tetradentate phosphine complexes, where ligand exerted a significant impact on the coordination of hydrazine to Ru (side-on [RuCl(κ^2 -N₂H₄)(κ^3 -PP₃^{ipr})]⁺ or end-on bound hydrazine [RuCl(κ^1 -N₂H₄)(κ^4 -PP₃^{Ph})]⁺) and the reactivity pathway of the resulting complexes.^[27] Apart from homogeneous catalysts there are several reports are available in the literature for the dehydrogenation of hydrazine using heterogeneous catalyst but the exploration of homogeneous complexes for hydrazine activation are particular importance because of several applications.^[28,29] However, anhydrous hydrazine is explosive in nature when exposed to a metal catalyst which makes it difficult to handle safely, whereas hydrous hydrazine (H₂NNH₂·H₂O), which also contains a large amount of hydrogen (7.9 wt %), is much safer and easy to handle.^[29]

Therefore, intrigued by the aforementioned findings, herein, we report the reactivity of iminopyridine based ruthenium-arene complexes with hydrazine and explored the base assisted catalytic dehydrogenation of hydrazine. ¹H NMR and mass spectrometric tools were probed to investigate and evidence the possible interactions between hydrazine and Ru and the generation of any possible organometallic intermediates.

2.2. Experimental Section

2.2.1. Materials. All experiments were carried out using the chemicals of higher purity purchased from Sigma Aldrich, TCI and Alfa Aesar unless otherwise specified, except the ligands and complexes prepared by us. Ru(II)-arene complexes were synthesized according to previous reports using, Ru(II)-arene precursors, $[{(\eta^6-benzene)RuCl_2}_2].^{[30]}$ **2.2.2. Instrumentation.** ¹H NMR (400 MHz) spectra were recorded at 298 K using CDCl₃, D₂O and DMSO-*d*₆ as a solvent on a Bruker Avance 400 spectrometer using tetramethylsilane (TMS) as an external standard. Chemical shifts (in ppm) are relative to the center of the singlet at 7.26 ppm for CDCl₃, 4.75 ppm for D₂O and 2.49 for DMSO-*d*₆ in ¹H NMR respectively. Coupling constant (*J*) values are reported in hertz (Hz), and the splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); br. (broad). ESI-mass spectra (Positive mode) were recorded on a micrOTF-Q II mass spectrometer. UV-visible absorption spectra were recorded on a Carry-60 UV- visible Spectrophotometer using 10 mm quartz cuvettes. GC–TCD analysis was performed on a Shimadzu GCMS-QP2010 Ultra and GC-2010 Plus system in EI (electron impact) mode using RT-Msieve 5A column.

2.2.3. Single-crystal X-ray diffraction Studies. Single crystal X-ray structure studies of complex [Ru]-4, from the suitable crystals grown by slow diffusion of diethyl ether into the methanol solution of complex [Ru]-4 was accomplished on a CCD Agilent Technologies (Oxford Diffraction) SUPERNOVA diffractometer. Crystal data for complexes [**Ru**]-4 was collected at 293(2) by the standard 'phi-omega' scan techniques and were scaled and reduced using CrysAlisPro RED software, using graphitemonochromated Cu K α radiation ($\lambda = 1.5418$ Å) based diffraction. The extracted data was 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 $F^{2,[31]}$ Direct methods determined the positions of all the atoms. All nonhydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2Ueq of their parent atoms. The CCDC number 1535290 contains the supplementary crystallographic data for [Ru]-4. The data is freely available at www.ccdc.cam.ac.uk (or can be procured from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

2.2.4. Catalytic dehydrogenation of hydrazine over ruthenium catalysts. A two neck round bottom flask attached to a condenser and equipped with a magnetic bar was charged with ruthenium catalyst (2.5 mol %), potassium tertiary butaoxide (20 mol%), THF-methanol (5.5 mL, 10:1 v/v). The resulting solution was heated at 80 °C for 15 minute until the colour changes from yellow to dark brown. Now the addition of hydrazine in the solution resulted in a colour change from dark brown to red-brown. The gas released during the reaction was passed through a hydrochloric acid solution (2.0 M) before being measured volumetrically by a water displacement method. Later, the presence of hydrogen in the generated gas was confirmed by GC-TCD.

2.2.5. Mass spectral studies to identify the hydrazine-coordinated ruthenium species [**Ru**]-**3A.** In a separate experiment, complex [**Ru**]-**3** (0.020 mg, 0.05 mmol) and an excess of hydrazine monohydrate (25 μ L, 0.5 mmol) were mixed in 1 mL solution of H₂O. The reaction mixture was stirred at room temperature for 5 minute, where a colour change from yellow to wine-red was observed. An aliquot of the reaction mixture was analysed by mass spectrometry to identify hydrazine coordinated Ru(II)-arene species ([**Ru**]-3A) at m/z 333.0. Similarly, under the catalytic reaction condition, an aliquot from the crude reaction mixture was taken out to analyse by mass spectrometry and similar intermediate species [**Ru**]-3A was observed.

2.2.6. NMR spectral studies to identify the hydrazine-coordinated ruthenium species [**Ru**]-3A. To confirm the identity of a plausible hydrazine coordinated species [**Ru**]-3A by ¹H NMR, complex [**Ru**]-3 (0.010 g) in D₂O (500 μ L) and hydrazine monohydrate (12.5 μ L) were taken into an NMR tube and analysed by ¹H NMR.

2.2.7. Recyclability experiments. For the recyclability experiment after every cycle the 20 mol% potassium tertiary butoxide added along with 1 mmol of hydrazine and gas was produced measured by volumetrically.

2.3. Results and Discussion

2.3.1. Synthesis and X-ray structure of ruthenium-arene complexes. To perform ruthenium catalyzed dehydrogenation of hydrazine, Ru(II)-arene complexes, $[(\eta^6 - \text{benzene})\text{Ru}(\text{N-hydroxy-iminopyridine})\text{CI}]^+$ (**[Ru]-3**), $[(\eta^6 - \text{benzene})\text{Ru}(\text{N-methoxy-iminopyridine})\text{CI}]^+$ (**[Ru]-4**), and $[(\eta^6 - \text{benzene})\text{Ru}(\text{N-isopropyl-iminopyridine})\text{CI}]^+$ (**[Ru]-5**), were synthesized following earlier reports (Figure 2.1a).^[32-34] Recrystallization of **[Ru]-4** gave orange colour crystals suitable for single-crystal structure determination (Figure 2.1b). Complex **[Ru]-4** adopted a *piano-stool* geometry, with bond lengths (Ru-Cl, Ru-N1, and Ru-N2, Ru-Ct) and bond angles (N_{py}-Ru-N_{imine} and N_{py/imine}-Ru-Cl) are in the expected range of the analogous ruthenium complexes provided in the following tables.^[33,34] Moreover, torsion angle N1-C5-C6-N2 (-1.2°) is suggesting the planar arrangement of the bidentate iminopyridine ligand.



Figure 2.1. (a) Ruthenium-arene catalyzed dehydrogenation of hydrazine, (b) X-ray crystal structure of complex [Ru]-4 with 30% ellipsoid probability. Counter ion (Cl⁻) are omitted for sake of clarity.

Table 2.1. Crystal refinement data for complexes [Ku]-4				
Empirical formula	$C_{13}H_{14}Cl_2N_2ORu$			
Formula weight	386.23			
Colour	orange solid			
Crystal size (mm)	0.23 x 0.18 x 0.13			
Crystal system	Triclinic			
Space group	<i>P</i> -1			
T (K)	150(2)			
λ (Å), radiation	1.5418, Cu Kα			
a (Å)	6.3745(2)			
b (Å)	9.7410(5)			
c (Å)	11.3179(5)			
α (°)	88.635(4)			
β (°)	83.291(3)			
γ (°)	82.905(3)			
V (Å ³)	692.59(5)			
Z	2			
D _{calcd.} (mg/m ³)	1.852			
F (000)	384			

Reflections collected / unique	4044/ 2589 [R(int) = 0.0318]
Data / restraints / parameters	2589/0/173
Final R indices [I>2sigma(I)]	R1 = 0.0479, wR2 = 0.1323
R indices (all data)	R1 = 0.0481, wR2 = 0.1327
GOF	1.072

Table 2.2. Bond lengths [Å] for [Ru]-4					

Table 2.3. Bond angles [deg] for [Ru]-4					
N(2)-Ru(1)-N(1)	75.80(14)	C(3)-C(4)-C(5)	118.8(5)		
N(2)-Ru(1)-C(8)	92.48(19)	C(3)-C(4)-H(4)	120.6		

N(1)-Ru(1)-C(8)	118.5(2)	C(5)-C(4)-H(4)	120.6
N(2)-Ru(1)-C(13)	117.4(3)	N(1)-C(5)-C(4)	122.1(4)
N(1)-Ru(1)-C(13)	94.94(18)	N(1)-C(5)-C(6)	115.3(4)
C(8)-Ru(1)-C(13)	38.4(3)	C(4)-C(5)-C(6)	122.5(4)
N(2)-Ru(1)-C(9)	96.05(19)	N(2)-C(6)-C(5)	114.0(4)
N(1)-Ru(1)-C(9)	155.3(3)	N(2)-C(6)-H(6)	123.0
C(8)-Ru(1)-C(9)	37.6(3)	C(5)-C(6)-H(6)	123.0
C(13)-Ru(1)-C(9)	67.8(2)	O(1)-C(7)-H(7A)	109.5
N(2)-Ru(1)-C(10)	122.4(3)	O(1)-C(7)-H(7B)	109.5
N(1)-Ru(1)-C(10)	161.6(3)	H(7A)-C(7)-H(7B)	109.5
C(8)-Ru(1)-C(10)	66.6(2)	O(1)-C(7)-H(7C)	109.5
C(13)-Ru(1)-C(10)	79.0(2)	H(7A)-C(7)-H(7C)	109.5
C(9)-Ru(1)-C(10)	35.9(3)	H(7B)-C(7)-H(7C)	109.5
N(2)-Ru(1)-C(11)	158.9(3)	C(9)-C(8)-C(13)	119.2(5)
N(1)-Ru(1)-C(11)	125.2(3)	C(9)-C(8)-Ru(1)	72.6(3)
C(8)-Ru(1)-C(11)	78.7(2)	C(13)-C(8)-Ru(1)	71.7(3)
C(13)-Ru(1)-C(11)	66.3(3)	C(9)-C(8)-H(8)	120.4
C(9)-Ru(1)-C(11)	65.4(3)	C(13)-C(8)-H(8)	120.4
C(10)-Ru(1)-C(11)	36.5(3)	Ru(1)-C(8)-H(8)	127.3
N(2)-Ru(1)-C(12)	154.2(3)	C(10)-C(9)-C(8)	120.4(6)
N(1)-Ru(1)-C(12)	99.0(2)	C(10)-C(9)-Ru(1)	72.2(3)
C(8)-Ru(1)-C(12)	67.4(3)	C(8)-C(9)-Ru(1)	69.8(3)
C(13)-Ru(1)-C(12)	37.0(3)	C(10)-C(9)-H(9)	119.8
C(9)-Ru(1)-C(12)	78.0(2)	C(8)-C(9)-H(9)	119.8
C(10)-Ru(1)-C(12)	65.7(3)	Ru(1)-C(9)-H(9)	130.9
C(11)-Ru(1)-C(12)	36.1(3)	C(9)-C(10)-C(11)	120.6(6)
N(2)-Ru(1)-Cl(1)	87.97(10)	C(9)-C(10)-Ru(1)	71.9(3)
N(1)-Ru(1)-Cl(1)	84.61(10)	C(11)-C(10)-Ru(1)	71.9(4)
C(8)-Ru(1)-Cl(1)	156.3(2)	C(9)-C(10)-H(10)	119.7
C(13)-Ru(1)-Cl(1)	153.8(3)	C(11)-C(10)-H(10)	119.7
C(9)-Ru(1)-Cl(1)	118.8(2)	Ru(1)-C(10)-H(10)	128.8

C(10)- $Ru(1)$ - $Cl(1)$	93.25(16)	C(12)-C(11)-C(10)	121.0(6)
C(11)-Ru(1)-Cl(1)	92.55(19)	C(12)-C(11)-Ru(1)	72.3(4)
C(12)-Ru(1)-Cl(1)	117.1(3)	C(10)-C(11)-Ru(1)	71.6(3)
N(2)-O(1)-C(7)	116.0(3)	C(12)-C(11)-H(11)	119.5
C(1)-N(1)-C(5)	118.3(4)	C(10)-C(11)-H(11)	119.5
C(1)-N(1)-Ru(1)	126.6(3)	Ru(1)-C(11)-H(11)	129.1
C(5)-N(1)-Ru(1)	115.0(3)	C(11)-C(12)-C(13)	120.4(6)
C(6)-N(2)-O(1)	120.9(4)	C(11)-C(12)-Ru(1)	71.6(4)
C(6)-N(2)-Ru(1)	119.8(3)	C(13)-C(12)-Ru(1)	70.4(3)
O(1)-N(2)-Ru(1)	119.2(3)	C(11)-C(12)-H(12)	119.8
N(1)-C(1)-C(2)	122.6(4)	C(13)-C(12)-H(12)	119.8
N(1)-C(1)-H(1)	118.7	Ru(1)-C(12)-H(12)	130.9
C(2)-C(1)-H(1)	118.7	C(12)-C(13)-C(8)	118.3(6)
C(1)-C(2)-C(3)	119.0(4)	C(12)-C(13)-Ru(1)	72.6(4)
C(1)-C(2)-H(2)	120.5	C(8)-C(13)-Ru(1)	69.9(3)
C(3)-C(2)-H(2)	120.5	C(12)-C(13)-H(13)	120.8
C(4)-C(3)-C(2)	119.1(4)	C(8)-C(13)-H(13)	120.8
C(4)-C(3)-H(3)	120.4	Ru(1)-C(13)-H(13)	128.8
C(2)-C(3)-H(3)	120.4		

2.3.2. Ruthenium catalyzed dehydrogenation of hydrazine. At an outset, dehydrogenation of hydrazine monohydrate (N_2H_4 · H_2O) was attempted over [**Ru**]-3 complex in water by using base (KOH) at 80 °C, where the evolution of gas from the reaction mixture was observed volumetrically (Table 2.4, entry 1). Further, an enhancement in TON and a two-fold increment in TOF were observed by performing the experiment in the presence of KO'Bu instead of KOH (Table 2.4, entry 2). In contrary to water, a significant enhancement in TON was observed for the dehydrogenation reaction performed in ethanol (Table 2.4, entry 3). Notably, an appreciable amount of gas evolution from the hydrazine solution in ethanol was also observed even in the absence of base, but the reaction was observed to be sluggish (Table 2.4, entry 4). Further in the search of a suitable solvent medium, [**Ru**]-3 catalyzed dehydrogenation of hydrazine was

performed in THF-methanol (10:1 v/v) at 80 °C in the presence of different bases KOH, NaOH and KO'Bu, where the highest TON and TOF were achieved with KO'Bu (Table 2.4, entries 5-7). Based on the amount of gas evolved, selectivity for H₂ gas (X) was found to be $0.46.^{[28-29,35]}$ Moreover, the presence of H₂ in the released gas was also analysed by GC-TCD (Figure 2.2).



Figure 2.2. GC-TCD analysis of gas produced for dehydrogenation of Hydrazine monohydrate (1.0 mmol) using KO^tBu (0.020 mmol), cat. **[Ru]-3** (2.5 mol %), THF-methanol (5.5 mL, 10:1 v/v) in Ar gas atmosphere at 80 °C.

Therefore, the overall hydrazine decomposition equation can be expressed which is as follows:

$$N_2H_4 \rightarrow 0.72NH_3 + 0.65N_2 + 0.92H_2$$
 eq. (2.1)

It should be noted that gas evolution was not observed in the absence of the catalyst (Table 2.4, entry 8). Furthermore, we performed control experiment under the optimised reaction condition in the absence of hydrazine. There were no traces of gas release was observed during the experiment, inferred that under the optimized reaction condition methanol dehydrogenation does not occurred (Table 2.4, entry 9). In addition,

analysis of reaction mixture obtained after the reaction does not show any other products, such as CO, CO₂, formate, acetal of formaldehyde, N-methylation of hydrazine. Moreover, using methanol is advantageous, as it increases the solubility of the studied complex in the solution. The above observations inferred that the observed gas release in the presence of hydrazine was due to catalytic dehydrogenation of hydrazine only, and that the presence of both catalysts and hydrazine is important for gas generation. Notably, in THF-methanol, an enhancement of three- and two-fold, respectively in the TOF was achieved compared to the catalytic dehydrogenation reaction performed in water and ethanol. Further performing the catalytic reaction at lower temperature (< 80 °C), TON and TOF of the catalytic dehydrogenation of hydrazine was significantly decreased (Table 2.4, entries 10-14). The apparent activation energy (Ea = 13.98 kcal mol⁻¹) for the catalytic dehydrogenation of hydrazine over [**Ru**]-**3** catalyst, as obtained by an Arrhenius plot (Figure 2.3), is in good agreement with other literature findings.^[35]



Figure 2.3. Linear fitting of log $[TOF(h^{-1})]$ vs 1/T for calculating activation energy from the graph (value for activation energy $E_a = 13.98 \text{ kcal} \cdot \text{mol}^{-1}$).

Entry	Catalyst	Solvent	Base	T (°C)/ t (min.)	Volume of gas (mL)	TON	TOF (h ⁻¹)
1	[Ru]-3	Water	КОН	80/53	8.0	-	-
2	[Ru]-3	Water	KO ^t Bu	80/36	11.0	3.5	5.8
3	[Ru]-3	Ethanol	KO ^t Bu	80/70	35.0	33.0	28.0
4	[Ru]-3	Ethanol	-	80/154	25.5	21.0	8.0
5	[Ru]-3	THF- methanol	KO'Bu	80/40	38.5	37.0	58.5
6	[Ru]-3	THF- methanol	КОН	80/57	36.5	35.0	37.0
7	[Ru]-3	THF- methanol	NaOH	80/75	32.0	29.0	23.0
8	-	THF- methanol	KO ^t Bu	80/120	-	-	-
9*	[Ru]-3	THF- methanol	KO ^t Bu	80/120	-	-	-
10	[Ru]-3	THF- methanol	KO ^t Bu	30/61	8	-	-
11	[Ru]-3	THF- methanol	KOʻBu	40/66	9.5	1.64	1.49
12	[Ru]-3	THF- methanol	KO ^t Bu	50/111	16.0	9.5	5.18
13	[Ru]-3	THF- methanol	KO ^t Bu	60/48	38.5	37.0	46.0
14	[Ru]-3	THF- methanol	KO'Bu	70/55	38.5	37.0	40.0
15	[Ru]-4	THF- methanol	KO ^t Bu	80/65	36.5	35.0	32.0

Table 2.4. Optimization of the reaction condition for the catalytic dehydrogenation of hydrazine over [Ru]-3 catalyst^a

16	[Ru]-5	THF-	KO ^t Bu	80/66	33.5	31.0	28.0
		methanol					

^{*a*}Reaction condition: N₂H₄·H₂O (1.0 mmol), base (20 mol %), catalyst (2.5 mol %), solvent (5.5 mL). THF-methanol (10:1 v/v). *Without hydrazine. TON = $n(H_2)/n(cat)$. TOF = $n(H_2)/\{n(cat)\cdot time\}$.

Further to evaluate the effect of substitutes at N_{imine} the studied ruthenium complexes [**Ru**]-3 – [**Ru**]-5, catalytic dehydrogenation of hydrazine was performed under the optimized reaction condition (hydrazine (1.0 mmol), catalyst (2.5 mol%) and KO'Bu (2.5 mol%) in THF-methanol (5.5 mL, 10:1 v/v) at 80 °C) (Table 4.1, entries 15-16, Figure 2.4a). Results inferred that among all the studied complexes having different steric and electronic properties, the (η^6 -benzene)Ru complex [**Ru**]-3 having N_{imine}-OH group outperformed and showed higher TOF (h⁻¹) over those having N_{imine}-OMe and N_{imine}-^{*i*}Pr substitution (Figure 2.4b), which can be attributed to the plausible involvement of the hydroxyl group in interaction with hydrazine coordinated with Ru and hence facilitating improved Ru to hydrazine interactions.^[36]



Figure 2.4. (*a-b*) Comparative catalytic efficacy (*a*) amount of gas released vs time and (*b*) TOF (h^{-1}) for the dehydrogenation of hydrazine monohydrate over ruthenium-arene catalysts. Reaction condition: hydrazine monohydrate (1.0 mmol) over various ruthenium catalysts (2.5 mol%) in the presence of KO^tBu (20 mol%) in THF-methanol (5.5 mL, 10:1 v/v) at 80 °C.

Notably, the outperforming **[Ru]-3** catalyst exhibited remarkably high recyclability up to six consecutive catalytic runs for the dehydrogenation of hydrazine under the optimized reaction condition (Figure 2.5).



Figure 2.5. Recyclability experiments for the catalytic dehydrogenation of hydrazine monohydrate over [*Ru*]-3 catalyst. Reaction condition: hydrazine monohydrate (1.0 mmol) over various ruthenium catalysts (2.5 mol%) in the presence of KO^tBu (20 mol%) in THF-methanol (5.5 mL, 10:1 v/v) at 80 °C.

Moreover, no remarkable change in the catalytic efficacy was observed during the reaction performed in the presence of Hg, suggesting the homogenous nature of the active form of the catalyst. To further investigate the role of Ru-catalyst in the catalytic dehydrogenation of hydrazine, several controlled and catalytic experiments were performed to identify the crucial organometallic intermediates which might be generated during the reaction due to the possible interactions between Ru-catalyst and hydrazine. In this context, control experiment performed using [**Ru**]-**3** catalyst in D₂O with an excess of hydrazine added, showed a peak at m/z 333.0 in mass spectra corresponding to the hydrazine coordinated Ru-species, [**Ru**]-**3A**. Coordination of hydrazine to ruthenium was further evidenced by ¹H NMR, where an upfield shifting in the peaks corresponding to iminopyridine ligand in [**Ru**]-**3** complex was observed (Figure 2.6).



Figure 2.6. ¹H NMR and mass spectral experiments evidenced the formation of a hydrazine coordinated Ru-species [Ru]-3A during the treatment of [Ru]-3 complex with an excess of N_2H_4 · H_2O in D_2O .

Further, an analogous behaviour in ¹H NMR was also observed when an excess of hydrazine was added in a solution of **[Ru]-3** complex in CD₃OD, and the corresponding mass data also showed an m/z value of 333.0 corresponding to the **[Ru]-3A** species. Moreover, mass spectral analysis of the reaction aliquot during the catalytic reaction condition also evidenced the formation of a hydrazine coordinated ruthenium species.

The catalysts [**Ru-3**] having N–OH substitution outperformed over [**Ru**]-4 and [**Ru**]-5 having N-OMe and N-^{*i*}Pr substitutions respectively, possibly because of the presence of protic group N–OH. In the presence of a base, the protic group N-OH deprotonated and thereby stabilised hydrazine coordinated monocationic ruthenium species [(η^6 –benzene)Ru(N-hydroxy-iminopyridine)N₂H₄]⁺ ([**Ru**]-3A), which was well characterised by mass (m/z 333.0) and NMR (Figure 2.6). Analogously, [**Ru**]-4 and [**Ru**]-5 complexes also showed the formation of corresponding hydrazine coordinated

ruthenium species and due to lack of protic group these ruthenium hydrazine species are dicataionc species **[Ru]-4A** (m/z 174.0) and **[Ru]-5A** (m/z 180.0) (Figure 2.7).



Figure 2.7. Mass spectral analysis for the hydrazine coordinated ruthenium species, [Ru]-3A, [Ru]-4A and [Ru]-5A, obtained by the addition of hydrazine to an aqueous solution of the corresponding complexes [Ru]-3, [Ru]-4 and [Ru]-5, respectively.

Moreover, the addition of hydrazine to a pale-yellow solution of [**Ru**]-3 in water resulted in an intense wine-red solution, suggested the formation of ruthenium-hydrazine species. The significant shift in the ¹H NMR spectra and the presence of a mass peak at m/z 333.0 corresponds to the [**Ru**]-3A species clearly evidenced the formation of ruthenium-hydrazine species. Further addition of an excess of dil. HCl in the above wine-red solution immediately resulted in the regeneration of pale yellow solution, thus straight forward evidenced the recovery of [**Ru**]-3, which was also supported by the reappearance of m/z peak at 337.0 (in the mass spectral analysis of the pale yellow solution) corresponding to the [**Ru**]-3 catalyst (Figure 2.8).



Figure 2.8. Mass spectral experiments showing the generation of a hydrazine coordinated ruthenium species ([Ru]-3A), which upon addition of a dilute solution of HCl regenerated the original ruthenium precursor ([Ru]-3).

Therefore, mass and ¹H NMR spectral results clearly evidenced the coordination of hydrazine to Ru center is a crucial step for the activation of hydrazine, which further transformed to Ru-H species via a well-established diazene intermediate. The temperature dependent ¹H NMR and corresponding mass analysis under the catalytic reaction condition also inferred the appearance of a ruthenium-hydrazine species with the increase in the reaction temperature (30-60 °C) (Figures 2.9 and 2.10).



Figure 2.9. Variable temperature ¹H NMR spectral experiments evidenced the formation of a hydrazine coordinated Ru-species during the treatment of **[Ru]-3** complex with an excess of N_2H_4 · H_2O in D_2O [Reaction condition: **[Ru]-3** (0.010 g) in D_2O (500 µL) and hydrazine monohydrate (12.5 µL)].



Figure 2.10. Mass analysis (at 30 °C – 60 °C) evidenced the formation of a hydrazine coordinated Ru-species [**Ru**]-3A during the treatment of [**Ru**]-3 complex with an excess of N_2H_4 · H_2O in H_2O . Along with the hydrazine coordinated ruthenium species ([**Ru**]-3A m/z 333.0), a water coordinated species [([$(\eta^6-C_6H_6)Ru(\kappa^2-L)(OH_2)$]⁺) at m/z 319.0 was also observed. All the observed mass spectra of various species identified were matching well with corresponding simulated patterns.

Analogous to hydrazine coordinated ruthenium species, phenylhydrazine also coordinated with the ruthenium metal, and such phenylhydrazine coordinated ruthenium species $[(\eta^6-\text{benzene})\text{Ru}(\text{N-hydroxy-iminopyridine})\{\text{N}_2\text{H}_3(\text{C}_6\text{H}_5)\}]^+$ (m/z 409.0) were analysed by ¹H NMR and mass. Whilst we were unable to observe the Ru-H and Ru-diazene intermediates during our investigations, presumably because of the lower stability of these species in the reaction medium, such species are expected to be involved in the dehydrogenation of hydrazine. Notably, X-ray structure of analogous ruthenium-diazene species $[(\eta^5-\text{Cp}*)\text{Ru}(\kappa^2-\text{HN}=\text{NH})\{\text{P}(\text{OEt})_3\}_2]^+$ was previously reported by Albertin *et al.*.^[4a] Also, Hillhouse *et al.* demonstrated the formation of metal-diazene and metal-hydride species from rhenium-hydrazine complexes.^[5] In this regard, treating 4-

methoxystyrene with hydrazine over **[Ru]-3** catalyst resulted in the formation of 1-ethyl-4-metoxy benzene in water-ethanol at 80 °C, suggesting the possible involvement of ruthenium-hydride species during the transfer hydrogenation via ruthenium-catalyzed activation of hydrazine.

In a recent report, Milstein *et al.* also demonstrated the crucial role of a hydrazinecoordinated Ru intermediate species $[(^{t}BuPNP)Ru(CO)(H)(N_{2}H_{4})]^{+}$ during a Ru-pincer complex catalyzed dehydrogenative coupling of alcohols with hydrazine with the release of H₂ gas.^[25] Similar activation of hydrazine, by the weakening of N-H bond of hydrazine upon coordination of hydrazine with molybdenum-terpyridine-phosphine has also been demonstrated.^[26] It has been observed that such metal hydrazine complexation lower the nitrogen-hydrogen bond dissociation free energy (34.6 kcal mol⁻¹) and hence enable H_2 evolution and hydrogenation of styrene.^[26] Analogous Ru-hydride and Ru-diazene intermediates were also observed during dehydrogenation of hydrazine over Rutetradentate phosphine complexes via a 'coordination induced activation pathway'.^[27] Based on the above findings and spectral data (mass and ¹H NMR) we proposed a plausible general reaction pathway for the hydrazine activation with ruthenium complexes shown in the Scheme 2.2. Moreover, the formation of hydrazine coordinated ruthenium species for all the complexes [Ru]-3, [Ru]-4 and [Ru]-5, suggesting that these complexes probably follow an analogous hydrazine dehydrogenation pathway, as illustrated in Scheme 2.2.



Scheme 2.2. Plausible reaction pathway for the dehydrogenation of hydrazine over the studied ruthenium catalysts.

2.4. Conclusions

We demonstrated catalytic dehydrogenation of hydrazine over ruthenium-arene catalysts containing N-substituted iminopyridine ligands at 80 °C in ethanol and THFmethanol in the presence of a base. Our findings suggested a ligand-accelerated dehydrogenation of hydrazine, where the ruthenium complex **[Ru]-3** containing Nhydroxyiminopyridine ligand outperformed over others. The evolved gas was analysed by GC-TCD. Our experimental findings along with ¹H NMR and mass studies evidenced the presence of a hydrazine coordinated ruthenium species. These observations suggesting a possible coordination assisted activation of hydrazine N-H bond over ruthenium catalyst to release hydrogen gas *via* a Ru-hydride species. Further efforts to explore more into the mechanistic aspect of the ruthenium catalyzed dehydrogenation of hydrazine are underway.

Note: The content of this chapter is published as Awasthi et al., Chem. Asian J., 2018, 13, 1424 -1431 (DOI: 10.1002/asia.201800315) and reproduced here with the permission of Willey-VCH.

2.5. References

- Barney B. M., Lukoyanov D., Yang T.-C., Dean D. R., Hoffman B. M., Seefeldt L. C. (2006), A methyldiazene (HN=N-CH3)-derived species bound to the nitrogenase active-site FeMo cofactor: Implications for mechanism, *Proc. Natl. Acad. Sci. USA.*, 103, 17113 (DOI: 10.1073/pnas.0602130103).
- Barney B. M., Lee H.-I., Santos P. C. D., Hoffman B. M., Dean D. R., Seefeldt L. C. (2006), Breaking the N₂ triple bond: insights into the nitrogenase mechanism, *Dalton Trans.*, 2277-2284 (DOI: 10.1039/B517633F).
- Albertin G., Antoniutti S., Botter A., Castro J. (2015), Hydrolysis of Coordinated Diazoalkanes To Yield Side-On 1,2-Diazene Derivatives, *Inorg. Chem.*, 54, 2091-2093 (DOI: 10.1021/ic502963n).
- 4. (a) Albertin G., Antoniutti S., Bortoluzzi M., Botter A., Castro J. (2016), Pentamethylcyclopentadienyl Half-Sandwich Diazoalkane Complexes of Ruthenium: Preparation and Reactivity, *Inorg. Chem.*, 55, 5592-5602 (DOI: 10.1021/acs.inorgchem.6b00671); (b) Ashworth T. V., Singleton E., Hough J. J. (1977), Cationic ruthenium(II) systems. Part 1. The preparation and reactivity of diene(hydrazine)ruthenium(II) cations, and the formation of aminobonded hydrazone complexes, *J. Chem. Soc., Dalton Trans.*, 1809-1815 (DOI: 10.1039/DT9770001809).
- Cbeng T.-Y., Peters J. C., Hillhouse G. L. (1994), Reactions of coordinated diazene in rhenium and tungsten complexes. Deprotonation of ligated NH:NH and subsequent hydrogen-migration to carbonyl ligands to give metal formyls, *J. Am. Chem. Soc.*, 116, 204-207 (DOI: 10.1021/ja00080a023).
- 6. (a) Wu B., Gramigna K. M., Bezpalko M. W., Foxman B. M., Thomas C. M. (2015), Heterobimetallic Ti/Co Complexes That Promote Catalytic N–N Bond Cleavage, *Inorg. Chem.*, 54, 10909-10917 (DOI: 10.1021/acs.inorgchem.5b01962); (b) Jia H.-P., Goure E., Monfort X. S., Castelbou J. L., Chow C., Taoufik M., Eisenstein O., Quadrelli E. A.

(2015), Hydrazine N–N Bond Cleavage over Silica-Supported Tantalum-Hydrides, *Inorg. Chem.*, 54, 11648-11659 (DOI: 10.1021/acs.inorgchem.5b01541).

- Saouma C. T., Moore C. E., Rheingold A. L., Peters J. C. (2011), A Five-Coordinate Phosphino/Acetate Iron(II) Scaffold That Binds N₂, N₂H₂, N₂H₄, and NH₃ in the Sixth Site, *Inorg. Chem.*, 50, 11285-11287 (DOI: 10.1021/ic2016066).
- Schwartz K. R., Mann K. R. (2011), Optical Response of a Cyclometalated Iridium(III) Hydrazino Complex to Carbon Dioxide: Generation of a Strongly Luminescent Iridium(III) Carbazate, *Inorg. Chem.*, 50, 12477-12485 (DOI: 10.1021/ic201286k).
- Crossland J. L., Zakharov L. N., Tyler D. R. (2007), Synthesis and Characterization of an Iron(II) η²-Hydrazine Complex, *Inorg. Chem.*, 46, 10476-10478 (DOI: 10.1021/ic702007r).
- Field L. D., Li H. L., Magill A. M. (2009), Base-Mediated Conversion of Hydrazine to Diazene and Dinitrogen at an Iron Center, *Inorg. Chem.*, 48, 5-7 (DOI: 10.1021/ic801856q).
- Crossland J. L., Balesdent C. G., Tyler D. R. (2009), Intermediates in the reduction of N₂ to NH₃: synthesis of iron η² hydrazido(1–) and diazene complexes, *Dalton Trans.*, 4420-4422 (DOI: 10.1039/B902524C).
- Sellmann D., Friedrich H., Knoch F., Moll M. (1993), Transition Metal Complexes with Sulfur Ligands, C*. Unexpectedly Facile Formation of Diazene Complexes and a New Type of Diastereomerism: [μ-N₂H₂{Fe(PPr₃)('S₄')}₂] and Analogous Complexes with [FeS]-Centers. ('S₄'²⁻ = 1,2-Bis(2-mercaptophenylthio)ethane(2-)), *Z. Naturforsch.*, 48b, 76-88 (DOI: 10.1515/znb-1994-0115).
- Sellman D., Hennige A. (1997), Direct Proof of *trans*-Diazene in Solution by Trapping and Isolation of the Trapping Products, *Angew. Chem. In. Ed. Engl.*, 36, 276-278 (DOI: 10.1002/anie.199702761).
- Crossland J. L., Balesdent C. G., Tyler D. R. (2012), Coordination of a Complete Series of N₂ Reduction Intermediates (N₂H₂, N₂H₄, and NH₃) to

an Iron Phosphine Scaffold, *Inorg. Chem.*, 51, 439-445 (DOI: 10.1021/ic201873a).

- Umehara K., Kuwata S., Ikariya T. (2013), N–N Bond Cleavage of Hydrazines with a Multiproton-Responsive Pincer-Type Iron Complex, J. Am. Chem. Soc., 135, 6754-6757 (DOI: 10.1021/ja3122944).
- Albertin G., Antoniutti S., Bordignon E., Menegazzo F. (2000), Synthesis and reactivity of hydrazine complexes of iridium(III), *J. Chem. Soc. Dalton Trans.*, 1181-1189 (DOI: 10.1039/A909404K).
- Albertin G., Antoniutti S., Bortoluzzi M., Castro J. (2018), Half-sandwich hydrazine complexes of iridium: Preparation and reactivity, *Inorg. Chim. Acta*. 470, 139-148 (DOI: 10.1016/j.ica.2017.04.016).
- Seino H., Saito A., Kajitani H., Mizobe Y. (2008), Properties and Reactivities of the Hydrido Ligands in Iridium Sulfido Clusters Relevant to Activation and Production of H₂, *Organometallics*, 27, 1275-1289 (DOI: 10.1021/om701207j).
- 19. (a) Kawano M., Hoshino C., Matsumoto K. (1992), Synthesis, properties, and crystal structure of a novel .mu.-hydrazine-bridged mixed-valence ruthenium(II,III) complex stabilized by hydrazine hydrogen bonds, [RuCl(TMP)2]2(.mu.-Cl)(.mu.-N2H4)(.mu.-S2) (TMP trimethyl = phosphite), Inorg. Chem., 31, 5158-5159 (DOI: 10.1021/ic00051a002); (b) Chatt J., Leigh G. J., Paske R. J. (1969), Reactions of complexes of ruthenium and osmium halides with ammonia, amines, and hydrazine, J. Chem. Soc. A, 854-859 (DOI: 10.1039/J19690000854); (c) Ashworth T. V., Singleton E., Hough J. J. (1977), Cationic ruthenium(II) systems. Part 1. The preparation and reactivity of diene(hydrazine)ruthenium(II) cations, and the formation of aminobonded hydrazone complexes, J. Chem. Soc., Dalton Trans., 1809-1815 (DOI: 10.1039/DT9770001809); (d) Albertin G., Antoniutti S., Bortoluzzi M., Castro-Fojo J., Garcia-Fontan S. (2004), Ruthenium Tris(pyrazolyl)borate Diazo Complexes: Preparation of Aryldiazenido, Aryldiazene, and Hydrazine Derivatives, Inorg. Chem., 43, 4511-4522 (DOI: doi.org/10.1021/ic0497275); (e) Zhang Q.-F., Zheng H.,

Wong W.-Y., Wong W.-T., Leung W.-H. (2000), Ruthenium(II) Ammine and Hydrazine Complexes with $[N(Ph_2PQ)_2]^-$ (Q = S, Se) Ligands, *Inorg. Chem.*, 39, 5255-5264 (DOI: 10.1021/ic000291c).

- Albertin G., Antoniutti S., Bacchi A., Bordignon E., Dolcetti P. M., Pelizzi G. (1997), Preparation of mono- and bis-(hydrazine) complexes of ruthenium(II), *J. Chem. Soc., Dalton Trans.*, 4435-4444 (DOI: 10.1039/A702712E).
- 21. Albertin G., Antoniutti S., Castro J. (2012), Preparation and reactivity of half-sandwich hydrazine complexes of ruthenium and osmium, *J. Organomet. Chem.*, 697, 6-14 (DOI: 10.1016/j.jorganchem.2011.09.011).
- Albertin G., Antoniutti S., Bonaldo L., Botter A., Castro J. (2013) Azo Complexes of Osmium(II): Preparation and Reactivity of Organic Azide and Hydrazine Derivatives, *Inorg. Chem.*, 52, 2870-2879 (DOI: 10.1021/ic302483e).
- 23. Cheng T.-Y., Peters J. C., Hillhouse G. L. (1994), Reactions of coordinated diazene in rhenium and tungsten complexes. Deprotonation of ligated NH:NH and subsequent hydrogen-migration to carbonyl ligands to give metal formyls, *J. Am. Chem. Soc.*, 116, 204-207 (DOI: 10.1021/ja00080a023).
- 24. Albertin G., Antoniutti S., Bordignon E., Menegazzo F. (2000), Synthesis and reactivity of hydrazine complexes of iridium(III), *J. Chem. Soc., Dalton Trans.*, 1181-1189 (DOI: 10.1039/A909404K).
- Bauer J. O., Leitus G., Ben-David Y., Milstein D. (2016), Direct Synthesis of Symmetrical Azines from Alcohols and Hydrazine Catalyzed by a Ruthenium Pincer Complex: Effect of Hydrogen Bonding, ACS Catal., 6, 8415-8419 (DOI: 10.1021/acscatal.6b02946).
- 26. Bezdek M. J., Guo S., Chirik P. J. (2016), Coordination-induced weakening of ammonia, water, and hydrazine X–H bonds in a molybdenum complex, *Science*, 354, 730-733 (DOI: 10.1126/science.aag0246).
- Field L. D., Li H. L., Dalgarno S. J., McIntosh R. D., (2013), Base-Induced Dehydrogenation of Ruthenium Hydrazine Complexes, *Inorg. Chem.*, 52, 1570-1583 (DOI: 10.1021/ic302449n).
- (a) Lee S., Fan C., Wu T., Anderson S. L. (2005), Hydrazine Decomposition over Ir_n/Al₂O₃ Model Catalysts Prepared by Size-Selected Cluster Deposition, *J. Phys. Chem. B*, 109, 381-388 (DOI: 10.1021/jp046086q); (b) Song J., Ran R., Shao Z. (2010), Hydrazine as efficient fuel for low-temperature SOFC through ex-situ catalytic decomposition with high selectivity toward hydrogen, *Int. J. Hydrogen Energy*, 35, 7919-7924 (DOI: 10.1016/j.ijhydene.2010.05.094); (c) Cao N., Yang L., Du C., Su J., Luo W., Cheng G. (2014), Highly efficient dehydrogenation of hydrazine over graphene supported flower-like Ni–Pt nanoclusters at room temperature, *J. Mater. Chem. A*, 2, 14344-14347 (DOI: 10.1039/C4TA02964J).
- (a) Singh S. K., Zhang X.-B., Xu Q. (2009), Room-Temperature Hydrogen Generation from Hydrous Hydrazine for Chemical Hydrogen Storage, *J. Am. Chem. Soc.*, 131, 9894-9895 (DOI: 10.1021/ja903869y); (b) Singh A. K., Yadav M., Aranishi K., Xu Q. (2012), Temperature-induced selectivity enhancement in hydrogen generation from Rh–Ni nanoparticle-catalyzed decomposition of hydrous hydrazine, *Int. J. Hydrogen Energy*, 37, 18915-18919 (DOI: 10.1016/j.ijhydene.2012.09.104).
- 30. (a) Bennett M. A., Huang T., Matheson T. W., Smith A. K. (1982), (η⁶-Hexamethylbenzene)Ruthenium Complexes, *Inorg. Synth.*, 21, 74-78 (DOI: 10.1002/9780470132524.ch16); (b) Zelonka R. A., Baird M. C. (1972), Benzene Complexes of Ruthenium(II), *Can. J. Chem.*, 50, 3063-3072 (DOI: 10.1139/v72-486).
- Sheldrick G. M. (2008), A short history of SHELX, *Acta Crystallogr.*, *Sect.* A, 64, 112-122 (DOI: 10.1107/S0108767307043930).
- 32. Ribeiro T. S., Prates A., Alves S. R., Oliveira-Silva J. J., Riehl C. A. S., Figueroa Villar J. D. (2012), The effect of neutral oximes on the reactivation of human acetylcholinesterase inhibited with paraoxon, J.

Braz. Chem. Soc., 23, 1216-1225 (DOI: 10.1590/S0103-50532012000700004).

- 33. (a) Gichumbi J. M., Friedrich H. B., Omondi B. (2016), Synthesis and characterization of half-sandwich ruthenium(II) complexes with N-alkyl pyridyl-imine ligands and their application in transfer hydrogenation of ketones, *Transition Met. Chem.*, 41, 867-877 (DOI: 10.1007/s11243-016-0089-5); (b) Gichumbi J. M., Friedrich H. B., Omondi B. (2016), Synthesis and characterization of piano-stool ruthenium complexes with *N,N'*-pyridine imine bidentate ligands and their application in styrene oxidation, *J. Organomet. Chem.*, 808, 87-96 (DOI: 10.1016/j.jorganchem.2016.02.015).
- Tyagi D., Rai R. K., Mobin S. M., Singh S. K. (2017), N-Substituted Iminopyridine Arene–Ruthenium Complexes for the Regioselective Catalytic Hydration of Terminal Alkynes, *Asian J. Org. Chem.*, 6, 1647-1658 (DOI: 10.1002/ajoc.201700396).
- 35. Zhao P., Cao N., Su J., Luo W., Cheng G. (2015), NiIr Nanoparticles Immobilized on the Pores of MIL-101 as Highly Efficient Catalyst toward Hydrogen Generation from Hydrous Hydrazine, ACS Sustainable Chem. Eng., 3, 1086-1093 (DOI: 10.1021/acssuschemeng.5b00009).
- Nieto I., Livings M. S., Sacci J. B., Reuther L. E., Zeller M., Papish E. T. (2011), Transfer Hydrogenation in Water via a Ruthenium Catalyst with OH Groups near the Metal Center on a bipy Scaffold, *Organometallics*, 30, 6339-6342 (DOI: 10.1021/om200638p).

Chapter 3

Hydrogen Production from Aromatic Alcohols over Ruthenium Catalyst

3.1. Introduction

Synthesis of carboxylic acids by oxidation of primary alcohols using a metal-based^[1-5,6(a)] oxidant is well established, but need either toxic strong oxidants or TEMPO with stoichiometric amount of sodium hypochlorite making it a less atom efficient process.^[6(b)] Alternatively, carboxylic acid can also be produced by alcohol dehydrogenation process.^[7-11] Alcohol dehydrogenation process is an atom economic process by generating hydrogen gas (a potential fuel) along with the desired carboxylic acid, and thus provide an opportunity to explore alcohols as potential hydrogen storage compounds. Interestingly, compared to the well explored oxidative syntheses of carboxylic acids using alcohols, catalytic dehydrogenation of alcohols (such as benzyl alcohol) are explored only in last decade using $Ir^{[8]}$, $Rh^{[9]}$ and $Ru^{[10-13]}$ based metal complexes.



Scheme 3.1. Literature reported active catalysts for the dehydrogenation of alcohol to carboxylic acid.

Moreover, the alcohol dehydrogenation reactions are explored either in presence of high base concentration in water or in organic solvents at higher temperature (≥ 110

°C) (Scheme 3.1).^[7-13] Yamaguchi et al. reported an Cp*Ir(III)-based dicationic complex having strongly electron-donating N-heterocyclic carbene (NHC) ligand and α hydroxypyridine moiety based bidentate ligand.^[8(a)] They have shown that α hydroxypyridine moiety plays an important role for the activation of secondary and primary alcohols to dehydrogenate in ketones and acids, respectively, in neutral water at 140 °C.^[8(a)] Recently, another Ir(III) complexes [Ir(2-PyCH₂(C₄H₅N₂))(COD)]OTf and [Ir(2-PyCH₂PBu²t)(COD)]OTf having NHC (2-((3-methyl-2,3-dihydro-1H-imidazol-1yl)methyl)pyridine) and N,P (2-((di-tert-butylphosphino)methyl) pyridine) ligands respectively, reported by Williams et al. for the catalytic acceptorless dehydrogenation of benzyl alcohol to benzoic acid (yield 98% in 40 h) in the presence of a base (KOH) in toluene at 120 °C.^[8(b)] Furthermore, the Rh-based complexes containing diolefin amido tridentate ligands are also explored for the catalytic dehydrogenation of alcohol using such as O₂/DMSO, 1-hexene acceptors and cyclohexanone at room temperature.^[9(a),9(b),9(c)] Recently, acceptorless dehydrogenation of alcohols using Rubased metal complexes are also explored using the tridentate pincer type ligand (PNN^[10(a)] and PNP^[10(b)]), N-heterocyclic carbene (NHC)^[10(c)] ligand and bidentate N,Ntype^[11] ligand. Milstein *et al.* reported that in the Ru-complex having a PNN-type tridentate pincer ligand, the PNN ligand undergoes dearomatized to form the catalytic active species for the dehydration of alcohols in an alkaline aqueous solution under reflux condition for 18 h.^[10(a)] Bera et al. explored Ru-hydride catalyst having N,N-type bidentate ligands for the catalytic dehydrogenation of alcohols in aqueous medium albeit in highly basic condition (18.5 mmol NaOH) at 110 °C.^[11] The only half-sandwich Ru-NHC complex $[(p-cymene)RuCl_2(IiPr)]$ (where IiPr = 1,3-diisopropyl-2,3-dihydro-1*H*imidazole) is reported by Madsen et al. for the catalytic alcohol dehydrogenation reaction in the presence of additive (PCy₃ and HBF₄) at 110 °C in toluene for 6h.^[12] Peng *et al.* investigated dehydrogenation of neat alcohol using Ru-complexes $[Ru(L)X(CH_3CN)_2]^+$ (L = 2,6-bis(benzimidazol-2-yl)) pyridine, X = Cl, OTf having N,N,N tridentate ligands, albeit at high temperature (150 °C) and in the presence of CsOH.^[13] Apart from noble metal based catalysts, recently, Liu et al. investigated Mn(I) based complexes having PNP-type pincer ligands for the catalytic acceptorless dehydrogenation of primary alcohols to carboxylic acids at 160 °C.^[14]

Therefore, it is evident that most of the Ru-based catalysts explored so far, for alcohol dehydrogenation requires either highly basic condition, additives or higher temperature. In recent past, we have also developed several arene-Ru(II)-based catalysts for the acceptorless dehydrogenation of hydrazine hydrate and formic acid, and found that ligands have a crucial role in tuning the catalytic activity.^[15] Herein, we synthesized several arene-Ru(II) complexes containing bidentate pyridylamine based ligands and explored for the acceptorless dehydrogenation of aromatic and aliphatic alcohols to carboxylic acids in toluene. Moreover, molecular structures of [**Ru**]-6, [**Ru**]-7 and [**Ru**]-10 are also authenticated by X-ray crystallography. Further, we probed mass investigation to elucidate the mechanistic pathway by identifying several crucial catalytic intermediate species under the catalytic and controlled reaction conditions.

3.2. Experimental Section

3.2.1. Materials. All experiments are carried out using the chemicals of high purity purchased from Sigma Aldrich, TCI and Alfa Aesar, unless otherwise specified, Ligand L4 is purchased from Alfa Aesar. The precursors $[\{(\eta^6-C_6H_6)RuCl_2\}_2]$, $[\{(\eta^6-C_{10}H_{14})RuCl_2\}_2]$ and $[\{(\eta^6-C_6Me_6)RuCl_2\}_2]$ are synthesized following the previous reported method.^[16]

3.2.2. Instrumentation. ¹H NMR (300, 400 and 500 MHz), ¹³C NMR (100 MHz) and ³¹P NMR (161.97 MHz) spectra are recorded at 298 K using DMSO- d_6 or CDCl₃ as the solvent on a Bruker Avance 300, 400 and 500 spectrometer. Tetramethylsilane (TMS) is used as an external standard and the chemical shifts in ppm are reported relative to the centre of the singlet at 7.26 ppm for CDCl₃, 2.49 ppm for DMSO- d_6 and multiplet at 3.30 ppm for CD₃OD in ¹H NMR, and to the centre of the triplet at 77.0 ppm for CDCl₃ and 39.50 ppm for DMSO- d_6 in ¹³C NMR. Suitable single crystals of complexes [**Ru**]-**6**, [**Ru**]-**7** and [**Ru**]-**10** subjected to single-crystal X-ray structural studies using Agilent Technologies Supernova CCD system. Coupling constant (*J*) values are reported in hertz (Hz), and the splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); br. (broad). ESI (positive mode), and high-resolution mass spectra (HRMS) are recorded on a micro TF-Q II mass spectrometer. GC-TCD analysis was performed on a Shimadzu GCMS-QP2010 Ultra and GC-2010 Plus system in EI (electron impact) mode using RT-Msieve 5A column.

3.2.3. Single-crystal X-ray diffraction studies. Single crystal was obtained by diffusion of diethyl ether into methanol solution of the complex [Ru]-6, [Ru]-7, and [Ru]-10 are performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data are collected at 150(2) K using graphite-monochromated Mo K α radiation ($\lambda \alpha = 0.71073$ A). The strategy for the data collection evaluated using the CrysAlisPro CCD software. The data are collected using the standard 'phi-omega' scans techniques, and are scaled and reduced using CrysAlisPro RED software. The structures are solved by direct methods using SHELXS-97, and refined using full matrix leastsquares with SHELXL-97, refining on F2.^[17] The positions of all the atoms are obtained by direct methods. All non-hydrogen atoms are refined anisotropically. The remaining hydrogen atoms are placed in geometrically constrained positions, and refined with isotropic temperature factors, generally 1.2 Ueq of their parent atoms. The crystal and refinement data are summarized in Tables 2.1. Selected bond lengths and bond angles are summarized in Tables 2.2 and 2.3. CCDC deposition numbers of the complex [Ru]-6 1872164, **[Ru]-7** is 1865341 and for **[Ru]-10** is 1872151. These data are freely available at www.ccdc.cam.ac.uk (or can be procured from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

3.2.4. General Procedure for the catalytic alcohol dehydrogenation reaction over pyridylamine-based (η^6 -arene)Ru(II) complexes. Typically, alcohol (1.0 mmol), catalyst (0.02 mmol), and KOH (1.1 mmol) are mixed in dry toluene (2 mL) in two necked round bottom flask equipped with a condenser and argon balloon. The reaction mixture is stirred at 110 °C for 6 h on an oil bath. After the desired reaction duration, solvent is removed under reduced pressure and the residue obtained is dissolved in deionized water (20 mL) and is acidified with 1 M HCl. Acidified solution is extracted with ethyl acetate (3 × 10 mL). The organic phase separated, dried over Na₂SO₄, and the organic solvent is removed under reduced pressure and remaining residue is dissolved in methanol, filtered and dried to yield the pure carboxylate salt.

3.2.5. Dehydrogenation of benzaldehyde



Benzaldehyde (1.0 mmol), **[Ru]-6** (2 mol%), and KOH (1.1 mmol) are mixed in dry toluene (2 mL) in two necked test tube equipped with a condenser. The reaction mixture is stirred at 110 °C on an oil bath under Argon atmosphere. The gas evolved is measured by water displacement method. After the reaction was over, the products are analyzed by ¹H NMR spectroscopy. The selectivity for benzoic acid and benzyl alcohol are respectively, 92% (89% isolated yield) and 8%.

3.2.6. General procedure for the synthesis of $(\eta^6-C_6H_6)Ru(II)$ complexes [Ru]-6 – [Ru]-10 and $(\eta^6-C_{10}H_{14})Ru(II)$ complexes [Ru]-11 – [Ru]-15. Complexes [Ru]-6 – [Ru]-15 are synthesized by treating *N*-substituted pyridylamine (L4 – L8) (0.59 mmol) with the respective precursor [{ $(\eta^6-arene)RuCl_2$ }_2](0.29 mmol) in acetonitrile (10 mL) at room temperature for 1 h under argon atmosphere. Later, the solvent is completely dried and dissolved in 5 mL ethanol, and then excess of NH₄PF₆ is added. The resulting solution is stirred for 30 minutes at room temperature. Adding 10 mL water in the reaction mixture resulted in the precipitation of the desired complexes, which is washed with water (2 × 5 mL) and diethyl ether (3 × 10 mL), and finally dried in air.

(a) Synthesis of $[(\eta^6-C_6H_6)RuCl(\kappa^2-(N,N)-2-(aminomethyl)-pyridine)]PF_6$ ([Ru]-6). Complex [Ru]-6 is synthesized following the above general procedure, by using 2-(aminomethyl)pyridine (L4) (0.59 mmol) and $[\{(\eta^6-C_6H_6)RuCl_2\}_2]$ (0.29 mmol). Yellow solid is obtained, yield 65%. [Ru]-6: ¹H NMR (400 MHz, DMSO-*d*_6): δ (ppm) = 9.21 (d, 1H, *J* = 4 Hz), 7.95 (t, 1H, *J* = 8 Hz), 7.55 (d, 1H, *J* = 8 Hz), 7.50 (t, 1H, *J*_1 = 4Hz, *J*_2 = 8Hz), 5.90 (s, 6H), 4.14 (t, 2H, *J*_1 = 8Hz, *J*_2 = 4Hz). ¹³C NMR (100 MHz, DMSO-*d*_6): δ (ppm) =161.49, 154.80, 139.19, 124.66, 121.16, 84.53, 52.10. ³¹P NMR (161.97 MHz, DMSO-*d*_6): δ (ppm) = -144.18 (sep, PF_6). MS (ESI): *m*/*z* calculated for [(η^6 -C₆H₆)RuCl(κ^2 -L4)]⁺ (L4 = 2-(aminomethyl) pyridine) [M]⁺ 322.9883, found 322.9986.

(b) Synthesis of $[(\eta^6-C_6H_6)RuCl(\kappa^2-(N,N)-N-(pyridin-2-ylmethyl)propan-2-amine)]PF_6$ ([Ru]-7). Complex [Ru]-7 is synthesized following the above general

procedure, by using *N*-(pyridin-2-ylmethyl)propan-2-amine (**L5**) (0.59 mmol) and [{(η^6 -C₆H₆)RuCl₂}₂] (0.29 mmol). Pale yellow solid is obtained, yield 68%. [**Ru**]-7: ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 9.06 (d, 1H, *J* = 4Hz), 7.99 (d, 1H, *J* = 8Hz), 7.63 (d, 1H, *J* = 8Hz), 7.54 (t, 1H, *J*₁ = 8Hz, *J*₂ = 4Hz), 5.93 (s, 6H), 4.33 (d, 2H, *J* = 8Hz), 3.92 - 3.87 (m, 1H), 1.41(d, 2H, *J* = 4Hz), 1.28 (d, 2H, *J* = 4Hz). ¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) =160.48, 154.72, 139.13, 124.93, 121.58, 85.28, 58.71, 56.62, 23.66, 20.14. ³¹P NMR (161.97 MHz, DMSO-*d*₆): δ (ppm) = -144.18 (sep, PF₆). MS (ESI): *m/z* calculated for [(η^6 -C₆H₆)RuCl(κ^2 -L5)]⁺ (L5 = *N*-(pyridin-2-ylmethyl)propan-2-amine)) [M]⁺ 365.0354, found 365.0436.

(c) Synthesis of $[(\eta^6-C_6H_6)RuCl(\kappa^2-(N,N)-N-(pyridin-2-ylmethyl)propan-1-amine)]PF_6 ([Ru]-8). Complex [Ru]-8 is synthesized following the above general procedure, by using N-(pyridin-2-ylmethyl)propan-1-amine (L6) (0.59 mmol) and [{(<math>\eta^6-C_6H_6$)RuCl_2}] (0.29 mmol). Pale yellow solid is obtained, yield 64%. [Ru]-8: ¹H NMR (400 MHz, DMSO-*d*_6): δ (ppm) = 9.08 (d, 1H, *J* = 4Hz), 8.01 (t, 1H, *J* = 8Hz), 7.61 (d, 1H, *J* = 8Hz), 7.54 (t, 1H, *J*_1 = 8Hz, *J*_2 = 4Hz), 5.93 (s, 6H), 4.38-4.26 (m, 2H), 3.52 (br, 1H), 3.16 (br, 1H), 1.78 (br, 1H), 1.6 (br, 1H), 0.96 (t, *J* = 8Hz). ¹³C NMR (100 MHz, DMSO-*d*_6): δ (ppm) = 159.70, 154.92, 139.17, 124.97, 121.43, 85.00, 62.01, 59.08, 21.77, 11.33. ³¹P NMR (161.97 MHz, DMSO-*d*_6): δ (ppm) = -144.18 (sep, PF_6). MS (ESI): *m*/*z* calculated for [(η^6 -C₆H₆)RuCl(κ^2 -L6)]⁺ (L6 =*N*-(pyridin-2-ylmethyl)propan-1-amine) [M]⁺ 365.0354, found 365.0449.

(d) Synthesis of $[(\eta^6-C_6H_6)RuCl(\kappa^2-(N,N)-N-(pyridin-2-ylmethyl)butan-1-amine)]PF_6 ([Ru]-9). Complex [Ru]-9 is synthesized following the above general procedure, by using N-(pyridin-2-ylmethyl)butan-1-amine (L7) (0.59 mmol) and [{(<math>\eta^6-C_6H_6$)RuCl_2}]_2] (0.29 mmol). Pale yellow solid is obtained, yield 71%. [Ru]-9: ¹H NMR (400 MHz, DMSO-*d*_6): δ (ppm) = 9.08 (d, 1H, *J* = 4Hz), 7.99 (t, 1H, *J* = 8Hz), 7.61 (d, 1H, *J* = 8Hz), 7.55 (t, 1H, *J*_1 = 4Hz, *J*_2 = 8Hz), 5.93 (s, 6H), 4.44 - 4.27 (m, 2H), 3.56 - 3.53 (m, 1H), 3.23 - 3.19 (m, 1H), 1.75 - 1.62 (m, 2H), 1.39 (t, 2H, *J*_1 = 4Hz, *J*_2 = 8Hz), 0.94 (t, 1H, *J*_1 = 8Hz, *J*_2 = 4Hz). ¹³C NMR (100 MHz, DMSO-*d*_6): δ (ppm) = 159.71, 154.93, 139.21, 125.03, 121.49, 85.04, 62.09, 57.19, 30.45, 19.17, 13.86. ³¹P NMR (161.97 MHz, DMSO-*d*_6): δ (ppm) = -144.17 (sep, PF_6). MS (ESI): *m/z* calculated for

 $[(\eta^6-C_6H_6)RuCl(\kappa^2-L7)]^+$ (L7 = *N*-(pyridin-2-ylmethyl)butan-1-amine) [M]⁺ 379.0510, found 379.0701.

(e) Synthesis of $[(\eta 6-C_6H_6)RuCl(\kappa^2-(N,N)-3-methyl-N-(pyridin-2-ylmethyl)butan-1-amine)]PF_6 ([Ru]-10). Complex [Ru]-10 is synthesized following the above general procedure, by using 3-methyl-$ *N* $-(pyridin-2-ylmethyl)butan-1-amine (L8) (0.59 mmol) and <math>[\{(\eta^6-C_6H_6)RuCl_2\}_2](0.29 mmol).$ Pale yellow solid is obtained, yield 62%. [Ru]-10: ¹H NMR (400 MHz, DMSO-*d*_6): δ (ppm) = 9.08 (d, 1H, *J* = 4Hz), 7.99 (t, 1H, *J* = 8Hz), 7.61 (d, 1H, *J* = 8Hz), 7.55 (t, 1H, *J*_1 = 4Hz, *J*_2 = 8Hz), 5.93 (s, 6H), 4.45-4.37 (m, 1H), 4.34-4.28 (m, 2H), 3.60-3.52 (m, 1H), 3.25-3.22 (m, 1H), 1.73-1.62 (m, 2H), 1.59-1.50 (m, 1H) 0.95 (t, 6H, *J* = 8Hz). ¹³C NMR (100 MHz, DMSO-*d*_6): δ (ppm) = 159.67, 154.92, 139.20, 125.01, 121.47, 85.03, 62.13, 55.86, 37.12, 30.69, 25.77, 22.53. ³¹P NMR (161.97 MHz, DMSO-*d*_6): δ (ppm) = -144.18 (sep, PF_6). MS (ESI): *m*/*z* calculated for [(η^6 -C₆H₆)RuCl(κ^2 -L8)]⁺ (L8 = 3-methyl-*N*-(pyridin-2-ylmethyl)butan-1-amine) [M]⁺ 393.0607, found 393.0860.

(f) Synthesis of $[(\eta^6-C_{10}H_{14})RuCl(\kappa^2-(N,N)-2-(aminomethyl)-pyridine)]PF_6$ ([Ru]-11). Complex [Ru]-11 is synthesized following the above general procedure, by using 2-(aminomethyl)pyridine (L4) (0.59 mmol) and $[\{(\eta^6-C_{10}H_{14})RuCl_2\}_2]$ (0.29 mmol). Yellow solid is obtained, yield 60%. [Ru]-11: ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 9.12 (d, 1H, *J* = 4 Hz), 7.96 (t, 1H, *J* = 8 Hz), 7.55 (d, 1H, *J* = 8 Hz), 7.51 (d, 1H, *J* = 4Hz), 5.91 (d, 1H, *J* = 4Hz), 5.85 (d, 1H, *J* = 4Hz), 5.73 (d, 1H, *J* = 8Hz), 5.67 (d, 1H, *J* = 8Hz), 4.21-4.10 (m, 2H), 2.72 (br, 1H), 1.9[5 (S, 3H), 1.12 (d, 6H, *J* = 8Hz). ¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) =161.22, 154.54, 139.13, 124.86, 121.14, 103.04, 98.01, 84.80, 83.05, 82.26, 82.70, 52.03, 30.22. 22.31, 21.42, 17.63. ³¹P NMR (161.97 MHz, DMSO-*d*₆): δ (ppm) = -144.18 (sep, PF₆). MS (ESI): *m/z* calculated for [(η^6 -C₁₀H₁₄)RuCl(κ^2 -L4)]⁺ (L4 = 2-(aminomethyl) pyridine) [M]⁺ 379.0510, found 379.0459.

(g) Synthesis of $[(\eta^6-C_{10}H_{14})RuCl(\kappa^2-(N,N)-N-(pyridin-2-ylmethyl)propan-2-amine)]PF_6$ ([Ru]-12). Complex [Ru]-12 is synthesized following the above general procedure, by using *N*-(pyridin-2-ylmethyl)propan-2-amine (L5) (0.59 mmol) and [{(η^6 -C₁₀H₁₄)RuCl₂}] (0.29 mmol). Yellow solid is obtained, yield 63%. [Ru]-12: ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 9.00 (d, 1H, *J* = 4 Hz), 8.00 (t, 1H, *J* = 8 Hz), 7.65 (d,

1H, J = 8 Hz), 7.56 (t, 1H, $J_1 = 8$ Hz, $J_2 = 4$ Hz), 5.91 (d, 1H, J = 4Hz), 5.82 (s, 2H), 5.71 (d, 1H, J = 8Hz), 4.32-4.25 (m, 2H), 3.84 (br, 1H), 2.09 (m, 1H), 1.98 (S, 3H), 1.38 (d, 3H, J = 4Hz), 1.31 (d, 3H, J = 4Hz), 1.09 (d, 3H, J = 8Hz), 1.00 (d, 3H, J = 8Hz). ¹³C NMR (100 MHz, DMSO- d_6): δ (ppm) = 159.97, 154.86, 139.17, 125.09, 121.79, 105.28, 96.56, 86.19, 84.92, 82.41, 80.38, 58.60, 56.18, 30.45, 23.42, 21.75, 21.64, 20.26, 17.38. ³¹P NMR (161.97 MHz, DMSO- d_6): δ (ppm) = -144.19 (sep, PF₆). MS (ESI): m/z calculated for [(η^6 -C₁₀H₁₄)RuCl(κ^2 -L5)]⁺ (L5 = *N*-(pyridin-2-ylmethyl)propan-2-amine) [M]⁺ 421.0981, found 421.0909.

 $[(\eta^6-C_{10}H_{14})RuCl(\kappa^2-(N,N)-N-(pyridin-2-ylmethyl)propan-1-$ (h) **Synthesis** of amine)]PF₆ ([Ru]-13). Complex [Ru]-13 is synthesized following the above general procedure, by using N-(pyridin-2-ylmethyl)propan-1-amine (L6) (0.59 mmol) and [{(η^6 - $C_{10}H_{14}$)RuCl₂]₂] (0.29 mmol). Pale Yellow solid is obtained, yield 72%. [**Ru**]-13: ¹H NMR (400 MHz, DMSO- d_6): δ (ppm) = 9.03 (d, 1H, J = 4 Hz), 8.00 (t, 1H, J = 8 Hz), 7.62 (d, 1H, J = 4 Hz), 7.56 (t, 1H, $J_1 = 8$ Hz, $J_2 = 4$ Hz), 5.86 (t, 2H, J = 4Hz), 5.83 (d, 1H, J = 4 Hz), 5.75 (d, 1H, J = 4Hz), 4.35-4.32 (m, 2H), 3.43-3.28 (br, 2H), 2.61 (br, 3H), 1.90 (s, 2H), 1.74-1.63 (m, 2H), 1.10-1.04 (dd, 6H, J = 8Hz), 0.96 (t, 3H, J = 8Hz). ¹³C NMR (100 MHz, DMSO- d_6): δ (ppm) =159.45, 154.88, 139.22, 125.13, 121.62, 105.14, 96.20, 85.54, 83.84, 82.64, 81.60, 61.12, 59.00, 30.53, 22.15, 21.14, 17.40, 11.25. ³¹P NMR (161.97 MHz, DMSO- d_6): δ (ppm) = -144.19 (sep, PF₆). MS (ESI): m/z calculated for $[(\eta^6-C_{10}H_{14})RuCl(\kappa^2-L6)]^+$ (L6 = N-(pyridin-2-ylmethyl)propan-1-amine) [M]⁺ 421.0981, found 421.0919.

(i) Synthesis of $[(\eta^6-C_{10}H_{14})RuCl(\kappa^2-(N,N)-N-(pyridin-2-ylmethyl)butan-1-amine)]PF_6 ([Ru]-14). Complex [Ru]-14 is synthesized following the above general procedure, by using N-(pyridin-2-ylmethyl)butan-1-amine (L7) (0.59 mmol) and <math>[(\eta^6-C_{10}H_{14})RuCl_2]_2$ (0.29 mmol). Yellow solid is obtained, yield 60%. [Ru]-14: ¹H NMR (400 MHz, DMSO-d_6): δ (ppm) = 9.03 (d, 1H, J = 8 Hz), 8.00 (t, 1H, J = 8 Hz), 7.62 (d, 1H, J = 8 Hz), 7.56 (t, 1H, J = 8 Hz), 5.88 (d, 2H, J = 8Hz), 5.83 (d, 1H, J = 8 Hz), 5.75 (d, 1H, J = 8Hz), 4.32 (m, 2H), 3.47-3.30 (br, 2H), 1.89 (s, 3H), 1.67 (m, 2H), 1.40 (m, 2H), 1.08 (t, 6H, J = 8Hz), 0.94 (t, 3H, J = 8Hz). ¹³C NMR (100 MHz, DMSO-d_6): δ (ppm) = 159.43, 154.86, 139.20, 125.12, 121.62, 105.23, 95.94, 85.71, 83.83, 82.40, 81.57, 61.21, 56.99, 30.55, 30.10, 22.14, 21.08, 19.61, 17.33, 13.78. ³¹P NMR (161.97)

MHz, DMSO-*d*₆): δ (ppm) = -144.19 (sep, PF₆). MS (ESI): *m*/*z* calculated for [(η^{6} -C₁₀H₁₄)RuCl(κ^{2} -L7)]⁺ (L7 = N-(pyridin-2-ylmethyl)butan-1-amine) [M]⁺ 435.1138, found 435.1072.

(j) Synthesis of $[(\eta^6-C_{10}H_{14})RuCl(\kappa^2-(N,N)-3-methyl-N-(pyridin-2-ylmethyl)butan-$ 1-amine)] PF₆ ([Ru]-15). Complex [Ru]-15 is synthesized following the above generalprocedure, by using 3-methyl-*N*-(pyridin-2-ylmethyl)butan-1-amine (L8) (0.59 mmol) $and [{(<math>\eta^6$ -C₁₀H₁₄)RuCl₂}₂] (0.29 mmol). Yellow solid is obtained, yield 63%. [Ru]-15: ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 9.02 (d, 1H, *J* = 4 Hz), 8.00 (t, 1H, *J* = 8 Hz), 7.62 (d, 1H, *J* = 8 Hz), 7.56 (t, 1H, *J* = 8Hz), 5.88 (t, 2H, *J* = 4Hz), 5.82 (d, 1H, *J* = 4 Hz), 5.75 (d, 1H, *J* = 4Hz), 4.33 (m, 2H), 3.50 (br, 1H), 3.30 (br, 1H), 2.61 (m, 2H), 1.89 (s, 3H), 1.70-1.54 (m, 4H), 1.08 (t, 6H, *J* = 8 Hz), 0.94 (t, 6H, *J* = 8Hz). ¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) =159.41, 154.85, 139.20, 125.12, 121.62, 105.31, 95.77, 85.84, 83.79, 82.37, 81.62, 61.29, 55.65, 36.77, 30.57, 25.60, 22.58, 22.37, 22.18, 21.02, 17.30. ³¹P NMR (161.97 MHz, DMSO-*d*₆): δ (ppm) = -144.19 (sep, PF₆). MS (ESI): *m/z* calculated for [(η^6 -C₁₀H₁₄)RuCl(κ^2 -L8)]⁺ (L8 = 3-methyl-*N*-(pyridin-2-ylmethyl)butan-1-amine) [M]⁺ 449.1294, found 449.1229.

3.3. Results and Discussion

3.3.1. Synthesis and characterization of arene-Ru complexes. *N*-substituted pyridylamine ligands, *N*-(pyridin-2-ylmethyl)propan-2-amine (L5), *N*-(pyridin-2-ylmethyl)propan-1-amine (L6), *N*-(pyridin-2-ylmethyl)butan-1-amine (L7) and 3-methyl-*N*-(pyridin-2-ylmethyl)butan-1-amine (L8) are synthesized following literature reports,^[16] except 2-(aminomethyl)-pyridine (L4) which is commercially available. The ligands L4 – L8 are treated with [{(η^6 -arene)RuCl₂}] in acetonitrile under argon atmosphere to obtain the monometallic (η^6 -arene)Ru(II) complexes [Ru]-6 – [Ru]-15 in good yields (Scheme 3.2). All the synthesized complexes displayed high stability in air and moisture, and are highly soluble in acetone. The spectro-analytical analysis of the synthesized complexes corroborated well with proposed structures. X-ray suitable crystal of [Ru]-6, [Ru]-7, and [Ru]-10 are grown using slow diffusion of diethyl ether in methanol/acetone (9:1 v/v) solution of the complexes. ESI-mass of all the synthesized complexes displayed prominent mass peak corresponding to the cationic mononuclear

species with general formula $[(\eta^6-C_6H_6)RuCl(\kappa^2-L)]^+$ and $[(\eta^6-C_{10}H_{14})RuCl(\kappa^2-L)]^+$, where L is pyridylamine ligands L4 – L8.



R^{*}= -H, -CH(CH₃)₂, -CH₂CH₂CH₃, -CH₂CH₂CH₂CH₃, -CH₂CH₂CH(CH₃)₂



Scheme 3.2. Synthesis of complexes [Ru]-6 – [Ru]-15.

In the ¹H NMR spectra of the complexes [**Ru**]-6 – [**Ru**]-15, the ortho C–H of pyridylamine resonated at downfield region 9.21 – 8.99 ppm in comparison to those of free ligands (L4 – L8) (8.50 – 8.29 ppm),^[18] which is consistent with the coordination of pyridylamine ligands with the (η^6 -arene)Ru(II) moiety.^[19] On introducing an alkyl substituent at the aminic nitrogen (N_{amine}), a significant upfield shift is observed for the ortho C-H proton of pyridine ring from 9.21 ppm in [**Ru**]-6 to 9.06 – 9.08 ppm in [**Ru**]-7 – [**Ru**]-10. Moreover, the Ru(II)-coordinated η^6 -C₆H₆ ring protons resonated as a singlet in the range of 5.90 – 5.93 ppm, suggesting the equivalence of all the carbon of the benzene ring. Analogous to (η^6 -C₆H₆)Ru complexes, [(η^6 -C₁₀H₁₄)RuCl(κ^2 -L)]⁺ complexes [**Ru**]-11 – [**Ru**]-15 also exhibited an upfield shift in the resonance of ortho C-H of pyridine ring from 9.12 ppm in [**Ru**]-11 to 8.99 – 9.03 ppm in [**Ru**]-12 – [**Ru**]-15, with the introducing of alkyl substituents at the aminic nitrogen (N_{amine}). The Ru(II) coordination with the *p*-cymene is also confirmed by the presence of peaks for the aromatic proton in the range of 5.88 – 5.73 ppm, methyl proton in the range of 1.95 – 1.89 ppm, and methyl protons of isopropyl group, respectively in the range

of 2.72 - 2.07 ppm and 0.98 - 1.38 ppm for [**Ru**]-11 – [**Ru**]-15. In ³¹P NMR the counter anion PF₆⁻ for the complexes [**Ru**]-6 – [**Ru**]-15 resonated at –144 ppm.^[18] Further, molecular structures of the complexes [**Ru**]-6, [**Ru**]-7 and [**Ru**]-10 are also authenticated by X-ray crystallography (Figure 3.1 and Table 3.1). The important bond lengths, bond angles and torsion angles are shown in Tables 3.2, 3.3 and 3.4.



Figure 3.1. X-ray crystal structures of the complex (a) [*Ru*]-6, (b) [*Ru*]-7 and (c) [*Ru*]-10 with 30% ellipsoid probability. Counter anions are omitted for the sake of clarity.

	[Ru]-6	[Ru]-7	[Ru]-10
empirical formula	$C_{12}H_{14}ClF_6N_2PRu$	$C_{15}H_{20}Cl_2N_2Ru$	C ₁₇ H ₂₄ ClF ₆ N ₂ PRu
formula wt	467.74	400.30	537.87
colour	yellow block	red block	golden yellow
			block
crystal size (mm)	0.23 x 0.17 x 0.13	0.26 x 0.22 x	0.23 x 0.18
		0.18	x 0.13
crystal system	Monoclinic	monoclinic	Triclinic
space group	<i>P</i> -21/n	<i>P</i> -21/c	<i>P</i> -1
<i>T</i> (K)	293(2)	293(2)	293(2)
λ (Å), radiation	0.71073, Mo Kα	0.71073, Mo	0.71073, Mo Kα
		Κα	
a (Å)	8.9736(8)	11.3850(2)	7.5042(3)
b (Å)	14.2623(12)	10.4973(3)	12.0015(5)
c (Å)	12.1118(11)	13.8742(4)	13.2949(5)
α (°)	90.00	90	115.000(4)
β (°)	95.125(7)	96.421(2)	94.297(3)
γ (°)	90.00	90	92.318(3)
$V(Å^3)$	1543.9(2)	1647.73(7)	1078.68(8)
Ζ	4	4	2
$\rho_{calcd.}$ (g/cm ³)	2.012	1.606	1.656
F (000)	920.0	800.0	540
no. of data collected /	15913 / 3789	17041 / 3965	9410 / 4982
unique data	[R(int) = 0.0820]	[R(int) =	[R(int) = 0.0357]
		0.0377]	
data / restraints /	3789/0/208	3965/0/183	4982 / 0 / 257
parameters			
final R indices	R1 = 0.0484, wR2	R1 = 0.0275,	R1 = 0.0445,
[I>2sigma(I)]	= 0.1354	wR2 = 0.0631	wR2 = 0.1157

<i>Table 3.1.</i>	Crystal	structure	refinement	data fe	or [Ru]]-6 ,	[Ru]-7 ,	and [Ru]]-10
-------------------	---------	-----------	------------	---------	-----------------	--------------	-----------------	-------------------	------

R indices (all data)	R1 = 0.0581, wR2	R1 = 0.0237,	R1 = 0.0522,
	= 0.1232	wR2 = 0.0643	wR2 = 0.1268
goodness of fit	1.039	0.973	0.919

Table 3.2. Important bond parameters of the complexes [Ru]-6, [Ru]-7, and [Ru]-10

	[Ru]-6	[Ru]-7	[Ru]-10
Bond length (Å)			
Ru-C _t	1.675	1.684	1.680
Ru-C _{avg}	2.186	2.193	2.168
$Ru-N_{py}$	2.083(4)	2.1033(17)	2.090(3)
Ru-N _{amine}	2.123(4)	2.1926(18)	2.138(3)
Ru-Cl	2.3923(12)	2.4308(6)	2.4007(10)
Namine-C ₆	1.478(6)	1.504(3)	1.490(5)
Bond Angles (°)			
N _{py} -Ru-N _{amine}	76.19(14)	77.98(7)	76.42(12)
N _{py} -Ru-Cl	84.23(11)	84.77(5)	85.61(9)
Namine-Ru-Cl	84.19(11)	93.48(5)	84.28(9)
N_{py} -Ru- C_t	131.64	130.28	129.06
Namine-Ru-Ct	132.12	128.61	133.52
Cl-Ru-Ct	129.34	126.14	129.29
Torsion Angles (°)			
Namine-C5-C6-Npy	28.5(5)	27.4(3)	27.2(5)

Table 3.3. Selected bond lengths for complexes [Ru]-6, [Ru]-7 and [Ru]-10

Bond Length(Å)	[Ru]-6	[Ru]-7	[Ru]-10
Ru1 N1	2.083(4)	2.1033(17)	2.090(3)
Ru1 N2	2.123(4)	2.1926(18)	2.138(3)
Ru1 C7	2.182(6)	-	-
Ru1 C8	2.175(5)	-	-
Ru1 C9	2.192(5)	-	-
Ru1 C10	2.191(5)	2.178(3)	-

Ru1 C11	2.202(6)	2.159(3)	-
Ru1 C12	2.173(5)	2.197(3)	2.172(5)
Ru1 C13	-	2.201(3)	2.168(5)
Ru1 C14	-	2.218(3)	2.139(4)
Ru1 C15	-	2.202(3)	2.159(5)
Ru1 C16	-	-	2.188(5)
Ru1 C17	-	-	2.182(5)
Ru1 Cl1	2.3923(12)	2.4308(6)	2.4007(10)
N1 C5	1.345(6)	1.356(3)	1.348(5)
N1 C1	1.343(6)	1.358(3)	1.340(5)
N2 C6	1.478(6)	1.504(3)	1.490(5
N2 C7	-	1.513(3)	1.479(5)
C1 C2	1.358(8)	1.388(4)	1.387(7)
C2 C3	1.393(8)	1.387(4)	1.365(8)
C3 C4	1.376(7)	1.390(4)	1.373(8)
C4 C5	1.379(7)	1.397(3)	1.372(6)
C5 C6	1.495(7)	1.502(3)	1.484(6)
C7 C8	1.430(9)	1.536(4)	1.506(5)
C8 C9	1.391(8)	-	1.539(6)
C9 C10	1.405(8)	-	1.520(7)
C10 C11	1.380(8)	1.438(6)	-
C11 C12	1.437(10)	1.416(5)	-
C12 C13	-	1.390(5)	1.363(10)
C13 C14	-	1.396(4)	1.406(10)
C14 C15	-	1.362(5)	1.359(9)
C15 C16		-	1.378(8)
C16 C17	-	-	1.354(9)
C7 C12	1.387(10)	-	-
C15 C10	-	1.426(6)	-
C7 C9	-	1.541(4)	-
C9 C11	-	-	1.540(8)

Bond Angles (deg)	[Ru]-6	[Ru]-7	[Ru]-10
N1-Ru-N2	76.19(14)	77.98(7)	76.42(12)
N1-Ru-Cl	84.23(11)	84.77(5)	85.61(9)
N2-Ru-Cl	84.19(11)	93.48(5)	84.28(9)
N2-Ru-Ct	131.64	130.28	129.06
N2-Ru-Ct	132.12	128.61	133.52
Cl-Ru-Ct	129.34	126.14	129.29
Ru-N1-C5	117.2(3)	115.59(14)	116.5(3)
Ru-N2-C6	109.0(3)	104.55(13)	106.9(2)
Ru-N1-C1	124.7(3)	125.12(15)	124.2(3)
N1-C5-C6	114.4(4)	115.19(18)	114.3(3)
N2-C6-C5	108.0(4)	111.32(18)	109.5(3)
C6-N2 –C7	-	116.07(18)	111.6(3)
C8-C7-C9	-	109.4(2)	-
C8-C7-N2	-	107.73(19)	112.2(3)
C9-C7-N2	-	113.2(2)	-
C9-C8-C7	-	-	113.1(4)
C8-C9-C10	-	-	110.3(5)
C8-C9-C11	-	-	109.8(5)
C10-C9-C11	-	-	110.1(4)

Table 3.4. Selected bond Angles for complexes [Ru]-6, [Ru]-7 and [Ru]-10

_

_

Complexes **[Ru]-6** and **[Ru]-7** crystallized in monoclinic crystal system with *P*-21/n and *P*-21/c space group respectively, whereas complex **[Ru]-10** crystallized in a triclinic crystal system with *P*-1 space group. Consistent with the NMR and mass results crystal structure of the complexes **[Ru]-6**, **[Ru]-7** and **[Ru]-10** confirmed the piano stool type geometry of these complexes, where the η^6 -C₆H₆ ring placed at the apex of the stool and the legs of the stool are occupied by the κ^2 -pyridylamine and chloro ligands. The bond angle from the benzene ring centroid (C_t) to each of the ligands are more than 120°,

which is consisted with the formation of piano stool geometries for these complexes. For complex [Ru]-6 the Ct-Ru-N_{py}, Ct-Ru-N_{amine} and Ct-Ru-Cl are found to be 131.64°, 132.12° and 129.34°, respectively.^[18,19] Similarly for [Ru]-7 and [Ru]-10, the respective bond angles are more than 120° suggesting the piano stool type geometry for these complexes also. Centroid (C_t) to Ru distance for [Ru]-7 (1.684 Å) and [Ru]-10 (1.680 Å) are higher than, those of [**Ru**]-6 (1.675), $^{[19(b)]}$ inferred the possible steric effect due to the alkyl substituents at the aminic nitrogen. The Ru-Cl bond lengths for [Ru]-6, [Ru]-7 and [Ru]-10 are 2.3923, 2.4308 and 2.4007Å, respectively.^[19] The Ru-N_{py} bond lengths $(2.0830 - 2.1033\text{\AA})$ are shorter than the Ru-N_{amine} bond lengths $(2.1230 - 2.1926\text{\AA})$, which is consistent with the sp² hybridized N_{py} and sp³ hybridized N_{amine} . Moreover, the Ru–N_{py} and Ru–N_{amine} bond lengths in [Ru]-6 are shorter than those in [Ru]-7 and [Ru]-10, presumably due to the strong coordination of L4 with the Ru center. The Ru-Namine bond lengths in [Ru]-6, [Ru]-7 and [Ru]-10 are 2.1230, 2.1926 and 2.1380 respectively, inferred that upon introducing the alkyl group at Namine, the Ru-Namine bond length also increases. The unusually higher Ru-N_{amine} bond length in [Ru]-7 is a typical nature of iso-propyl substituted nitrogen atoms.^[20]

3.3.2. Catalytic dehydrogenation of alcohols to carboxylic acids. Catalytic performance of the synthesized complexes [**Ru**]-6 – [**Ru**]-15 along with their precursors for the acceptorless alcohol dehydrogenation to carboxylic acid/carboxylate is evaluated using benzyl alcohol (**1a**) as a model substrate at 110 °C in toluene using 1.1 equiv. of KOH (Table 3.5 and 3.6). Typically, dehydrogenation of alcohols to carboxylic acids involves two steps, firstly alcohols converted to aldehyde with the release of one equivalent of H₂ gas and finally diols, generated from aldehyde with the aid of a base, further dehydrogenated to carboxylic acid with the release of an another equivalent of H₂ gas. Therefore, with the release of two equivalents of hydrogen gas and the quantitative yield of carboxylic acid, alcohol dehydrogenation is considered as an atom economic reaction. Preliminary investigation inferred that among the arene-ruthenium precursors, [{(η^6 -C₆H₆)RuCl₂}₂], [{(η^6 -C₁₀H₁₄)RuCl₂}₂] and [{(η^6 -C₆Me₆)RuCl₂}₂], the [{(η^6 -C₆H₆)RuCl₂}₂] exhibited higher conversion for benzyl alcohol dehydrogenation at 110 °C in toluene (Table 3.6). Therefore, further exploration for catalytic benzyl alcohol dehydrogenation is performed using [(η^6 -C₆H₆)RuCl(κ^2 -L)]⁺ ([**Ru**]-6 – [**Ru**]-10).

Moreover, the catalytic performance of analogous $[(\eta^6-C_{10}H_{14})RuCl(\kappa^2-L)]^+$ (**[Ru]-11** – **[Ru]-15**) are also explored. Our results inferred that among the complexes **[Ru]-6** – **[Ru]-15** explored for benzyl alcohol dehydrogenation, $[(\eta^6-C_6H_6)RuCl(\kappa^2-L)]^+$ (**[Ru]-6** – **[Ru]-10**) exhibited higher catalytic activity, wherein **[Ru]-6** outperformed over others with 94% yield (>99% conversion) of benzoic acid with quantitative yield of H₂ gas in 6h (Table 3.5, entries 1-5, and Table 3.6).

OH 1a	1. Catalyst (2) KOH (1.1 ec 110 °C, 6h, 2. 1M HCI	mol%), quiv.) Ar►	OH O 1b
Entry	Catalyst	temperature (°C)	isolated yield (1b) (%)
1.	[Ru]-6	110	94 $(1.9)^b$
2.	[Ru]-7	110	88 $(1.6)^b$
3.	[Ru]-8	110	90
4.	[Ru]-9	110	91
5.	[Ru]-10	110	92
6.	[Ru]-6	100	72
7.	[Ru]-6	90	39

Table 3.5. Screening of the catalyst [Ru]-6 – [Ru]-10 for benzyl alcohol dehydrogenation^a

^{*a*}Reaction condition: **1a** (1 mmol), catalyst (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 6

h. ^bH₂ gas released (in mmol)

Table 3.6. Screening of the catalyst for benzyl alcohol dehydrogenation^a



3.	[{(n ⁶ -C ₆ Me ₆)RuCl ₂ } ₂]	110	22
4.	[Ru]-6	110	>99
5.	[Ru]-11	110	76
6.	[Ru]-12	110	73
7.	[Ru]-13	110	77
8.	[Ru]-14	110	72
9.	[Ru]-15	110	63

^{*a*}Reaction condition: **1a** (1 mmol), catalyst (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 6 h. ^{*b*}conv. determined using ¹H NMR.

The amount of gas produced during the reaction is measured by water displacement method and is identified as hydrogen by GC-TCD (Figure 3.2, and Figure 3.3).



Figure 3.2. GC-TCD (using Argon as carrier gas) of (a) H_2 gas (Pure sample) (b) evolved gas from the reaction mixture. Reaction condition: 1a (1 mmol), catalyst (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 110 °C.



Figure 3.3. Hydrogen gas generation profile for benzyl alcohol dehydrogenation to benzoic acid over [*Ru*]-6 and [*Ru*]-7 catalysts. Reaction condition: 1a (1 mmol), catalyst (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 110 °C.

The trend of the catalytic activity for [Ru]-6 – [Ru]-10 complexes is observed as [Ru]-6 > [Ru]-10 > [Ru]-9 > [Ru]-8 > [Ru]-7. Interestingly, the observed trend in the catalytic activity is in good correlation with the basicity of the aminic nitrogen of the complexes [Ru]-6 - [Ru]-10.^[19] Complex [Ru]-7, having N-isopropyl substituted pyridylamine ligand (L2), exhibited the lowest activity (benzoic acid, yield 81%), attributed to the lower basicity of N_{amine} and the steric crowding at α -carbon.^[20] Further the activity increases with the increase in carbon chain length or branches from complexes [Ru]-8 – [Ru]-10. However, the marginal increase in benzoic acid yield from 90% [Ru]-8 to 92% [Ru]-10 may be substantiated by the fact that with the increase in alkyl carbon chain length or branches the basicity of Namine increases, but it may also increase the steric hindrance at Namine. As also inferred, from the respective single-crystal X-ray Ru-Namine bond lengths in complexes [Ru]-6, [Ru]-7 and [Ru]-10, the Ru-N_{amine} is the shortest (2.123 Å) for [Ru]-6 and the longest (2.1926 Å) for [Ru]-7. The observed trend suggesting the high basicity of N_{amine} in [Ru]-6 compared to [Ru]-7 and [Ru]-10, which is well in accordance with the observed trend in the catalytic activity for alcohol dehydrogenation. To further optimize the reaction condition, catalytic dehydrogenation of **1a** to **1b** is investigated over the high performing catalyst **[Ru]-6** using various bases and varying reaction temperature. Results showed that base exerts significant effect on the catalytic activity, where a strong base (NaOH and KOH) facilitated the higher conversion of **1a**, while with weak base (K_2CO_3 , Na_2CO_3 and $NaHCO_3$) poor conversion is observed (Table 3.7).

	∕он	1. Catalyst (2 mol%), base (1.1 equiv.) 110 °C, 6h, Ar	OH
1a		2. 1M HCI	1b
entry	Catalyst	Base	conv. (1b) (%)
1.	[Ru]-6	КОН	>99
2.	[Ru]-6	NaOH	62
3.	[Ru]-6	K ₂ CO ₃	3
4.	[Ru]-6	Na ₂ CO ₃	2
5.	[Ru]-6	NaHCO ₃	<1

Table 3.7. Screening of the base for benzyl alcohol dehydrogenation^a

^{*a*}Reaction condition: **1a** (1 mmol), catalyst (2 mol%), base (1.1 equiv.), toluene (2 mL), 6 h, 110 °C.

Results also showed that decreasing the reaction temperature to 100 °C and 90 °C, the yield of the product also decreased to 72% and 39% respectively (Table 3.4). The estimated activation energy is calculated to be 17.3 kcal/mol for the dehydrogenation of **1a** to **1b** over **[Ru]-6** catalyst (Figure 3.4).



Figure 3.4. (a) Dehydrogenation of benzyl alcohol (*1a*) over [*Ru*]-6 catalyst at various temperatures. (b) Arrhenius plot of TOF values. Reaction condition: *1a* (*1 mmol*), catalyst (2 mol%), KOH (1.1 equiv.), toluene (2 mL).

Moreover, performing the reaction using benzyl alcohol (1a) and [Ru]-6 catalyst in absence of base in toluene, revealed in the formation of only aldehyde with 6 % conversion of 1a in 6h, suggesting the crucial role of the base in alcohol dehydrogenation reaction (Figure 3.5).



Figure 3.5. ¹H NMR spectra after the reaction of benzyl alcohol in absence of base

3.3.3. Substrate screening. Further, the generality and the scope of the superior catalyst of the [Ru]-6 catalyst is further investigated for the acceptorless dehydrogenation of other substrates under the optimized reaction condition ([Ru]-6 (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 110 °C). A wide range of substrates including aliphatic alcohols (2a-5a), p-substituted benzyl alcohols (6a-9a), (hetero) aromatic alcohols (12a) and other alcohols (10a-11a) are efficiently transformed to their respective carboxylic acid products in moderate to good yields (upto 86%). The lower yield of *iso*-butyric acid (2b, 20%) can be attributed to the lower boiling point of *iso*-butyl alcohol (2a) (Table 3.8, entry 1). However, the n-butyl alcohol (3a, boiling point 117-119 °C) converted efficiently to *n*-butyric acid (3b) with an isolated yield of 80 % (Table 3.8, entry 2). 2-Methoxyethanol (4a) and 2-(methylamino)ethanol (5a) are also transformed to their respective carboxylic acids (4b and 5b) in good yields (Table 3.8, entries 3 and 4). Further *p*-substituted benzyl alcohols (**6a–9a**) also transformed to their corresponding carboxylic acids (**6b–9b**) in good yield (Table 3.8, entries 5-8). Among several *p*-substituted benzyl alcohols explored for this reaction, those having p-methyl (8a) and p-methoxy (9a) substituents exhibited higher yield of the corresponding carboxylic acid (86%, 8b and 80%, 9b). Notably, *p*-chloro and *p*-bromo substituted benzyl alcohols (6a and 7a) displayed moderate to good yield for the corresponding *p*-halogen substituted benzoic acid (6b and 7b). The lower yield of *p*-bromobenzoic acid (7b) is presumably due to the cleavage of p-Br/C bond under the catalytic reaction conditions (Table 3.8, entry 6). [**Ru**]-6 can also catalyzed the dehydrogenation of phenyl ethyl alcohol (10a), albeit with lower yield of the desired phenyl acetic acid (10b) (Table 3.8, entry 9). 2-Naphthoic acid (11b) is also obtained with 65% yield from 2-naphthyl methanol (11a) (Table 3.7, entry 10). Notably, pyridine-2-methanol (12a) is also efficiently converted into pyridine-2carboxylic acid (12b) in 85% yield (Table 3.8, entry 11).

entry	Alcohol	Product	isolated
			yield (%)
1.) 2а ОН	O 2b OH	20
2.	OH 3a	O J 3b	80
3.	O 4a OH	O 4b OH	52
4.	H N 5a OH	H N 5b	75
5.	CI 6a	CI 6b OH	72
6.	Br 7a	Br 7b	59
7.	H ₃ C 8a	O H ₃ C 8b	86
8.	OH 9a	O O 9b	80

Table 3.8. Substrate scope for alcohol dehydrogenation using [Ru]-6 catalyst^a



^aReaction conditions: **2a–12a** (1 mmol), catalyst (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 110 °C, 6 h

3.3.4. Bulk reaction for the catalytic alcohol dehydrogenation reaction. Further, our catalytic system can also be applied for the gram scale synthesis of carboxylic acids. 10 mmol of benzyl alcohol (1a) is dehydrogenated to benzoic acid (1b) in the presence of 1.1 equiv. of KOH in toluene. 0.97 g of benzoic acid is obtained after 9 h, along with the release of the *ca* 16 equiv. of H₂ gas over [**Ru**]-6 catalyst with turnover number (TON) of 400. Further, 62% (TON 620) yield of benzoic acid (1b) is obtained over 0.1 mol% of [**Ru**]-6 catalyst in 24 h under the catalytic reaction condition (Table 3.9).





2.	[Ru]-6 (0.5)	toluene (2 mL)	24	110	76
3.	[Ru]-6 (0.1)	toluene (2 mL)	24	110	62

Reaction condition: 1a (1 mmol), [Ru]-6, KOH (1.1 equiv.), 110 °C.

The high catalytic activity (TON 620) studied (arene)Ru(II) pyridylamine-based complex is of significant importance and the obtained results are superior or as par with several of present reports for alcohol dehydrogenation. The only previous report using (arene)RuNHC complex [(*p*-cymene)RuCl₂(IiPr)]in toluene needs 300 mol% of KOH and a catalytic amount of PCy₃ and HBF₄ as additives at 110 °C. Although, Williams *et al.* reported an efficient formation of benzyl alcohol to benzoic acid in 98% yield using 0.2 mol% of [Ir(2-PyCH₂PBu²t)(COD)]OTf catalyst, but reaction takes 40 h at 120 °C.^[8(b)] On the other hand, with [**Ru**]-6 catalyst, 80% yield of benzoic acid can be obtained in lesser duration (9 h) and temperature (110 °C) in toluene (TOF 44 h⁻¹). Moreover, TON as high as 1378 (TOF 57 h⁻¹) is also achieved over [**Ru**]-6 catalyst for a bulk reaction of benzyl alcohol (**1a**).



Figure 3.6. Hydrogen generation profile for gram scale dehydrogenation of benzyl alcohol (*1a*) to benzoic acid (*1b*) over [*Ru*]-6 catalyst. Reaction conditions: *1a* (10 mmol), [*Ru*]-6 (0.2 mol%), KOH (1.1 equiv.), toluene (10 mL), 9 h, 110 °C.

3.3.5. Mechanism. To elucidate the possible pathway for the dehydrogenation of alcohol to carboxylate as catalyzed by (η^6 -C₆H₆)Ru(II) pyridylamine-based complexes, several controlled experiments and extensive mass investigation are conducted to identify catalytic intermediate species involved in alcohol dehydrogenation reaction (Figures 3.7-3.10).



Figure 3.7. (*a*) *ESI-MS* analysis in water, *[Ru]-6*, *KOH* (*b*) *ESI-MS* analysis in water, *[Ru]-6*, *KOH*, *p*-methylbenzaldehyde.



Figure 3.8. ESI-MS analysis of the reaction mixture after heating at 110 °C in catalytic reaction condition using the [**Ru**]-8 (2 mol%), KOH (1.1 equiv.), benzyl alcohol (1 mmol), toluene (2 mL) in 30 min and 1 h.



Figure 3.9. ESI-MS analysis of the reaction aliquot for benzyl alcohol dehydrogenation after heating at 110 °C for 1 h under controlled reaction condition using the catalyst [*Ru*]-8 (0.1 mmol), benzyl alcohol (0.3 mmol) and KOH (0.3 mmol) in toluene (2 mL).



Figure 3.10. ¹*H* NMR of the reaction aliquot (diluted with methanol- d_4) for benzyl alcohol dehydrogenation after heating at 110 °C for 1 h under controlled reaction condition using the catalyst **[Ru]-8** (0.1 mmol), benzyl alcohol (0.3 mmol) and KOH (0.3 mmol) in toluene (2 mL).

Treating the complex [**Ru**]-6 with KOH (1 equiv.) in water gave a clear wine red solution, which is analyzed as $[(\eta^6-C_6H_6)Ru(\kappa^2-L4)]^+$ [**Ru**]-6A showing a dominant mass peak at m/z 287. Analogously, mass analysis of the catalytic reaction mixture in toluene also showed the presence of a mass peak at m/z 287 ([**Ru**]-6A), suggesting the involvement of this species in the catalytic reaction. Notably, an intense wine-red color appeared upon addition of *p*-methylbenzyl alcohol (**8a**) to the reaction mixture containing [**Ru**]-6 catalyst and KOH at room temperature, and catalytic reaction condition in toluene.

Notably, alcohol coordinated catalytic species are the most obvious species in such kind of catalytic reaction.^[8(b)] For instance, *p*-methoxy benzyl alcohol coordinated Ir species is reported to formed by treating the Ir(COD)NHC complex with *p*-methoxy benzyl alcohol in the presence of KOH in C₆D₆ at room temperature.^[8(b)] On the other hand, upon addition of an excess of *p*-methyl benzaldehyde in an aqueous solution of **[Ru]-6** in presence of KOH, an intense brown-red color appeared. Mass analysis of the reaction mixture inferred the presence of an aldehyde coordinated Ru species with a dominant mass peak at m/z 407 for $[(\eta^6-C_6H_6)Ru(\kappa^2-L4)(p-methylbenzaldehyde)]^+$. Analogous, aldehyde coordinated Ru species $[(\eta^6-C_6H_6)Ru(\kappa^2-L6)(p-methylbenzaldehyde)]^+$.

methylbenzaldehyde)]⁺ (m/z 449) is also observed upon treatment of [**Ru**]-8 with *p*methyl benzaldehyde in toluene or water. Notably, gentle heating (85 °C) of the above reaction mixture resulted in the disappearance of the mass peak at m/z 449 and a new peak appeared at m/z 467 corresponding to the diol coordinated Ru species ([**Ru**]-8D) (Figure 3.11).



Figure 3.11. (a) *ESI-MS* analysis in water before heating, *[Ru]-8*, KOH, pmethylbenzaldehyde (b) *ESI-MS* analysis in water after heating, *[Ru]-8*, KOH, pmethylbenzaldehyde, gentle heating (85 °C).

Further, the involvement of these (η^6 -C₆H₆)Ru intermediate species is also investigated for the alcohol dehydrogenation reaction performed under real catalytic condition (**[Ru]-8** catalyst (0.02 mmol), KOH (1.1 mmol) and benzyl alcohol (**1a**) (1 mmol) at 110 °C in toluene (2 mL)). The mass analysis of the reaction aliquots collected at 30 min and 1 h, showed the presence of several (η^6 -C₆H₆)Ru based catalytic intermediate species including {(η^6 -C₆H₆)Ru(κ^2 -L6)}⁺ (**[Ru]-8A**) and the aldehyde coordinated species {(η^6 -C₆H₆)Ru(κ^2 -L6)(benzaldehyde)}⁺ (**[Ru]-8D**) (Figure 3.9). These results suggesting that η^6 -C₆H₆-to-Ru bond remains intact under the catalytic reaction condition. To further authenticate this, we conducted a controlled reaction using

the stoichiometric ratio (3:1 molar ratio) of benzyl alcohol and [Ru]-8 catalyst in the presence of 1 equiv. of KOH in toluene (2 mL) at 110 °C. Mass spectral analysis (Figure 3.9) of the reaction mixture obtained after 1 hour, clearly evidenced the presence of prominent peaks corresponding to the aldehyde coordinated species $\{(\eta^6-C_6H_6)Ru(\kappa^2-$ L6)(benzaldehyde)}⁺ ([Ru]-8D) at m/z 435.1 along with the species [Ru]-8A ($\{(\eta^6 C_{6}H_{6}$ $Ru(\kappa^{2}-L6)$ ⁺ m/z 329.1). Further, the ¹H NMR (in methanol-d₄) of the above reaction mixture also evidenced the presence of $(\eta^6-C_6H_6)Ru$ based species, which is consistence with the mass studies (Figure 3.10). These findings further authenticated the intactness of the η^6 -C₆H₆-to-Ru bond under the catalytic reaction condition of benzyl alcohol dehydrogenation over the studied (η^6 -C₆H₆)Ru-pyridylamine catalysts. Since no induction period is observed for the catalytic benzyl alcohol dehydrogenation, it can be anticipated that various (η^6 -C₆H₆)Ru based catalytic species (such as [Ru]-8A and [Ru]-**8D**) observed during the initial hours of the catalytic reactions are presumably the crucial catalytic species involved in the alcohol dehydrogenation reaction. Though our findings clearly suggested that arene ring of $(\eta^6-C_6H_6)Ru$ is not lost under the catalytic dehydrogenation reaction conditions, we cannot completely exclude the displacement of arene ring.^[21]

Earlier reports showed that the alcohol dehydrogenation may go through the Tishchenko-like reaction pathway, but we could not observe any traces of ester formation in our catalytic reaction condition. Notably, aromatic aldehydes readily undergo disproportionation to benzyl alcohol and carboxylate in the presence of KOH.^[12] Under our dehydrogenation condition, only 8% benzyl alcohol is observed during the reaction of benzaldehyde with **[Ru]-6** catalyst, suggesting the possibility of Cannizzaro reaction. However, it should be noted that dehydrogenation of aldehyde to carboxylic acid occurred at a faster rate as *ca* 92% of benzoic acid formation is observed within initial 1 hour over the **[Ru]-6** catalyst. Moreover, in contrast to the earlier reports under our reaction condition immediately dehydrogenation start and *ca*. 8.2 equiv. of H₂ gas (approx. 80% conversion) is achieved (Figure 3.12-3.13).



Figure 3.12. Hydrogen generation from benzaldehyde to benzoic acid using [*Ru*]-6 catalyst. Reaction condition: benzaldehyde (1 mmol), [*Ru*]-6 (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 1 h, 110 °C.



Figure 3.13. ¹*H NMR spectra after the reaction of benzaldehyde.*

Analogously, 95% isolated yield of *p*-methyl benzoic acid with equivalent amount of H_2 gas is generated from *p*-methyl benzaldehyde over **[Ru]-6** catalyst (Figure 3.14).



Figure 3.14. Hydrogen generation from p-methyl benzaldehyde to benzoic acid using [*Ru*]-6 catalyst. Reaction condition: p-methyl benzaldehyde (1 mmol), [*Ru*]-6 (2 mol%), KOH (1.1 equiv.), toluene (2 mL), 1 h, 110 °C.

Based on the experimental and mass investigations, a proposed pathway for the catalytic alcohol dehydrogenation is illustrated in Scheme 3.3. We believe that **[Ru]** precatalyst transferred to the active **[Ru]-6A** catalytic species in the presence of KOH. The first step involved the coordination of alcohol to **[Ru]-6A** species to from **[Ru]-6B**, which undergoes β -hydride elimination to yield aldehyde and a Ru-hydride species (**[Ru]-6C**). Further, the **[Ru]-6C** species undergoes dehydrogenation to regenerate **[Ru]-A** species. Upon coordination with aldehyde, **[Ru]-6A** species further generated a Ru-aldehyde species (**[Ru]-6D**), which later transformed to a diol coordinated species **[Ru]-6E**. Diol in **[Ru]-6E** species undergoes β -hydride elimination to release one equiv. of H₂ gas and carboxylate to regenerate the catalytic active species **[Ru]-6A**.



Scheme 3.3. A proposed mechanistic pathway for the dehydrogenation of alcohol

3.4. Conclusions

We synthesized several pyridylamine ligated (η^6 -arene)Ru(II) cationic complexes [**Ru**]-**6** – [**Ru**]-15 and confirmed the structures of three complexes by single crystal X-ray diffraction. We employed these complexes to achieve efficient acceptorless dehydrogenation of benzyl alcohol (1a) to benzoic acid (1b) with the quantitative release of 2 equiv. of H₂ gas, in toluene at 110 °C. Results inferred that N_{amine} basicity and steric crowding at N_{amine} influenced the overall catalytic activity of the studied pyridylamine-(arene)-Ru(II) complexes, where the picolylamine ligated (η^6 -C₆H₆)Ru(II) complex ([**Ru**]-6) displayed superior catalytic performance. The optimized catalytic protocol is
also employed to a wide range of substrates including aliphatic, aromatic and (hetero) aromatic alcohols to obtain the respective carboxylic acids in good yields (up to 86%). Extensive mass spectral investigations evidenced the presence of several important organometallic species, such as aldehyde and diol coordinated (η^6 -arene)Ru species, under the catalytic and controlled reaction conditions. Moreover, highly active [**Ru**]-6 catalyst also exhibited superior catalytic performance for the gram/bulk scale catalytic reaction to achieve the turnover number of 1378, which is superior or on par with several active Ru and Ir based complexes available in the literature.

Spectral data for dehydrogenation products of alcohols^[8,10-13]

Isobutyric acid (2b): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 1.17-1.18 (d, 6H, J = 5 Hz), 2.54-2.64 (m, 1H).



Butyric acid (3b): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 2.33-2.36 (t, 2H, *J1*= 10 Hz, *J2*= 5 Hz), 1.64-1.71 (m, 2H), 0.96-0.99 (t, 2H, *J1*= 5 Hz, *J2*= 10 Hz).



2-methoxyacetic acid (4b): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 4.09 (s, 2H), 3.48 (s, 3H).



Potassium-2-(methylamino)acetate (5b): ¹H NMR (300 MHz, D₂O): δ (ppm) = 3.35 (s, 2H), 2.49 (s, 3H).

4-chlorobenzoic acid (6b): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 8.02-8.04 (d, 2H, J = 10 Hz), 7.44-7.45 (d, 2H, J = 5 Hz).



4-bromobenzoic acid (7b): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.96-7.98 (d, 2H, *J* = 10 Hz), 7.62-7.64 (d, 2H, *J* = 10 Hz).



4-methylbenzoic acid (8b): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 8.00-8.02 (d, 2H, J = 10 Hz), 7.27-7.29 (d, 2H, J = 10 Hz), 2.44(s, 1H).



4-methoxybenzoic acid 2-phenylacetic acid (9b): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 8.06-8.08 (d, 2H, J = 10 Hz), 6.94-6.96 (d, 2H, J = 10 Hz), 3.88 (s, 1H).



2-phenylacetic acid (10b): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.33-7.36 (m, 2H), 7.27-7.30 (m, 3H), 3.66 (s, 2H).



2-naphthoic acid (11b): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 8.74 (s, 1H), 8.13-8.15 (d, 1H, *J* = 10 Hz), 7.99-8.01 (d, 1H, *J* = 10 Hz), 7.90-7.94 (t, 1H, *JI* = 10 Hz, *J2* = 10 Hz), 7.62-7.65 (t, 1H, *JI* = 10 Hz, *J2* = 5 Hz), 7.56-7.59 (t, 1H, *JI* = 5 Hz, *J2* = 10 Hz).



potassium picolinate (12b): ¹H NMR (500 MHz, CD₃OD): δ (ppm) = 8.54-8.55 (d, 1H, J = 5 Hz), 7.97-7.99 (d, 1H, J = 10 Hz), 7.81-7.85 (t, 1H, JI = 10 Hz, J2 = 10 Hz), 7.38-7.40 (t, 1H, JI = 5 Hz, J2 = 5 Hz).



Spectral data for synthesized complexes



¹H NMR spectra of complex **[Ru]-6**



³¹P NMR spectra of complex [Ru]-6



¹H NMR spectra of complex [Ru]-7



³¹P NMR spectra of complex [Ru]-7



¹H NMR spectra of complex [Ru]-8



³¹P NMR spectra of complex [Ru]-8



¹H NMR spectra of complex [Ru]-9







ESI-MS spectra of complex [Ru]-9



¹H NMR spectra of complex **[Ru]-10**



³¹P NMR spectra of complex [Ru]-10



¹H NMR spectra of complex [Ru]-11



³¹P NMR spectra of complex [Ru]-11



¹H NMR spectra of complex [Ru]-12



³¹P NMR spectra of complex [Ru]-12



¹H NMR spectra of complex [Ru]-13



³¹P NMR spectra of complex [Ru]-13



¹H NMR spectra of complex [Ru]-14



³¹P NMR spectra of complex [Ru]-14



¹H NMR spectra of complex [Ru]-15



³¹P NMR spectra of complex [Ru]-15



ESI-MS spectra of complex [Ru]-15

Note: The content of this chapter is published as Awasthi et al., Inorg. Chem., 2019, 58, 21, 14912–14923, (DOI: 10.1021/acs.inorgchem.9b02691) and reproduced here with the permission of American Chemical Society.

3.5. References

- 1. Fatiadi A. J. (1987), The Classical Permanganate Ion: Still a Novel Oxidant in Organic Chemistry, *Synthesis*, 85–127 (DOI: 10.1055/s-1987-27859).
- Lee D. G., Ribagorda, M., Adrio, J. (2001), Potassium Permanganate. In Encyclopedia of Reagents for Organic Synthesis; Wiley: Chichester, U.K., (DOI: 10.1002/047084289X.rp244).
- Freeman F. (2001), Chromic Acid. In Encyclopedia of Reagents for Organic Synthesis; Wiley: Chichester, U.K., (DOI: 10.1002/047084289X.rc164).
- Piancatelli G. (2001), Pyridinium Dichromate. In Encyclopedia of Reagents for Organic Synthesis; Wiley: Chichester, U.K., (10.1002/047084289X.rp290).
- Martin V. S., Palazon J. M., Rodriguez C. M., Nevill, C. R., Hutchinson D. K., (2001), Ruthenium(VIII) Oxide. In *Encyclopedia of Reagents for Organic Synthesis*; Wiley: Chichester, U.K., (DOI: 10.1002/047084289X.rr009).
- (a) Galvin J. M., Jacobsen E. N., Palucki M., Frederick M. O. (2001) Sodium Hypochlorite. In Encyclopedia of Reagents for Organic Synthesis; Wiley: Chichester, U.K., (DOI: 10.1002/047084289X.rs084). (b) Jr L. Q., Tolman W. B. (2008), Biologically inspired oxidation catalysis, *Nature*, 455, 333–340 (DOI: 10.1038/nature07371).
- Hu P., Milstein D. (2019), Conversion of Alcohols to Carboxylates Using Water and Base with H₂ Liberation. *Top. Organometal. Chem.*, 63, 175-192 (DOI: 10.1007/3418_2018_20).
- (a) Fujita K., Tamura R., Tanaka Y., Yoshida M., Onoda M., Yamaguchi R. (2017), Dehydrogenative Oxidation of Alcohols in Aqueous Media Catalyzed by a Water-Soluble Dicationic Iridium Complex Bearing a Functional N-Heterocyclic Carbene Ligand without Using Base, ACS Catal., 7, 7226–7230 (DOI: 10.1021/acscatal.7b02560); (b) Cherepakhin V., Williams T. J. (2018), Iridium Catalysts for Acceptorless Dehydrogenation of Alcohols to Carboxylic Acids: Scope and Mechanism, ACS Catal., 8, 3754–3763 (DOI: 10.1021/acscatal.8b00105).
- 9. (a) Zweifel T., Naubron J., Grützmacher H. (2009), Catalyzed Dehydrogenative Coupling of Primary Alcohols with Water, Methanol, or Amines, *Angew. Chem.*,

Int. Ed., 48, 559–563 (DOI: 10.1002/anie.200804757); (b) Trincado M., Grützmacher H., Vizza F., Bianchini C. (2010), Domino Rhodium/Palladium-Catalyzed Dehydrogenation Reactions of Alcohols to Acids by Hydrogen Transfer to Inactivated Alkenes, *Chem. - Eur. J.*, 16, 2751–2757 (DOI: 10.1002/chem.200903069); (c) Annen S., Zweifel T., Ricatto F., Grützmacher H. (2010), Catalytic Aerobic Dehydrogenative Coupling of Primary Alcohols and Water to Acids Promoted by a Rhodium(I) Amido N-Heterocyclic Carbene Complex, *ChemCatChem*, 2, 1286–1295 (DOI: 10.1002/cctc.201000100).

- (a) Balaraman E., Khaskin E., Leitus G., Milstein D. (2013), Catalytic Transformation of Alcohols to Carboxylic Acid Salts and H₂ Using Water as the Oxygen Atom Source, *Nat. Chem.*, 5, 122–125 (DOI: 10.1038/nchem.1536); (b) Choi J., Heim L. E., Ahrens M., Prechtl M. H. G. (2014), Selective Conversion of Alcohols in Water to Carboxylic Acids by in situ Generated Ruthenium Trans Dihydrido Carbonyl PNP Complexes, *Dalton Trans.*, 43, 17248–17254 (DOI: 10.1039/C4DT01634C); (c) Malineni J., Keul H., Möller M. (2015), A Green and Sustainable Phosphine-Free NHC-Ruthenium Catalyst for Selective Oxidation of Alcohols to Carboxylic Acids in Water, *Dalton Trans.*, 44, 17409–17414 (DOI: 10.1039/C5DT01358E).
- Sarbajna A., Dutta I., Daw P., Dinda S., Rahaman S. M. W., Sarkar A., Bera J. K. (2017), Catalytic Conversion of Alcohols to Carboxylic Acid Salts and Hydrogen with Alkaline Water, ACS Catal., 7, 2786–2790 (DOI: 10.1021/acscatal.6b03259).
- Santilli C., Makarov I. S., Fristrup P., Madsen R. J. (2016), Dehydrogenative Synthesis of Carboxylic Acids from Primary Alcohols and Hydroxide Catalyzed by a Ruthenium N-Heterocyclic Carbene Complex, *J. Org. Chem.*, 81, 9931–9938 (DOI: 10.1021/acs.joc.6b02105).
- 13. Dai Z., Luo Q., Meng X., Li R., Zhang J., Peng T. (2017), Ru(II) Complexes Bearing 2,6-Bis(benzimidazole-2-yl)pyridine Ligands: a New Class of Catalysts for Efficient Dehydrogenation of Primary Alcohols to Carboxylic Acids and H₂ in the Alcohol/CsOH System, *J. Organomet. Chem.*, 830, 11–18 (DOI: 10.1016/j.jorganchem.2016.11.038).

- 14. Shao Z., Wang Y., Liu Y., Wang Q., Fub X., Liu Q. (2018), A general and efficient Mn-catalyzed acceptorless dehydrogenative coupling of alcohols with hydroxides into carboxylates, *Org. Chem. Front.*, 5, 1248-1256 (DOI: 10.1039/C8QO00023A).
- 15. (a) Awasthi M. K., Tyagi D., Patra S., Rai R. K., Mobin S. M., Singh S. K. (2018), Ruthenium complexes for catalytic dehydrogenation of hydrazine and transfer hydrogenation reactions, *Chem. Asian J.*, 13, 1424 -1431 (DOI: 10.1002/asia.201800315); (b) Patra S., Awasthi M. K., Rai R. K., Hemanta D., Mobin S. M., Singh S. K. (2019), Dehydrogenation of Formic Acid Catalyzed by Water-Soluble Ruthenium Complexes: X-ray structure and mechanistic investigations, *Eur. J. Inorg. Chem.*, 1046-1053 (DOI: 10.1002/ejic.201801501).
- 16. (a) Bennett M. A., Huang T.-N., Matheson T. W., Smith A. K. (1982), *Inorg. Synth.*, 21, 74-78 (DOI: 10.1002/9780470132524.ch16); (b) Zelonka R. A., Baird M. C. (1972), Benzene Complexes of Ruthenium(II), Can. J. Chem., 50, 3063-3072 (DOI: 10.1139/v72-486); (c) Bennett M. A., Smith A. K. (1974), Arene ruthenium(II) complexes formed by dehydrogenation of cyclohexadienes with ruthenium(III) trichloride, *J. Chem. Soc., Dalton Trans.*, 233-241 (DOI: 10.1039/dt9740000233).
- Sheldrick G. M. (2008), A short history of SHELX, *Acta Crystallogr.*, *Sect. A*, 64, 112-122 (DOI: 10.1107/S0108767307043930).
- Dwivedi A. D., Sahu V. K., Mobin S. M., Singh S. K. (2018), Cyclopentadienyl–Ru(II)–Pyridylamine Complexes: Synthesis, X-ray Structure, and Application in Catalytic Transformation of Bio-Derived Furans to Levulinic Acid and Diketones in Water, *Inorg. Chem.*, 57, 4777-4787 (DOI: 10.1021/acs.inorgchem.8b00536).
- (a) Gomez J., Garcıa-Herbosa G., Cuevas V. J., Arnaiz A., Carbayo A., Munoz A., Falvello L., Fanwick E. P. (2006), Diastereospecific and Diastereoselective Syntheses of Ruthenium(II) Complexes Using N,N' Bidentate Ligands Aryl-pyridin-2-ylmethyl-amine ArNH-CH₂-2-C₅H₄N and Their Oxidation to Imine Ligands, *Inorg. Chem.*, 45, 2483-2493 (DOI: 10.1021/ic051590a); (b) Tyagi D.,

Rai R. K., Mobin S. M., Singh S. K. (2017), N-Substituted Iminopyridine Arene– Ruthenium Complexes for the Regioselective Catalytic Hydration of Terminal Alkynes, *Asian J. Org. Chem.*, 6, 1647-1658 (DOI: 10.1002/ajoc.201700396).

- 20. (a) Chakraborty A. K., Bischoff K. B., Astarita G., Damewood, J. R. (1988), Molecular orbital approach to substituent effects in amine-CO₂ interactions, J. Am. Chem. Soc., 110, 6947–6954 (DOI: 10.1021/ja00229a003); (b) Graton J., Berthelot M., Laurence C. (2001), Hydrogen-bond basicity pKHB scale of secondary amine, J. Chem. Soc., Perkin Trans., 2, 2130–2135 (DOI: 10.1039/b105082f).
- 21. (a) Zhang Y., Chen C., Ghosh S. C., Li Y., Hong S. H. (2010), Well-Defined N-Heterocyclic Carbene Based Ruthenium Catalysts for Direct Amide Synthesis from Alcohols and Amines, *Organometallics*, 29, 1374–1378 (DOI: 10.1021/om901020h); (b) Delaude L.. Delfosse S., Richel A., Demonceau A., Noels A. F. (2003), Tuning of ruthenium *N*-heterocyclic carbene catalysts for ATRP, *Chem. Commun.*, 1526–1527 (DOI: 10.1039/b301733h).

Chapter 4

Hydrogen Production from Formaldehyde over Ruthenium Catalyst in Water

4.1. Introduction

Globally efforts are being made to search for a sustainable and renewable energy resource to cope with the current scenario of depleting fossil fuels resources and deteriorating environmental condition. In this regard, 'Hydrogen gas' is identified as a potential clean fuel for both stationary and mobile application, as it has very high energy density and it produces only water when combine with oxygen in a fuel cell.^[1] Despite that hydrogen is the third most abundant element on earth, it is mostly found in its various chemical forms, and its presence as hydrogen gas in the earth's atmosphere is extremely rare (about 1 ppm by volume).^[1, 2] Though efforts are being made to store hydrogen gas in tanks under high pressure and/or as liquid under cryogenic condition, the low volumetric energy density of hydrogen gas and potential safety issues has made its storage and transport a critical challenge.^[3]

In addition to the extensive efforts to store hydrogen in porous structures and metal hydrides, storing hydrogen in chemical bonds in a suitable liquid hydrogen storage material has also received considerable global attention.^[2,4] These liquid hydrogen storage materials can release hydrogen gas in the presence of a suitable catalyst and can be recovered back via hydrogenation.^[5-13] In this regard, formic acid, formaldehyde and methanol have been identified as efficient hydrogen carriers.^[6-13] Further, most of these liquid hydrogen storage materials have appreciably high gravimetric density of hydrogen, are inexpensive, ready-to-use and can be obtained from renewable resources. Advantageously being liquid, these liquid hydrogen storage materials would be compatible with the existing infrastructure for dispensing fossil fuels. In line with methanol^[6,9] and formic acid,^[7] formaldehyde^[8-13] is also emerging a promising liquid hydrogen storage material. Compared to formic acid, formaldehyde has a gravimetric hydrogen density of 8.4 wt%, and for the aqueous formaldehyde (37 wt%) (H₂CO-H₂O)

the gravimetric hydrogen density is 5.0 wt%.^[8-13] The favorable thermodynamics (Δ Hr = - 35.8 kJ mol⁻¹) for hydrogen production from formaldehyde-water dehydrogenation (CH₂O + H₂O \rightarrow 2H₂ + CO₂), makes formaldehyde a potential source of hydrogen gas. Typically, in water formaldehyde exists in the form of a stable methanediol, and in the presence of a suitable catalyst produces hydrogen and carbon dioxide (Scheme 4.1).^[8-13]



Scheme 4.1. Literature known homogeneous catalysts for hydrogen production from formaldehyde.

Recently, several Ru and Ir-based homogenous catalysts have been reported for hydrogen production from formaldehyde and paraformaldehyde (Scheme 4.1).^[8-14] Among one of the first report on H₂ production from formaldehyde, Prechtl et al. used ruthenium para-cymene dimer complex ($[(\eta^6-C_{10}H_{14})RuCl_2]_2$) to achieve a turnover number of 700 for hydrogen production from formaldehyde in water at 95 °C.^[10] A water soluble Ir(III) complex [$(\eta^5-C_5Me_5)Ir(4-(1H-pyrazol-1-yl)benzoic acid)(H_2O)]^+$ was also reported for hydrogen production from paraformaldehyde under basic reaction conditions (pH 11) at 25 °C (TON 24), where the *in situ* generated active catalytic species Ir(III)hydroxo species was found to be crucial for this reaction.^[11] Fujita *et al.* investigated Ir(III)-bipyridionate complex ($[(\eta^5-C_5Me_5)Ir(6,6'-dionato-2,2'-bipyridine)(OH)]^-$) for H₂ production (TON 178) from formaldehyde in the presence of NaOH, where the bipyridionate ligand plays crucial role in the catalytic reaction.^[9] Ru(II) hydrido complex was also reported for the dehydrogenation of formaldehyde to H₂ at 60 °C, albeit required a strong basic reaction conditions (2.72 mol L⁻¹ KOH).^[12] Recently, Himeda et al. employed (η^6 -C₆Me₆)Ru(II)-diamine complexes for H₂ production from aqueous formaldehyde at 95 °C.^[13] Using paraformaldehyde a total turnover number of 24000 was achieved over the catalyst $[(\eta^6-C_6Me_6)Ru(\kappa^2-bipyridyl-2,2'-diamine)OH_2]SO_4$ at 95 °C.^[13] Very recently, we also explored arene-Ru(II)-pyridine-2-ylmethanol complex $\lceil (\eta^6 C_{10}H_{14}$)Ru(κ^2 -pyridine-2-ylmethanol)(Cl)]⁺ for hydrogen production from aqueous formaldehyde to achieve an impressive initial TOF of 1072 h⁻¹ (TON 1838) (Scheme 4. 1).^[14] Therefore, it is evident from these reports that the development of efficient catalytic system for hydrogen production from aqueous formaldehyde without the use of any organic solvent is highly desirable. Herein, we report hydrogen production for formaldehyde and paraformaldehyde in water by utilizing ruthenium catalysts in the presence of a suitable ligand. In the presence of a suitable ligand, *in situ* generated highly active ruthenium catalyst exhibited high yields and selectivity of hydrogen gas from formaldehyde and paraformaldehyde with high TON and TOF under moderate reaction conditions.

4.2. Experimental section

4.2.1 Materials. All experiments were carried out using the chemicals of higher purity purchased from Sigma Aldrich, TCI and Alfa Aesar unless otherwise specified. Ru(II)- arene complexes were synthesized according to previous reports using, Ru(II)-arene precursors, [{(η^6 -C₁₀H₁₄)RuCl₂}].¹⁵

4.2.2. Instrumentation. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra are recorded at 298 K using D₂O or CDCl₃ as the solvent on a Bruker Avance 400 spectrometer. Tetramethylsilane (TMS) is used as an external standard and the chemical shifts in ppm are reported relative to the centre of the singlet at 7.26 ppm for CDCl₃ and 4.75 ppm for D₂O in ¹H NMR, and to the centre of the triplet at 77.0 ppm for CDCl₃ in ¹³C NMR. Suitable single crystals of complex [**Ru**]-16 and [**Ru**]-18 subjected to single-crystal X-ray structural studies using Bruker APEX SMART D8 Venture CCD diffractometer and Agilent Technologies Supernova CCD system respectively. Coupling

constant (*J*) values are reported in hertz (Hz), and the splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); br. (broad). ESI (positive mode), and high-resolution mass spectra (HRMS) are recorded on a micro TF-Q II mass spectrometer. The GC-TCD analyses are performed on a Shimadzu GC-2014 system using a shin carbon-ST packed column.

4.2.3. Single-crystal X-ray diffraction studies: X-ray suitable single crystals of **[Ru]**-16 and [Ru]-18 are grown by diffusion of diethyl ether into methanol solution of complexes. Solid state structure of [Ru]-18 is obtained using a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer while the [Ru]-16 is collected using a Bruker APEX SMART D8 Venture CCD diffractometer. Data were collected at 293(2) K using graphite-monochromated Mo K α radiation ($\lambda \alpha = 0.71073$ A). The strategy for the data collection is evaluated using the CrysAlisPro CCD software. The data are collected using the standard 'phi-omega' scans techniques, and are scaled and reduced using CrysAlisPro RED software. The structures are solved by direct methods using SHELXS-97 and SHELXS-2014, and refined using full matrix leastsquares with SHELXL-97 and SHELXS-2014, refining on F2.^[16] The positions of all the atoms are obtained by direct methods. All non-hydrogen atoms are refined anisotropically. The remaining hydrogen atoms are placed in geometrically constrained positions, and refined with isotropic temperature factors, generally 1.2 Ueq of their parent atoms. CCDC deposition numbers of the complex [Ru]-18 and [Ru]-16 is 1994921 and 1994922 respectively. These data are freely available at www.ccdc.cam.ac.uk (or can be procured from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

4.2.4. General Procedure for the catalytic formaldehyde dehydrogenation reaction over in situ generated complexes. Typically, formaldehyde (13.55 mol L⁻¹, 1.07 mL), **[Ru]-2** precursors [{(η^6 -C₁₀H₁₄)RuCl₂}] (13 µmol), and ligands (**L9-L16**) (26 µmol) are mixed in two necked test-tube equipped with a condenser and water displacement setup. The reaction mixture is stirred at 95 °C on an oil bath. Analogous reactions are also performed for the catalytic dehydrogenation of aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL). **4.2.5.** Procedure for the synthesis of $(\eta^6-C_{10}H_{14})Ru(II)$ complexes [Ru]-17 – [Ru]-19. Complex synthesized via treating imidazole ligands in 2, 4 and 6 equivalent with respect to the precursor [{ $(\eta^6-C_{10}H_{14})RuCl_2$ }] at room temperature.

(a) Synthesis of $[(\eta^6-C_{10}H_{14})Ru(L14)Cl_2]$ ([Ru]-17). Complex [Ru]-17 is synthesized following the literature reported procedure,^[17] by using imidazole (L14) (0.41 mmol) and $[\{(\eta^6-C_{10}H_{14})RuCl_2\}_2]$ (0.2 mmol) in refluxing toluene (30 mL). The yellow solid is precipitated out and filtered. The precipitate was dissolved in methanol and dichloromethane mixture (v/v; 9:1) and layered with diethyl ether yielded the [Ru]-17 as yellow color solid, yield 62%. [Ru]-17: ¹H NMR (400 MHz, CDCl_3): δ (ppm) = 10.47 (s, 1H), 7.47 (s, 1H), 6.93 (s, 1H), 6.57 (s, 1H), 5.39 (d, 2H, *J* = 4Hz), 5.20 (d, 2H, *J* = 4Hz) 2.90-2.83 (m, 1H), 2.06 (s, 3H), 1.27 (d, 6H, *J* = 8Hz). ¹³C NMR (100 MHz, CDCl_3): δ (ppm) = 138.42, 129.72, 117.58, 102.78, 97.10, 82.46, 81.40, 65.82, 30.64, 22.20, 18.33, 15.23. MS (ESI): *m/z* calculated 339.0197 ([M-Cl]⁺), found 339.0241.

(b) Synthesis of $[(\eta^6-C_{10}H_{14})Ru(L14)_2Cl]Cl([Ru]-18)$. Complex [Ru]-18 is synthesized following the literature reported procedure,^[17] by using imidazole (L14) (0.81 mmol) and $[\{(\eta^6-C_{10}H_{14})RuCl_2\}_2]$ (0.20 mmol) in methanol (30 mL) and refluxed for 3h. Pale yellow solid is obtained on adding the diethyl ether in the concentrated solution of reaction mixture. Dried under vacuum yielded 69% of [Ru]-18 as yellow color solid. [Ru]-18: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 13.01 (s, 2H), 8.27 (s, 2H), 7.30 (s, 2H), 6.87 (s, 2H), 5.71 (d, 2H, *J* = 4Hz), 5.60 (d, 2H, *J* = 4Hz) 2.44-2.39 (m, 1H), 1.69 (s, 3H), 1.08 (d, 6H, *J* = 4Hz). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 138.69, 129.54, 117.14, 103.14, 100.28, 86.01, 81.61, 65.81, 30.68, 22.20, 17.76, 15.23. MS (ESI): *m/z* calculated 407.0572 ($[M]^+$), found 407.0571.

(c) Synthesis of $[(\eta^6-C_{10}H_{14})Ru(L14)_3]Cl_2$ ([Ru]-19). Complex [Ru]-19 is synthesized, by using imidazole (L14) (1.3 mmol) and $[\{(\eta^6-C_{10}H_{14})RuCl_2\}_2]$ (0.20 mmol) in 30 mL dichloromethane. Pale yellow solid is obtained as precipitate washed with diethylether and dried and stored under vacuum, yield 64%. [Ru]-19: ¹H NMR (400 MHz, D₂O): δ (ppm) = 7.63 (s, 3H), 7.24 (s, 3H), 6.89 (s, 3H), 6.01 (d, 2H, *J* = 4Hz), 5.76 (d, 2H, *J* = 8Hz), 2.39-2.31 (m, 1H), 1.74 (s, 3H), 1.06 (d, 6H, *J* = 8Hz). ¹³C NMR (100 MHz, D₂O):

 δ (ppm) = 139.57, 130.53, 118.52, 105.33, 103.32, 86.77, 82.90, 30.18, 21.38, 17.08. MS (ESI): *m*/*z* calculated 220.0628 ([M]²⁺), found 220.0739.

[(η⁶-C₁₀H₁₄)₂Ru₂(μ-H)(μ-OOCH)(μ-Cl)]PF₆: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 6.81 (s, 1H), 6.53 (d, 2H, J = 4Hz), 6.19 (d, 2H, J = 4Hz), 5.77 (d, 2H, J = 8Hz), 5.42 (d, 2H, J = 4Hz) 2.73-2.63 (m, 2H), 2.10 (s, 6H), 1.29 (t, 12H, J = 8Hz), -7.29 (s, 1H). ¹³C NMR (100 MHz, D₂O): δ (ppm) = 172.36, 102.15, 95.23, 83.64, 81.83, 78.42, 76.33, 29.06, 20.48, 19.57, 16.83. ³¹P NMR (161.97 MHz, CDCl₃): δ (ppm) = -144.09 (sep, PF₆). MS (ESI): m/z calculated 553.0024 ([M]⁺), found 552.9792.

4.2.6. Mercury poisoning experiment. A two neck testtube attached to a condenser and equipped with a magnetic bar was charged with ruthenium catalyst (**[Ru]-2**), 0.013 mmol), and ligand (**L14**, 0.026 mmol) with aqueous formaldehyde (13.55 mmol) and mercury (250 mg). The resulting solution was stirred at room temperature for 2 h then heated at 95 °C, the reaction start to produce the gas, which measured by using the water displacement method.

4.2.7. Recyclability experiment: Initially, aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), [**Ru**]-2 precursors [{(η^6 -C₁₀H₁₄)RuCl₂}] (13 µmol), and ligand (**L14**) (26 µmol) are mixed in two necked test-tube equipped with a condenser and water displacement setup. The reaction mixture is stirred at 95 °C on an oil bath. For subsequent catalytic run 1.5 mmol of formaldehyde added in each cycle and release of gas was monitored by water displacement process. Equivalence of gas calculated using the eq. (4.1)

HCHO + H₂O \longrightarrow 2H₂ + CO₂ eq. (4.1) So 1 equivalent of formaldehyde produced the 3 equivalent of gas.

4.2.8. TON and TOF calculation:

TON calculations are performed using formula-

TON = η (gas produced in mmol) / η (catalyst used) for TOF calculation-

TOF = TON / time (h)

e.g. for the bulk reaction the total gas produced was 1580 mL (64.5 mmol) from 60 mmol of formaldehyde over 0.005 mmol of catalyst.

$$TON = 64.5/0.005$$

So, the calculated TON of the reaction is 12905.

4.3. Results and discussion

Firstly, hydrogen production from aqueous formaldehyde was examined over *in*situ generated ruthenium catalyst obtained using $[(\eta^6-C_{10}H_{14})RuCl_2]_2$ (**[Ru]-2**) in the presence of various mono-dentate nitrogen based ligands at 95 °C in water (Scheme 4.2 and Table 4.1). The reaction setup was equipped with a gas burette to monitor the release of gas, and further the composition of the released gas was determined by gas chromatography (Figure 4.1). Among various ligands (**L9-L16**) screened for hydrogen production from formaldehyde in the initial 1 h, aniline (**L11-L13**) and imidazole (**L14-L16**) based ligands outperformed over others (**L9-L10**). In the presence of aniline (**L11)**, the release of 258 moles of gas per mol of catalyst was achieved, whereas using substituted aniline (**L12-L13**) could not significantly enhance the amount of gas released over the ruthenium catalyst. On the other hand, the release of 281 moles of gas per mol of catalyst was achieved in the initial 1 h and 515 moles of gas per mol of catalyst was released in 3 h over the catalyst [**Ru]-2** in the presence of imidazole (**L14**) (Figure 4.2).



Figure 4.1. GC- TCD of (a) H_2 gas (Pure sample) (b) CO₂ gas (Pure sample) and (c-f) gas evolved from aqueous formaldehyde at different time interval of the catalytic reaction. (Reaction condition: aq. formaldehyde (13.55 mmol, 1.07 mL), catalyst **[Ru]-2** (13 µmol) and ligand **L14** (26 µmol) at 95 °C) (Analyses performed using Argon as carrier gas).



Figure 4.2. Initial time course for hydrogen production from aqueous formaldehyde. (Reaction condition: aq. formaldehyde (13.55 mol L^{-1} , 1.07 mL), catalyst **[Ru]-2** (13 μ mol) and ligand **L14** (26 μ mol) at 95 °C).

Further, using substituted imidazole ligands (L15-L16) could not significantly increase the release of gas from formaldehyde. Nevertheless, the turnover number of 454 and 421 achieved respectively with L15 and L16 in 3 h is higher than that observed under ligand-free condition for hydrogen production from formaldehyde over [Ru]-2 at 95 °C (Table 4.1).



Scheme 4.2. Comparative TON for the catalytic hydrogen production from aqueous formaldehyde (13.55 mmol, 1.07 mL) over catalyst [Ru]-2 (13 μ mol) in the presence of ligands (L9-L16, 26 μ mol) at 95 °C.
The observed >35% enhancement in TON (515 in 3h) with [**Ru**]-2 in the presence of ligand **L14** (**L14/Ru**) as compared to TON of 380 with [**Ru**]-2 without ligand inferred that presumably the ruthenium-imidazole (**L14**) interaction is playing a crucial role. Notably with **L14/Ru** catalyst, higher catalytic turnover of 688 moles of gas per mol of catalyst (with an initial TOF of 850 h⁻¹) was achieved to produce 438 mL of hydrogen gas from aqueous formaldehyde in 7 h at 95 °C.

Table 4.1. Optimization of reaction parameters for hydrogen production fromformaldehyde in water catalyzed by $[Ru]-2^{[a]}$

cat. [Ru]-2 (0.1mol%) O Iligand L9-L16 (0.2 mol%) □ → 2H₂ + CO₂				
н∕∼н	95	°C		
Entry	Cat./ligand	Evolved Gas [mL]	TOF [h ⁻¹] ^[e]	
1	Ru	242 (334) ^[b]	560	
2	Ru/ L9	255	539	
3	Ru/ L10	(103) ^[c]	498	
4	Ru/L11	290	788	
5	Ru/L12	270	788	
6	Ru/ L13	270	808	
7	Ru/ L14	328 (438) ^[d]	850	
8	Ru/ L15	289	850	
9	Ru/ L16	268	725	

[a] Reaction was performed with aqueous formaldehyde (13.55 mol L⁻¹, 1.07 mL), catalyst **[Ru]-2** (13 μ mol) and ligands **L9-L16** (26 μ mol) at 95 °C for 3 h. [b] Total gas evolved in 6 h. [c] Evolved gas in 1 h. [d] Total gas evolved in 7 h. [e] Average TOF for initial 10 min.

Further, the content of ligand **L14** per ruthenium was found to be highly influential in tuning the amount of hydrogen gas released from formaldehyde. Figure 4.3 displayed the time-course plot for hydrogen production from formaldehyde over **[Ru]-2** catalyst in the presence of varying **L14/Ru** ratio of 1, 2 and 3. Further, despite the initial

faster rate of gas generation observed with **L14/Ru** ratio of 3, reaction ceased after the release of 224 mL of gas in 75 min with a maximum TON of 352. On the other hand, 352 mL of gas was produced from formaldehyde for **L14/Ru** ratio of 2, before the reaction ceased in 180 min (TON of 553) (Figure 4.3a). In contrary to the reaction performed with higher **L14/Ru** ratios, a noteworthy steady release of gas was observed for the reaction performed with **L14/Ru** ratio of 1, and reaction remains active even after 6 h to yield over 400 mL of gas (TON of 688) (Figure 4.3a and Table 4.1).



Figure 4.3. (a) Time course for hydrogen production from aqueous formaldehyde (13.55 mol L^{-1} , 1.07 mL) over catalyst **[Ru]-2** (13 µmol) in the presence of 1, 2 and 3 equiv. of ligand **L14** at 95 °C and (b) The H₂/CO₂ ratios in the produced gas mixture from aqueous formaldehyde.

These results further suggesting the crucial role of the imidazole ligand (**L14**) in ruthenium catalyzed hydrogen production from formaldehyde. Notably, hydrogen production from formaldehyde in water (methanediol, 8.4 wt% H₂) involves two-step dehydrogenation pathways: (a) methanediol to formic acid with the release of one equivalent of H₂, and (b) dehydrogenation of formic acid to H₂ and CO₂. Previous studies revealed that dehydrogenation of formic acid requires base to achieve efficient dehydrogenation of formic acid.^[7h,7i] On the other hand, dehydrogenation of formaldehyde in water can occur even in the absence of base, but the presence of base may enhance the efficiency of catalytic dehydrogenation reaction.^[10] As analyzed by GC- TCD, the gas released during the dehydrogenation of formaldehyde in water over the studied **L14/Ru** catalyst (**L14/Ru** ratio of 1) at 95 °C inferred higher H₂ content in the initial hours of the dehydrogenation reaction, which is consistent with the two-step dehydrogenation pathway of formaldehyde in water (Figure 4.3b).

The high hydrogen selectivity of ~90% in the initial hours, suggesting the conversion of methanediol to hydrogen gas and formic acid/formate in the first step, which is followed by the second step of formic acid/formate conversion to H₂ and CO₂ resulting in gradual decrease in H₂/CO₂ ratio to 1:1. Moreover, we analysed the reaction mixture by ¹H NMR during the initial 1h of the formaldehyde (13.55 mol L⁻¹) dehydrogenation reaction (Figure 4.4).



Figure 4.4. (a) The H_2/CO_2 ratios in the produced gas mixture and (b) ¹H NMR yield of HCOOH during the catalytic dehydrogenation of aqueous formaldehyde in the initial 1 h of the reaction. (Reaction condition: aq. formaldehyde (13.55 mol L⁻¹, 1.07 mL), catalyst [**Ru**]-2 (13 µmol) and ligand **L14** (26 µmol), at 95 °C. HCOOH yield was determined using dioxane as an internal standard).

Results inferred the generation of formic acid in the initial 30 min, and later the content of formic acid starts decreasing. This trend clearly suggesting the initial decomposition of methanediol to formic acid and H₂, followed by the conversion of formic acid to H₂ and CO₂ in an exergonic pathway.^[10] Further, we observed that the studied **L14/Ru** catalyst also catalysed the dehydrogenation of formic acid in the absence of base to release 112 mL of gas (TON of 176) in the initial 1 h and 186 mL (TON of 292 in 3 h) with an initial TOF of 528 h⁻¹ (in 10 min) (Figure 4.5). Similarly, at lower

concentration of formic acid (1.5 mol L⁻¹), higher conversion of formic acid to H₂ and CO₂ is achieved with an initial TOF of 453 h⁻¹ (in 5 min) (Figure 4.5). Therefore, the observed trend in the formic acid generation and consumption during the formaldehyde dehydrogenation is consistent with the H₂/CO₂ ratio in the evolved gas.



Figure 4.5. Time course for hydrogen production from formic acid (a) 13.55 *mol* L^{-1} , 1.07 *mL and (b)* 1.5 *mol* L^{-1} , 1.07 *mL over catalyst* **[Ru]-2** (13 µmol) *in the presence of ligand L*14 (26 µmol) *at* 95 °C.

Notably, analysis of the catalytic reaction mixture by mass spectrometry evidenced the presence of several imidazole coordinated ruthenium species. The presence of mass peak at m/z 339 ([M-Cl]) for the reaction performed with L14/Ru ratio of 1 was assigned to an *in situ* formed (arene)Ru-imidazole species $[(\eta^6-C_{10}H_{14})Ru(L14)Cl_2]$, under the both catalytic and controlled reaction conditions (Figure 4.6). Analogously, for the reaction performed with higher L14/Ru ratio of 2 and 3, prominent mass peaks corresponding to the monocationic bis-imidazole ruthenium $[(\eta^6-C_{10}H_{14})Ru(L14)_2Cl]^+$ (m/z 407) and dicationic tris-imidazole ruthenium species $[(\eta^6-C_{10}H_{14})Ru(L14)_3]^{2+}$ (m/z 220), respectively were also observed (Figure 4.6). Therefore, these results inferred that the coordination behaviour of the imidazole ligand (L14) to ruthenium significantly tune the catalytic hydrogen production from formaldehyde. The observed increase in the catalytic activity upon increasing the imidazole contents (L14/Ru) in the reaction medium from 1 to 3, can be attributed to the formation of highly active Ru-imidazole species. However, during the course of the reaction the higher content of imidazole favors

the formation of bi-imidazole and tris-imidazole ruthenium species in the reaction, as confirmed by mass studies of the reaction mixture (Figure 4.6). On the other hand, monocationic bis-imidazole ruthenium $[(\eta^6-C_{10}H_{14})Ru(L14)_2Cl]^+$ was observed for the reaction mixture for L14/Ru ratio of 1, and it persist throughout the dehydrogenation reaction of formaldehyde. Mass investigations also evidenced the presence of methanediol coordinated ruthenium-imidazole species $[(\eta^6-C_{10}H_{14})Ru(L14)(HC(OH)O-)(H_2O)]^+$ (m/z 369) for the reaction performed with L14/Ru ratio of 1 (Figure 4.6).



Figure 4.6. (a) Ruthenium-imidazole (L14/Ru ratio of 1) species, (b) methanediol coordinated ruthenium-imidazole (L14/Ru ratio of 1), (c) ruthenium-bis-imidazole (L14/Ru ratio of 2), and (d) ruthenium-tris-imidazole (L14/Ru ratio of 3) coordinated species observed during mass studies.

Further, along with the ruthenium-imidazole species, mass peak at m/z 553 corresponding to the dinuclear ruthenium hydride species $[{(\eta^6-C_{10}H_{14})Ru}_2(\mu-H)(\mu-HCO_2)(\mu-Cl)]^+$ (**[Ru]-16**) was also observed during the catalytic reaction. We also obtained the solid state structure of the PF₆⁻ salt of this diruthenium species by single-

crystal X-ray diffraction, which inferred that two (η^6 -C₁₀H₁₄)Ru species are bridged with Cl⁻, H⁻ and HCOO⁻, analogous to the previously reported X-ray structure of its BF₄ salt by Perchtl *et. al* (Figure 4.7).^[9]



Figure 4.7. (a) X-ray crystal structures of the complex [Ru]-16 (with 30% ellipsoid probability and counter anion PF_6^- is omitted for the sake of clarity).

This diruthenium hydride species is considered to be one of the prominent species involved in the catalytic dehydrogenation of formaldehyde.^[9] Nevertheless, mass investigation of the reaction aliquots collected at regular intervals for the catalytic reaction performed with **L14/Ru** ratio of 1, inferred that the mass peaks corresponding to the ruthenium-imidazole persist throughout the dehydrogenation reaction of formaldehyde. These finding suggesting the possible involvement of the ruthenium-imidazole species in the catalytic dehydrogenation of formaldehyde.

As mass investigation evidenced the *in situ* generation of ruthenium-imidazole species during the catalytic dehydrogenation of formaldehyde, we further synthesized purified mono-, bis- and tris-imidazole ruthenium complexes, $[(\eta^6-C_{10}H_{14})Ru(L14)Cl_2]$ (**[Ru]-17**), $[(\eta^6-C_{10}H_{14})Ru(L14)_2Cl]Cl$ (**[Ru]-18**), and $[(\eta^6-C_{10}H_{14})Ru(L14)_3]Cl_2$ (**[Ru]-**

19), as the chloride salts. All the complexes were fully characterized, and the molecular structure of the ruthenium-bisimidazole complex $[(\eta^6-C_{10}H_{14})Ru(L14)_2Cl]Cl$ (**[Ru]-18**) was also confirmed by single-crystal X-ray diffraction. Unfortunately, its crystal refinement data is not suitable for publication. Nevertheless, the molecular structure and the arrangement of all the ligands around the Ru metal center corroborated well with the piano stool geometry in complex **[Ru]-18**, where $\eta^6-C_{10}H_{14}$ is placed on the top of Ru, while two imidazole and a chloro ligand occupied the three legs (Figure 4.8).



Figure 4.8. X-ray crystal structure of the complex *[Ru]-18* with 30% ellipsoid probability (Counter anions are omitted for the sake of clarity).

Further, we performed catalytic reactions for hydrogen production from aqueous formaldehyde with these purified ruthenium-imidazole complexes under the reaction condition analogous to that utilized for the *in situ* generated ruthenium catalysts. To our delight, we observed a close agreement of the gas evolution performance of these purified ruthenium-imidazole complexes with the *in situ* generated ruthenium-imidazole catalysts for hydrogen production from formaldehyde (Figure 4.9). Consistent with our findings, the mono-imidazole ruthenium complex [**Ru**]-17 outperformed over others with a steady rate of gas generation to yield over 400 mL of gas in 6 h (300 mL in 180 min). Analogously, with bis-imidazole ruthenium complex [**Ru**]-18, a total of 333 mL of gas

was generated in 180 min, which is also consistence with the trend observed with the *in situ* generated catalyst (**L14/Ru** ratio of 2) (Figure 4.9).



Figure 4.9. Time course for hydrogen production from aqueous formaldehyde (13.55 mol L⁻¹, 1.07 mL) in the presence of catalyst [*Ru*]-2 *(13 μmol) (with ligand L14),* [*Ru*]-17 *(26 μmol) and* [*Ru*]-16 *(26 μmol).*

On the other hand, we observed that earlier Perchtl et al. reported the production of ~300 mL of gas in 200 min over $[(\eta^6-C_{10}H_{14})RuCl_2]_2$ catalyst under base free condition, while employing the dinuclear diruthenium species $[\{(\eta^6-C_{10}H_{14})Ru\}_2(\mu-H)(\mu-HCO_2)(\mu-Cl)]^+$ only 180 mL of gas is released in 200 min.^[10] However, when reaction was performed in the presence of a base K₃PO₄, higher amount of gas generation (340 mL in 180 min) for $[\{(\eta^6-C_{10}H_{14})Ru\}_2(\mu-H)(\mu-HCO_2)(\mu-Cl)]^+$ was observed.^[10] These results inferred that indeed the dinuclear diruthenium species is involved in the dehydrogenation of formaldehyde, but is presumably not the most active catalytic species involved in the dehydrogenation of formaldehyde. Through literature, it has been observed that Prechtl *et al.* found this dinuclear diruthenium species more active for self-hydrogenation of formaldehyde to methanol.^[18] In contrary to the above, we observed that the monoimidazole ruthenium complex $[(\eta^6-C_{10}H_{14})Ru(L14)Cl_2]$ ([Ru]-17) yields much higher gas generation of 300 mL in 180 min (414 mL of gas in 6 h, TON of 471 in 3 h). Further, the clear resemblance of the catalytic performance of the purified mono-imidazole ruthenium complex [**Ru**]-17 with that of *in situ* generated ruthenium-imidazole catalyst using **L14/Ru** ratio of 1, evidenced the involvement of the ruthenium-imidazole species as the most prominent species in the catalytic production of hydrogen gas from formaldehyde in water at 95 °C. Based on the experimental evidences and the identification of various imidazole coordinated ruthenium species, we proposed a plausible reaction pathway, where presumably imidazole ligand plays a crucial role in proton exchange during the dehydrogenation process (Scheme 4.3). Initially Rumethanediol species ([**Ru**]-17B) was formed upon the coordination of H₂ (*via* a Ru-H intermediate), a ruthenium-formate species ([**Ru**]-17C) was formed. Consequently, [**Ru**]-17C undergoes decarboxylation to generate a Ru-H species ([**Ru**]-17D). Further, with the aid of imidazole ligand, an equivalent of H₂ molecule is released from [**Ru**]-17D.



Scheme 4.3. A plausible pathway for dehydrogenation of aqueous formaldehyde over [Ru]-17.

Notably, hydrogen production from formaldehyde was also observed at a temperature as low as 65 °C, where over 108 mL of gas was produced in the initial 180 min in the presence of **L14/Ru** catalyst (**L14/Ru** ratio of 1). A linear Arrhenius plot for the catalytic reaction performed in the temperature range of 65 °C – 95 °C suggesting activation energy of 18.7 kcal mol⁻¹ for the production of hydrogen from formaldehyde (Figure 4.10).^[13]



Figure 4.10. (a) Temperature dependent hydrogen production from aqueous formaldehyde and (b) the corresponding Arrhenius plot of initial TOF values (initial 10 min). (Reaction condition: aq. formaldehyde (13.55 mol L^{-1} , 1.07 mL), catalyst **[Ru]-2** (13 µmol) and ligand **L14** (26 µmol) at 95 °C).

Further to check the homogeneity of the reaction, the reaction performed with and without mercury and results inferred the homogenous nature of the catalyst with comparable gas generation in 3 h (Figure 4.11).



Figure 4.11. Mercury poisoning test for the catalytic reaction for hydrogen production from aqueous formaldehyde (13.55 mol L^{-1} , 1.07 mL) over the catalyst **[Ru]-2** (13 µmol) in the presence of ligand **L14** (26 µmol) at 95 °C (with/without added Hg).

Moreover, a distinct effect of the concentration of formaldehyde over the amount of gas released in the presence of **L14/Ru** catalyst was observed, where the rate of gas release increased markedly as the concentration of formaldehyde increase from 1.1 mol $L^{-1} - 13.55$ mol L^{-1} (Table 4.2 and Figure 4.12).



Figure 4.12. Hydrogen production from varying concentration of aqueous formaldehyde $(1.1-13.55 \text{ mol } L^{-1})$ over the catalyst [**Ru**]-2 (13 µmol) and ligand **L14** (26 µmol) at 95 °*C*.

Entry	Formaldehyde	Time	Evolved	Conv. (%)	Equivalents of
	$(mol L^{-1})$	(min)	gas (mL)		evolved gas
1.	1.1	65 min	75	93	2.8
2.	1.35	125 min	90.2	91	2.7
3.	1.5	92 min	108	98	2.9
4.	2	200 min	114.4	78	2.3
5.	6.75	200 min	268.2	54	1.6
6.	13.55	350 min	427.4	43	1.3

Table 4.2. Hydrogen production from varying concentration of formaldehyde

Reaction conditions: aqueous formaldehyde (1.07 mL), catalyst **[Ru]-2** (13 μmol), ligand **L14** (26 μmol) at 95 °C.

Results inferred that higher conversion (>98%) with the release of >2.94 equivalents of gas per mol of formaldehyde was achieved with **L14/Ru** catalyst for a diluted aqueous formaldehyde solution (1.5 mol L⁻¹) at 95 °C (Figure 4.13 and Table 4.3).



Figure 4.13. Time course plot for hydrogen production from aqueous formaldehyde. (Reaction condition: aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst [*Ru*]-2 (13 μ mol) and ligands *L9*, *L11* and *L14* (26 μ mol) at 95 °C).

Entry	Cat./ligand	Evolved Gas (equiv.)	$TOF (h^{-1})^{[b]}$
1	Ru	2.46	415
2	Ru/L9	2.42	406
3	Ru/L11	2.17	471
4	Ru/L14	2.94	509

Table 4.3. Hydrogen production from formaldehyde in water: Effect of ligands^[a]

^[a]Reaction was performed with aqueous formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst [**Ru]-2** (13 μmol), ligands **L9**, **L11** and **L14** (26 μmol) in 90 min at 95 °C. ^[b]Average TOF for initial 10 min.

Moreover, the generation of formic acid in the initial duration of the formaldehyde dehydrogenation and its further consumption observed during aq. formaldehyde (1.5 mol L^{-1}) dehydrogenation reaction is analogous to that observed with the dehydrogenation of 13.55 mol L^{-1} aq. formaldehyde (Figure 4.14).



Figure 4.14. (a) The H_2/CO_2 ratios in the produced gas mixture and (b) ¹H NMR yield of HCOOH during the catalytic dehydrogenation of aqueous formaldehyde in the initial 1 h of the reaction. (Reaction condition: aq. formaldehyde (1.5 mol L⁻¹, 1.07 mL), catalyst [**Ru**]-2 (13 µmol) and ligand L14 (26 µmol), at 95 °C. HCOOH yield was determined using dioxane as an internal standard).

Further, we also screened other ligands (L9 and L11) for the catalytic dehydrogenation of aq. formaldehyde at this optimal concentration. Results inferred an analogous trend to that observed with the dehydrogenation of 13.55 mol L^{-1} aq.

formaldehyde, where with the ligand **L14** superior catalytic activity was observed as compared to that observed with ligands **L9** and **L11**. Moreover, results also inferred a significant improvement in TOF in the presence of **L14**, as compared to the reaction performed without ligand or with other ligands.

Based on these findings, we performed reaction for bulk hydrogen production as well as for recyclability of catalyst from 1.5 mol L⁻¹ formaldehyde concentration catalyzed by **L14/Ru** under the optimized reaction condition. As shown from the time course plot of the bulk reaction (Figure 4.15), a TOF of 5715 h⁻¹ for the initial 10 min was achieved. Notably, we accomplished the long term bulk production of hydrogen gas for over 33 h with the turnover number of 12905, which is the second largest TON reported till date.^[13] Further, ¹H NMR of the spent reaction mixture inferred the presence of 24 mmol of formic acid. Advantageously, the average rate of gas production (426 mL min⁻¹ g_{cat}⁻¹) is also several folds higher than that reported earlier values under analogous condition.^[13]



Figure 4.15. Hydrogen production from a paraformaldehyde-water solution (inset shows the GC traces for the evolved gas in initial 5 min). (Reaction conditions: paraformaldehyde-water (1.5 mol L^{-1} , 40 mL), catalyst [**Ru**]-2 (2.5 µmol) and ligand **L14** (5 µmol) at 95 °C).

Further, we performed recyclability experiments to investigate the long term stability of the catalyst for the catalytic dehydrogenation of aq. formaldehyde solution

(1.5 mol L⁻¹). As inferred from Figure 4.16, the L14/Ru catalyst exhibited high catalytic activity for 8 consecutive cycle runs with an appreciably good conversion (>80%), evidenced the robustness of the L14/Ru catalyst. In contrary to the high performance of L14/Ru, a significant loss (even in the 4th catalytic run) in the catalytic activity for formaldehyde dehydrogenation was observed with catalyst [Ru]-2 in the absence of the ligand L14 under analogous reaction condition (Figure 4.17 and 4.18). These results clearly evidenced the crucial role of the ligand L14 in achieving high catalytic performance and catalyst robustness for formaldehyde dehydrogenation.



Figure 4.16. Long term stability and recyclability experiment for catalytic hydrogen production from aq. formaldehyde over the catayst [*Ru*]-2 in the presence of ligand *L14*. (Reaction condition: aq. formaldehyde (1.5 mol L^{-1} , 1.07 mL), catalyst [*Ru*]-2 (13 µmol) and ligand *L14* (26 µmol) at 95 °C, 1.5 mmol of formaldehyde added in each cycle).



Figure 4.17. Long term stability and recyclability experiment for hydrogen production from aqueous formaldehyde over complex [*Ru*]-2. (Reaction condition: aq. formaldehyde)

(1.5 mol L^{-1} , 1.07 mL), catalyst **[Ru]-2** (13 µmol) at 95 °C; 1.5 mmol of formaldehyde added in each cycle).



Figure 4.18. TOF comparison graph for hydrogen production from aqueous formaldehyde over [**Ru**]-2/L14 and [**Ru**]-2. (Reaction condition: aq. formaldehyde (1.5 mol L^{-1} , 1.07 mL), catalyst [**Ru**]-2 (13 µmol) and ligands L14 (26 µmol) at 95 °C).

4.4. Conclusion

In summary, we develop an efficient catalytic system for the production of hydrogen gas from formaldehyde and paraformaldehyde in water using ruthenium-imidazole catalysts under moderate condition. This catalytic system produces hydrogen from formaldehyde without the use of an external base and works effectively at 95 °C in water. We also achieve appreciably higher turnover number (>12000) and appreciably good TOF (5175 h^{-1}) in a long-term bulk hydrogen production from a paraformaldehyde-water solution over ruthenium-imidazole catalyst. Further, the studied catalyst also exhibited high catalyst recyclability for formaldehyde dehydrogenation in water. The present catalytic system may provide new insights to explore rather simple systems for efficient hydrogen production from liquid organic hydrogen carriers.

Spectral data for synthesized complexes



¹³C NMR spectra of complex [Ru]-17



¹H NMR spectra of complex [Ru]-18







ESI-MS spectra of complex [Ru]-18



¹³C NMR spectra of complex [Ru]-19



¹H NMR spectra of complex [Ru]-16



³¹P NMR spectra of complex [Ru]-16



ESI-MS spectra of complex [Ru]-16

Note: The content of this chapter is published as Awasthi et al., Sustainable Energy Fuels, 2021, 5, 549-555 (DOI: 10.1039/D0SE01330G) and reproduced here with the permission of Royal Society of Chemistry.

4.5. References

- Bockris J. O'M. (1972), A Hydrogen Economy, Science, 176, 1323 (DOI: 10.1126/science.176.4041.1323). (b) Armaroli N., Balzani V. (2011), The Hydrogen Issue, ChemSusChem, 4, 21-36 (DOI: 10.1002/cssc.201000182).
- Singh S. K., Xu Q. (2013), Nanocatalysts for hydrogen generation from hydrazine, *Catal. Sci. Technol.*, 3, 1889-1900 (DOI: 10.1039/C3CY00101F).
- Eberle U., Felderhoff M., Schuth F. (2009), Chemical and Physical Solutions for Hydrogen Storage, Angew. Chem., Int. Ed., 48, 6608–6630 (DOI: 10.1002/anie.200806293).
- 4. (a) Sartbaeva A., Kuznetsov V. L., Wells S. A., Edwards P. P. (2008), Hydrogen nexus in a sustainable energy future, Energy Environ. Sci., 1, 79-85 (DOI: 10.1039/B810104N); (b) Singh S. K., Singh A. K., Aranishi K., Xu Q. (2011), Noble-Metal-Free Bimetallic Nanoparticle-Catalyzed Selective Hydrogen Generation from Hydrous Hydrazine for Chemical Hydrogen Storage, J. Am. Chem. Soc., 133, 19638-19641 (DOI: 10.1021/ja208475y); (c) Singh S. K., Xu Q. (2009), Complete Conversion of Hydrous Hydrazine to Hydrogen at Room Temperature for Chemical Hydrogen Storage, J. Am. Chem. Soc., 131, 18032-18033 (DOI: 10.1021/ja908037t); (d) Singh S. K., Zhang X.-B., Xu Q. (2009), Room-Temperature Hydrogen Generation from Hydrous Hydrazine for Chemical Hydrogen Storage, J. Am. Chem. Soc., 131, 9894-9895 (DOI: 10.1021/ja903869y) (e) Awasthi M. K., Tyagi D., Patra S., Rai R. K., Mobin S. M., Singh S. K. (2018), Ruthenium complexes for catalytic dehydrogenation of hydrazine and transfer hydrogenation reactions, Chem. Asian J., 13, 1424 -1431 (DOI: 10.1002/asia.201800315).
- Jiang H. L., Singh S. K., Yan J. M., Zhang X. B., Xu Q. (2010), Liquid-phase chemical hydrogen storage: catalytic hydrogen generation under ambient conditions, *ChemSusChem*, 3, 541–549 (10.1002/cssc.201000023).
- 6. (a) Nielsen M., Alberico E., Baumann W., Drexler H.-J., Junge H., Gladiali S., Beller M. (2013), Low-temperature aqueous-phase methanol dehydrogenation to hydrogen and carbon dioxide, Nature, 495, 85–89 (DOI: 10.1038/nature11891);
 (b) Rodriguez-Lugo R. E., Trincado M., Vogt M., Tewes F., Santiso- Quinones

G., Grutzmacher H. (2013), A homogeneous transition metal complex for clean hydrogen production from methanol-water mixtures, Nat. Chem., 5, 342–347 (DOI: 10.1038/nchem.1595); (c) Hu P., Diskin-Posner Y., Ben-David Y., Milstein D. (2014), Reusable Homogeneous Catalytic System for Hydrogen Production from Methanol and Water, ACS Catal., 4, 2649-2652 (DOI: 10.1021/cs500937f); (d) Bielinski E. A., Forster M., Zhang Y., Bernskoetter W. H., Hazari N., Holthausen M. C. (2015), Base-Free Methanol Dehydrogenation Using a Pincer-Supported Iron Compound and Lewis Acid Co-catalyst, ACS Catal., 5, 2404–2415 (DOI: 10.1021/acscatal.5b00137); (e) Klankermayer J., Wesselbaum S., Beydoun K., Leitner W. (2016), Selective Catalytic Synthesis Using the Combination of Carbon Dioxide and Hydrogen: Catalytic Chess at the Interface of Energy and Chemistry, Angew. Chem. Int. Ed., 55, 7296–7343 (DOI: 10.1002/anie.201507458); (f) Kothandaraman J., Kar S., Sen R., Goeppert A., Olah G. A., Prakash G. K. S. (2017), Efficient Reversible Hydrogen Carrier System Based on Amine Reforming of Methanol, J. Am. Chem. Soc., 139, 2549-2552 (DOI: 10.1021/jacs.6b11637).

7. (a) Hull J. F., Himeda Y., Wang W. H., Hashiguchi B., Periana R., Szalda D. J., Muckerman J. T., Fujita E. (2012), Reversible hydrogen storage using CO₂ and a proton-switchable iridium catalyst in aqueous media under mild temperatures and pressures, Nat. Chem, 4, 383–388 (DOI: 10.1038/nchem.1295); (b) Wang W. H., Himeda Y., Muckerman J. T., Manbeck G. F., Fujita E., CO₂ Hydrogenation to Formate and Methanol as an Alternative to Photo- and Electrochemical CO₂ Reduction, Chem. Rev.. 2015. 115. 12936-12973 (DOI: 10.1021/acs.chemrev.5b00197); (c) Wang L., Onishi N., Murata K., Hirose T., Muckerman J. T., Fujita E., Himeda Y. (2017), Efficient Hydrogen Storage and Production Using a Catalyst with an Imidazoline-Based, Proton-Responsive Ligand, ChemSusChem, 10, 1071–1075 (DOI: 10.1002/cssc.201601437); (d) Li Z. P., Xu Q., Acc. Chem. Res., 2017, 50, 1449–1458; (e) Papp G., Csorba J., Laurenczy G., Joo F. (2011), A Charge/Discharge Device for Chemical Hydrogen Storage and Generation, Angew. Chem. Int. Ed., 50, 10433–10435 (DOI: 10.1002/anie.201104951); (f) Burgess S. A., Appel A. M., Linehan J. C., Wiedner E. S. (2017), Changing the Mechanism for CO₂ Hydrogenation Using Solvent-Dependent Thermodynamics, Angew. Chem., Int. Ed., 56, 15002–15005 (DOI: 10.1002/anie.201709319); (g) Bernskoetter W. H., Hazari N. (2017), Reversible Hydrogenation of Carbon Dioxide to Formic Acid and Methanol: Lewis Acid Enhancement of Base Metal Catalysts, Acc. Chem. Res., 50, 1049-1058 (DOI 10.1021/acs.accounts.7b00039); (h) Guan C., Zhang D.-D., Pan Y. P., Iguchi M., Ajitha M. J., Hu J. S., Li H. F., Yao C. G., Huang M. -H., Min S. X., Zheng J. R., Himeda Y., Kawanami H., Huang K.-W. (2017), Dehydrogenation of Formic Acid Catalyzed by a Ruthenium Complex with an N,N'-Diimine Ligand, Inorg. Chem., 56, 438-445 (DOI: 10.1021/acs.inorgchem.6b02334); (i) Singh A. K., Singh S., Kumar A. (2016), Hydrogen energy future with formic acid: a renewable chemical hydrogen storage system, Catal. Sci. Technol., 6, 12-40 (DOI: 10.1039/C5CY01276G); (j) Mellmann D., Sponholz P., Junge H., Beller M. (2016), Formic acid as a hydrogen storage material – development of homogeneous catalysts for selective hydrogen release, Chem. Soc. Rev., 45, 3954-3988 (DOI: 10.1039/C5CS00618J); (k) Eppinger J., Huang K.-W., ACS Energy Lett., 2017, 2, 188–195; (1) Sordakis K., Tang C. H., Vogt L. K., Junge H., Dyson P. J., Beller M., Laurenczy G. (2018), Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols, Chem. Rev., 118, 372-433 (DOI: 10.1021/acs.chemrev.7b00182).

- Trincado M., Grützmacher H., Prechtl M. H. G., CO₂-based hydrogen storage Hydrogen generation from formaldehyde/water, Phys. Sci. Rev., 2018, 3, 20170013 (DOI: 10.1515/psr-2017-0013).
- Fujita K. -I., Kawahara R., Aikawa T., Yamaguchi R. (2015), Hydrogen Production from a Methanol–Water Solution Catalyzed by an Anionic Iridium Complex Bearing a Functional Bipyridonate Ligand under Weakly Basic Conditions, Angew. Chem., Int. Ed., 54, 9057–9060 (DOI: 10.1002/anie.201502194).
- Heim L. E., Schlorer N. E., Choi J.-H., Prechtl M. H. G., (2014), Selective and mild hydrogen production using water and formaldehyde, Nat. Commun., 5, 3621 (DOI: 10.1038/ncomms4621).

- Suenobu T., Isaka Y., Shibata S., Fukuzumi S. (2015), Catalytic hydrogen production from paraformaldehyde and water using an organoiridium complex, Chem. Commun., 51, 1670–1672 (DOI: 10.1039/C4CC06581F).
- 12. Trincado M., Sinha V., Rodriguez-Lugo R. E., Pribanic B., Bruin B. D., Grutzmacher, H. (2017), Homogeneously catalysed conversion of aqueous formaldehyde to H_2 and carbonate, Nat. Commun., 8, 14990 (DOI: 10.1038/ncomms14990).
- Wang L., Ertem M. Z., Kanega R., Murata K., Szalda D. J., Muckerman J. T., Fujita E., Himeda Y. (2018), Additive-Free Ruthenium-Catalyzed Hydrogen Production from Aqueous Formaldehyde with High Efficiency and Selectivity, ACS Catal., 8, 8600–8605 (DOI: 10.1021/acscatal.8b02088).
- Patra S., Singh S. K. (2020), Hydrogen Production from Formic Acid and Formaldehyde over Ruthenium Catalysts in Water, Inorg. Chem., 59, 4234–4243 (DOI: 10.1021/acs.inorgchem.9b02882).
- (a) Bennett M. A., Huang T.-N., Matheson T. W., Smith A. K. (1982), Inorg. Synth., 21, 74-78 (DOI: 10.1002/9780470132524.ch16); (b) Zelonka R. A., Baird M. C. (1972), Benzene Complexes of Ruthenium(II), Can. J. Chem., 50, 3063-3072 (DOI: 10.1139/v72-486).
- Sheldrick G. M. (2008), A short history of SHELX, *Acta Crystallogr.*, *Sect. A*, 64, 112-122 (DOI: 10.1107/S0108767307043930).
- 17. Vock C. A., Scolaro C., Phillips A. D., Scopelliti R., Sava G., Dyson P. J. (2006), Synthesis, Characterization, and in Vitro Evaluation of Novel Ruthenium(II) η^6 -Arene Imidazole Complexes, J. Med. Chem., 49, 5552-5561 (DOI: 10.1021/jm0604950).
- Waals D. v. d., Heim L. E., Vallazza S., Gedig C., Deska J., Prechtl M. H. G. (2016), Self-Sufficient Formaldehyde-to-Methanol Conversion by Organometallic Formaldehyde Dismutase Mimic, *Chem. Eur. J.*, 22, 11568 11573 (DOI: 10.1002/chem.201602679).

Chapter 5

Low-Temperature Hydrogen Production from Methanol over Ruthenium Catalyst in Water

5.1. Introduction

Hydrogen is a potential clean energy carrier, and when used in fuel cell it produces only water as a byproduct. Unfortunately, the presence of hydrogen gas in the earth's atmosphere is extremely low (≈ 1 ppm by volume). Therefore, one of the major hurdles in exploring hydrogen economy with full potential is the safe production and storage of hydrogen gas. Notably, carrying big and heavy hydrogen cylinders with high pressure has critical safety and economical challenges. On the other hand, using liquid hydrogen storage materials (such as HCHO, CH₃OH, HCOOH) in the fuel tank of existing vehicles (using petroleum products) and generate hydrogen on-board to supply to Fuel Cell is not only a viable concept but is also very economical.^[1-12] In this context, methanol, which contains an appreciably high gravimetric content of hydrogen 12.5 wt% is a promising candidate for on-board and off-board (stationary) large-scale production of hydrogen gas.^[13-20] Notably, methanol offers several advantages, such as it is an inexpensive liquid, low carbon content (C1 alcohol), easy to store, and is being produced on large scale from biomass resources and hydrogen and carbon monoxide, or as industrial byproducts.^[13-20] Traditionally, hydrogen gas is being produced from methanol steam reforming process at a high-temperature range (200 °C - 350 °C), while catalyst assisted hydrogen production from methanol in water is more energy efficient as it operates at low temperature (< 190°C).

In principle, hydrogen production from methanol is mildly endothermic, therefore a suitable catalyst may activate methanol to produce hydrogen gas.^[14-24] Experimental evidences revealed that in the presence of a catalyst the dehydrogenation of methanol may follow the three consecutive pathways: initially, the dehydrogenation of methanol to formaldehyde and hydrogen (eq. 5.1), followed by the dehydrogenation of formaldehyde in the presence of water (gem-diol) to hydrogen and formic acid (eq. 5.2), and finally dehydrogenation of formic acid to hydrogen and CO₂ (eq. 5.3).

$$CH_3OH \rightarrow H_2CO + H_2 (\Delta H = 129.8 \text{ kJ mol}^{-1})$$
(5.1)

$$H_2CO + H_2O \rightarrow HCOOH + H_2 (\Delta H = -30.7 \text{ kJ mol}^{-1})$$
(5.2)

$$HCOOH \rightarrow CO_2 + H_2 (\Delta H = 31.6 \text{ kJ mol}^{-1})$$
(5.3)

A wide range of catalysts has been explored to utilize methanol, as a potential liquid hydrogen storage material, for the production of hydrogen gas at low-temperature with regulated emission of unwanted CO and methane.^[21,25] Recently, homogeneous catalysts based on Ru, Ir, Fe, and Mn have been explored to dehydrogenate methanol in presence of water and produce H₂ without or very low ppm of CO at the temperature below 100 °C.^[14,21,25-30] In particular, ruthenium-pincer based molecular catalysts exhibited higher activity to produce hydrogen from methanol in basic condition.^[25-26] In contrary to the above, heterogeneously catalyzed reforming of methanol to produce hydrogen and carbon dioxide has been continuously studied and developed, using different metal-based catalysts such as CuO/ZnO/Al₂O₃,^[31] Pd/CeO₂-ZrO₂,^[32] Pt₃Ni,^[33] and Ni-Fe-Mg^[34] alloys, but most of these catalysts require higher temperature over 200 °C and pressure. On the other hand, industrially viable heterogeneous catalysts for lowtemperature hydrogen production are rarely explored, until recently when Pt/MoC catalyst was explored for hydrogen production from methanol, but this catalyst worked effectively only at the higher temperature (150-190 °C) and using an expensive Pt catalyst.^[35]

Notable, the development of catalysts for the selective transformation of methanol to hydrogen gas (eq. 1) with the generation of formic acid is of critical importance, as it eliminates the energy-intensive process of CO₂ scrubbing from H₂ and CO₂ mixture obtained from complete transformation of methanol (eq. 5.1 and 5.2). Furthermore, the byproduct formic acid is also a worthful product and a potential hydrogen storage material.^[9] Herein, we synthesized ruthenium nanoparticles *in-situ* from an organometallic ruthenium complex and a ligand and utilized it to achieve efficient catalytic activity to produce hydrogen gas and formate/formic acid from methanol in the water at the lower temperature (90-130 °C). The structure of the ruthenium catalyst was established by TEM, XPS, P-XRD, ICP, TGA and several reaction parameters were

evaluated to achieve high catalytic activity for the low-temperature conversion of methanol to hydrogen gas and formate over the ruthenium catalyst in water.

5.2. Experimental section

5.2.1. Materials. All reactions were performed under Argon gas atmosphere using chemicals of high purity procured from Sigma Aldrich and Alfa Aesar unless otherwise specified. [$\{(\eta^6\text{-benzene})\text{RuCl}_2\}_2$] and [$\{(\eta^6\text{-}p\text{-}cymene)\text{RuCl}_2\}_2$] were synthesized using literature reports.

5.2.2. Instrumentation. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra are recorded at 298 K using D₂O as the solvent on a Bruker Avance 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm relative to the centre of the singlet at 4.75 ppm for D₂O in ¹H NMR. SEM images and EDS data were collected on Carl Zeiss supra 55 equipped with OXFORD instrument EDS X-ray spectrometer. Electron microscopy (TEM and HAADF-STEM) experiments and elemental analysis (EDX) were performed with a FEI Tecnai F20 ST TEM (operating voltage 200 kV) equipped with a field emission gun and EDAX EDS X-ray spectrometer [Si(Li) detecting unit, super ultrathin window, active area 30 mm² resolution 135 eV (at 5.9 keV)]. For TEM and SEM analysis, a few droplets of the nanoparticle suspension were deposited onto amorphous carbon-coated 400 mesh copper grids and eventually air-dried. Powder XRD measurements were performed on the dried particles on a Rigaku SmartLab, Automated Multipurpose x-ray Diffractometer at 40 kV and 30 mA using Cu K α radiation (λ = 1.5418 Å). The XPS analyses were conducted over PHI 5000 Versa Prob II,FEI Inc. Charge correction was based on the position of C 1s (C 284.6 eV) and to assigned the oxidation state of Ru in the catalyst, CuO used as an standard (Cu²⁺3p_{3/2} 933.5 eV in CuO). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was achieved with ARCOS, simultaneous ICP spectrometer of SPECTRO analytical instruments (SPECTRO Analytical Instruments). Thermogravimetric analysis (TGA) was performed over Mettler Toledo TGA instrument of the dried samples, under pure N₂ gas flow 50 mL min⁻¹ at a linear heating rate of 5°C min⁻¹. ESI-mass spectra are recorded on a micrOTFQ II mass spectrometer. The GC-TCD analyses are performed on a Shimadzu GC-2014 system using a shin carbon-ST packed column.

5.2.3. Catalytic hydrogen production from methanol. Typically, an appropriate amount of $[{(\eta^6-\text{benzene})\text{RuCl}_2}_2]$ **[Ru]-1** (0.05 mmol) (or other precursors) and ligand (0.1 mmol - 0.2 mmol) in methanol-water solution $(n(\text{CH}_3\text{OH})/n(\text{H}_2\text{O}) = 1:0 \text{ to } 1:2)$ was taken in a 5 mL test tube reaction vessel and was added an appropriate base (1.1 equiv. with respect to methanol). Then the reaction vessel, connected equipped with a condenser (-10 °C) and water displacement setup, was de-aerated and flushed with Ar. Further, the reaction mixture was stirred at a suitable temperature on an oil bath. The amount of gas generated per unit time was quantified by the water displacement method, and the composition of the released gas was confirmed by GC-TCD. The turnover number (TON) was calculated by the formula $[n(\text{H}_2)/n(\text{catalyst})]$. The turnover frequency (TOF) was calculated as TON/time. After the catalytic reaction, the supported ruthenium nanoparticles were collected by centrifugation and dried in a vacuum oven and weight to ~14 mg of catalysts (as obtained from 25 mg of [**Ru]-1** used in the catalytic reaction) which can be used for the further catalytic cycles.

5.2.4. Catalytic hydrogen production from ethanol/*n*-**propanol.** Catalytic hydrogen production from ethanol/n-propanol was performed following the procedure used for methanol, by using ethanol/n-propanol (16.08 mmol), **Ru/L9** catalyst (0.625 mol%, $n([\mathbf{Ru}]-\mathbf{1})/n(\mathbf{L9}) = 1:2$) and potassium hydroxide (1.2 equiv.) in water (1 equiv.). Then the 5 mL test tube reaction vessel, connected equipped with a condenser (-10 °C) and water displacement setup, was de-aerated and flushed with Ar. Further, the reaction mixture was stirred at 110 °C on an oil bath. The amount of gas generated per unit time was quantified by the water displacement method, and the composition of the released gas was confirmed by GC-TCD. The turnover number (TON) was calculated by the formula [$n(\mathrm{H}_2)/n(\mathrm{catalyst})$]. The turnover frequency (TOF) was calculated as TON/time.

5.2.5. Synthesis of ruthenium nanoparticles. Ru nanoparticles were synthesized by adding the dropwise of an aqueous solution of NaBH₄ (0.025 g, in 5 mL of water) in an aqueous solution of RuCl₃.3H₂O (0.026 g, 0.1 mmol, in 5 mL of water) and PVP (0.05 g). The content of the flask was sonicated for 10 min to obtain a black suspension of Ru nanoparticles, which were collected by centrifugation and was washed with distilled water (10 mL x 02).

5.2.6. Long term stability and recyclability experiments. Initially, the Ru/L9 catalyst (0.625 mol%, n([Ru]-1)/n(L9) = 1:2) in methanol (16.08 mmol) and water (1 equiv.) was taken in a 5 mL test tube reaction vessel, and was added KOH (1.2 equiv.). Then the reaction vessel, connected equipped with a condenser (-10 °C) and water displacement setup, was de-aerated and flushed with Ar. Further, the reaction mixture was stirred at 130 °C on an oil bath. The amount of gas generated per unit time was quantified by the water displacement method. For the subsequent catalytic run, the reaction mixture was centrifuged to separate the catalyst. Further, the catalyst was transferred to the reaction vessel, and methanol (16.08 mmol), water (1 equiv.) and KOH (1.2 equiv.) were added to the reaction vessel, and the reaction mixture was stirred at 130 °C on an oil bath under Argon atmosphere. The release of gas was monitored by water displacement process, and the composition of the released gas was confirmed by GC-TCD.

5.2.7. Estimating the performance of Ru/L9 catalyst for hydrogen production from methanol for industrial application. Considering the worldwide aggressive initiatives to promote hydrogen fueled vehicles, there will be a requirement of installing a huge number of hydrogen gas fueling stations. Hence, a huge infrastructure will be required to produce hydrogen gas in bulk scale and to be transported to recharge these fueling station. Alternatively, small and efficient hydrogen production units can be installed at the fueling stations to on-demand production of hydrogen gas. In this context, we estimated that 1 kg of H₂ gas can be produced from 14.5 L of methanol using the Ru/L9 catalyst at 130 °C. These estimated values are impressive, comparing to that observed for earlier reported highly active catalysts, 0.2%Pt/ α -MoC catalyst (1 kg H₂ per 546.5 L of methanol at 190 °C) and Ru-PNP complex (1 kg H₂ per 57.9 L methanol). Therefore, the Ru/L1 catalytic system represents a cost effective and industrially viable candidate to meet the requirement for bulk hydrogen production for application in recharging H₂ fueling stations for fuel cell-based vehicles and cater other related H₂-based energy requirements.

5.3. Results and discussion

At an outset, we employed $[{(\eta^6-\text{benzene})\text{RuCl}_2}_2]$ (**[Ru]-1**) as a pre-catalyst for hydrogen production from methanol (2:1 molar ratio of CH₃OH:H₂O) at 110 °C in the presence of 1.2 equiv. KOH, where we observed the release of 73 mol H₂ per mol of Ru (initial TOF 9 h⁻¹) (Table 5.1, entry 1). The evolved gas was identified as hydrogen by GC-TCD. Notably, the initial dark brown color of the reaction solution turned to a black suspension, which was identified as Ru nanoparticles (*ca.* 18.7 nm) by TEM (Figure 5.1).



Figure 5.1. TEM images of ruthenium nanoparticles obtained from **[Ru]-1** *in the absence of the ligand.*

Further, recent studies revealed that pyridine-based ligands can act as an internal base and play a crucial role in C-H activation reaction.^[36-37] We, therefore, investigated the role of 2-hydroxy pyridine (**L9**) as a promoter in the ruthenium-catalyzed hydrogen production from methanol. For **Ru/L9** catalyst (pre-catalyst [**Ru**]-1 in the presence of **L9**), we observed a significant enhancement of *ca*. 82% in the initial TOF with the release of 0.66

mol of H_2 per mol of methanol (TON of 106 mol H_2 per mol of Ru) (Table 5.1, entry 2 and Figure 5.2a).



Figure 5.2. Effect of (a) ligand L9 and (b) methanol to water molar ratio on the Ru/L9 catalyzed hydrogen production from methanol at 110 °C. (Reaction condition: methanol (16.08 mmol), Ru catalyst (0.625 mol%, n([Ru]-1)/n(L9) 1:2), KOH (1.2 equiv.) and methanol to water molar ratio (1:1), argon, ^amethanol to water molar ratio is 2:1, and ^b[Ru]-2 precursor is used).

When the reaction was performed using CH₃OH:H₂O molar ratio of 1:1, the intrinsic activity increased further to yield a TON of 134 mol of H₂ per mol of Ru (0.83 mol of H₂ per mol of methanol) with an improved initial TOF of 20 h⁻¹ (Table 5.1, entry 5 and Figure 5.2b). Notably, further increasing the water content (1:2 molar ratio of CH₃OH:H₂O) resulted in lower catalytic activity for H₂ production from methanol over **Ru/L9** catalyst (Table 5.1, entry 6, and Figure 5.2b), as compared to the reaction performed with high methanol content (CH₃OH:H₂O molar ratio of 1:1, 2:1 or 4:1) (Table 5.1 and Figure 5.2a). Literature reports on aqueous methanol dehydrogenation outlined the beneficial role of water in methanol dehydrogenation reaction.^[11,14] For instance, Grützmacher *et al.* achieved dehydrogenation of methanol using CH₃OH/H₂O 1:1 molar ratio, and mentioned that in the presence of water high gravimetric content of hydrogen can be achieved form methanol.^[111] Beller and other researchers also highlighted the role of water-promoted dehydrogenation of formaldehyde to formic acid and H₂ during methanol dehydrogenation reaction.^[25,38] Notably, Lin *et al.* also reported efficient hydrogen

production from methanol over Pt/α -MoC using higher water content (CH₃OH/H₂O molar of 1:3 and 1:1).^[35]

Entry	Cat.	<i>n</i> (alc.)/ <i>n</i> (H ₂ O)	T (°C)	KOH (equiv.)	<i>n</i> (H ₂)/ <i>n</i> (alc.)	<i>n</i> (H ₂)/ <i>n</i> (cat.)	TOF ^h (h ⁻¹)
1^b	Ru	2:1	110	1.2	0.45	73	9
2	Ru/L19	2:1	110	1.2	0.66	106	18
3	Ru/L9	4:1	110	1.2	0.68	109	13
4	Ru/L9	neat	110	1.2	0.63	102	14
5	Ru/L9	1:1	110	1.2	0.83	134	20
6	Ru/L9	1:2	110	1.2	0.25	40	14
7 ^c	Ru/L9	1:1	110	-	0.67	107	19
8	Ru/L9	1:1	130	1.2	1.42	229	49
9	Ru/L9	1:1	90	1.2	0.24	38	5
10^d	Ru/L9	1:1	110	1.2	0.50	81	11
11 ^e	RuNP/L 9	1:1	110	1.2	0.13	21	12
12^{f}	Ru/L9	1:1	110	1.2	0.61	98	20
13 ^g	Ru/L9	1:1	110	1.2	0.69	111	16

Table 5.1. Screening of catalyst to producing hydrogen from methanol^{*a*}

^{*a*}Reaction condition: alcohol (16.08 mmol), Ru catalyst (0.625 mol%, n([Ru]-1)/n(L9) 1:2), KOH (1.2 equiv.), 10 h, argon, ^{*b*} in the absence of ligand L9, ^{*c*} reaction with NaOMe in place of CH₃OH, ^{*d*} with [Ru]-2 and L9 (n([Ru]-

2)/n(**L9**) 1:2), ^{*e*}with pre-synthesised Ru nanoparticles and **L9** (1 equiv.), ^{*f*}using ethanol as reactant, ^{*g*}using *n*-propanol as reactant and ^{*h*}average turnover frequency (TOF) at 1 h.

Notably, we found that base played a crucial role in generating the active Ru nanoparticles in the initial hour of the reaction. Moreover, lower activity was observed while using less content of KOH (0.42 equiv.) (Table 5.2). Results inferred that compared to KOH, reaction with other bases such as NaOH, K'OBu, and K_2CO_3 exhibited either lower activity or no reaction (Table 5.3).

 Table 5.2. Effect of base concentration on catalytic hydrogen production from methanol

 over Ru/L9 catalyst

entry	base (equiv.)	n(H ₂)/n(methanol)	$n(H_2)/n(cat.)$
1	КОН (1.2)	0.66	106 (173) ^a
2	KOH (0.42)	0.23	38 (52) ^b

Reaction condition: methanol (16.08 mmol), Ru/L1 catalyst (0.625 mol%, n([Ru]-A)/n(L9) = 1:2), base, water (0.5 equiv.), 110 °C, 10 h, Argon. ^{*a*}29 h, ^{*b*}23 h 35 min.

Table 5.3. Effect of base on catalytic hydrogen production from methanol over Ru/L9 catalyst

entry	base	n(H ₂)/n(methanol)	n(H ₂)/n(cat.)
1	КОН	0.83	134
2	NaOH	0.77	123
3	K ^t OBu	0.45	72
4	K ₂ CO ₃	Nr	Nr

Reaction condition: methanol (16.08 mmol), Ru/L1 catalyst (0.625 mol%, $n([\mathbf{Ru}]-1)/n(\mathbf{L9}) = 1:2)$, base (1.2 equiv.), water (1 equiv.), 110 °C, 10 h, Argon. nr = no reaction.

It is worth noting that almost a similar amount of H_2 was released when NaOMe was used as a substrate instead of methanol, in absence of base, suggesting that presumably content of base is crucial for the deprotonation of methanol (Table 5.1, entry 7, and Figure 5.3).


Figure 5.3. Hydrogen production from NaOMe over Ru/L9 catalyst. Reaction condition: NaOMe (16.08 mmol), Ru/L1 catalyst (0.625 mol%, n([Ru]-1)/n(L9) = 1:2), water (1 equiv.), 110 °C, Argon.

Moreover, kinetic isotope effect (KIE) studies indicated that CD_3OD is more influential than D_2O in tuning the reaction rate for the **Ru/L9** catalyzed hydrogen production from methanol (Figure 5.4).



Figure 5.4. Kinetic isotope effect (KIE) experiments for hydrogen production from methanol over Ru/L9 catalyst. Reaction condition: CH₃OH/CD₃OD (16.08 mmol), Ru/L9 catalyst (0.625 mol%, n([Ru]-1)/n(L9) = 1:2), KOH (1.2 equiv.), H₂O/D₂O (1 equiv.), 110 °C, Argon.

These results inferred that the activation of methanol C-H bond is presumably the ratedetermining step and not the proton assisted release of hydrogen gas from methanol. Further, ¹³C NMR of the reaction aliquot after the completion of the catalytic reaction inferred the presence of formate with traces of carbonate, suggesting that decomposition of formate does not take place. Notably, performing the reaction with the spent **Ru/L9** catalyst resulted in no formate decomposition and no traces of carbonate was detected in ¹³C NMR (Figure 5.5).



Figure 5.5. ¹³*C NMR* spectra of the reaction mixture obtained after the reaction performed using the recovered catalyst. Reaction condition: methanol (16.08 mmol), spent **Ru/L9** catalyst, KOH (1.2 equiv.), water (1 equiv.), 110 °C, Argon.

Furthermore, the amount of formate formed as a co-product was also quantified to nearly half of the mol of H_2 gas generated during the reaction. GC-TCD analysis of the evolved gas is in good agreement with the observation of only purified hydrogen gas. When reaction temperature was increased to 130 °C, initial TOF increased by over ten-folds to 49 mol H_2 per mol Ru per hour as compared to the reaction performed at 90 °C (TOF of 5 mol H_2 per mol of Ru per hour) (Table 5.1, entries 5, 8, 9, and Figure 5.6).



Figure 5.6 (a) Temperature dependent hydrogen production from aqueous methanol, and (b) the corresponding Arrhenius plot of initial TOF values (initial 10 min). Reaction condition: methanol (16.08 mmol), Ru/L9 catalyst (0.625 mol%, n([Ru]-1)/n(L9) = 1:2), KOH (1.2 equiv.), water (1 equiv.), 110 °C – 130 °C Argon.

Notably, the **Ru/L9** catalyst exhibited the generation of 1.42 mol H₂ per mol of methanol (~71% conv.) (at 130 °C), which is several-folds higher than that reported for 0.2% Pt/ α -MoC catalyst (0.037 mol H₂ per mol of methanol at 190 °C).³⁵ The apparent activation energy for the conversion of methanol to H₂ over **Ru/L9** catalyst was estimated as 18.3 kcal/mol (Figure 5.6). Therefore, it is evident from these results that **Ru/L9** is active even at lower reaction temperature of 90 °C – 130 °C.

Further to detect various species that might form during the dehydrogenation of methanol, the reaction mixture at various time intervals (0, 15 and 60 min) was analyzed by ¹H and ¹³C NMR, where no traces of formaldehyde, methanediol, paraformaldehyde and trioxane were detected. Consistent with the literature reports, this can be attributed to the faster transformation of formaldehyde to formic acid and hydrogen in water as compared to methanol dehydrogenation to formaldehyde.^[11,18,38] Furthermore, we performed the catalytic dehydrogenation of aqueous formaldehyde (37 wt.%) under analogous reaction condition to methanol dehydrogenation and analyzed the evolved gas by GC-TCD and the reaction aliquots by NMR. Results inferred that indeed in the presence of base only pure hydrogen and formate was produced from formaldehyde dehydrogenation as confirmed by GC-TCD and NMR, respectively. Therefore, these results evidenced that

during methanol dehydrogenation under the optimized reaction condition, the possible intermediates such as formaldehyde or methanediol formed during the reaction may also undergo faster transformation to formic acid and H₂ gas, and therefore formaldehyde was not detected in the reaction solution. However, we have detected and isolated the formic acid generated during the methanol dehydrogenation reaction under the studied reaction condition.

Further, to obtain insights into the role of pyridine ligand, catalytic conversion of methanol to H_2 was also examined using 2-methoxy pyridine (**L17**) where a significant decline in the initial TOF (15 mol H_2 per mol Ru per hour) was observed with Ru/L17 catalyst as compared to the TOF of 20 mol H_2 per mol Ru per hour obtained with Ru/L9 catalyst (Figure 5.7).



Figure 5.7. Effect of ligands (*L9*, *L17* – *L19*) on the ruthenium catalyzed hydrogen production from methanol. Reaction condition: methanol (16.08 mmol), *Ru/Ligand catalyst* (0.625 mol%, n([Ru]-1)/n(Ligand) = 1:2), *KOH* (1.2 equiv.), water (1 equiv.), 3 h, 110 °C, Argon.

Further, the reaction performed using Ru/pyridine (L18) and Ru/phenol (L19) showed even lower activity (Figure 5.2c and Figure 5.7). These observations suggested the possible involvement of the 2-hydroxy pyridine ligand (L9) in promoting the facile activation of methanol over Ru nanoparticles to produce hydrogen gas with higher

activity. Notably, performing the catalytic reaction with the larger content of the ligand L1 (**Ru/L9** 1:4) resulted in lower activity yielding only 46 mol H₂ per mol Ru in 8 h as compared to 62 mol H₂ per mol of Ru for **Ru/L9** ratio of 1:2, presumably because excess ligands may poison the catalyst. Moreover, using [{(η^6 -p-cymene)RuCl₂}₂] ([**Ru**]-2) precursor instead of [**Ru**]-1 could not improve the catalytic activity (Table 5.1, entry 10).

Further, performing the catalytic reaction in the presence of pre-synthesized Ru nanoparticles with L9 resulted in only lower activity, suggesting that *in-situ* generated Ru nanoparticles in the presence of L9 in the more suitable condition to generate active Ru nanoparticle catalysts (Table 5.1, entry 11). Moreover, to know the nature of real catalyst for methanol dehydrogenation, we performed a series of poisoning experiments using Whitesides' mercury test.^[25] Results inferred that the catalytic reaction quenched in the presence of Hg(0) (>300 equiv.) due to the poisoning of the **Ru/L9** catalyst by amalgam formation. In contrary to the control reaction, the addition of Hg(0) (>300 equiv.) at the beginning of the reaction resulted in complete quenching of the catalytic methanol dehydrogenation, suggesting the heterogeneous nature of the Ru/L9 catalyst. Further, in another experiment, the spent Ru/L9 catalyst was also stirred with an excess of added Hg(0) (>300 equiv.), before employing it as a catalyst for methanol dehydrogenation reaction under the optimized reaction condition, but no gas release was observed. It is worth noting here, that the spent Ru/L9 catalyst was found to be highly active (in the absence of Hg(0)), supports the heterogeneous nature of the studied catalysts. Moreover, the Ru/L9 catalyst also exhibited appreciable long-term stability, where a total turnover number (TON) of 762 mol of H_2 per mol of Ru was achieved in a 7-cycle recyclability experiment generating 186 L of H_2 gas per gram of Ru (Figure 5.8).



Figure 5.8. Long term stability and recyclability experiment for Ru/L9 catalyzed production of H_2 from methanol at 130 °C.

On the other hand, continuing the reaction with the reaction solution (supernatant), obtained after the removal of Ru/L9 catalyst, resulted in no release of gas even after extending the catalytic reaction for a longer duration (10 h). The literature revealed that reaction performed under reducing condition may result in the transformation of organometallic Ru precursor to Ru(0) nanoparticles.^[39-43] Chaudret et al. established the mechanism and the process for the transformation of organometallic ruthenium complexes to Ru nanoparticles.^[42-43] Similarly some other groups have also established the transformation of organometallic ruthenium complexes to Ru nanoparticles.^[40] Therefore, in absence of induction period during the in-situ transformation of **[Ru]-1** to Ru nanoparticles can be attributed to the highly reducing reaction condition due to the presence of KOH, H₂ gas and 110-130 °C. Further, ICP-OES analysis of the recovered nanoparticles inferred the presence of ~54 wt.% of Ru, whereas no traces of metal were detected (detection limit of 0.01 ppm) in the supernatant, evidence the absence of ruthenium species in the reaction mixture also supports the complete transformation of **[Ru]-1** precursor to Ru nanoparticles. Moreover, the liquid portion (supernatant) was also analyzed by ESI-MS, where any isotopic patterns corresponding to ruthenium was not observed, further suggesting that ruthenium complex is converted to ruthenium nanoparticles during the reaction and no residual ruthenium species is

present in the solution. Therefore, the above findings evidenced the heterogeneous nature of the **Ru/L9** catalyst for methanol dehydrogenation. Furthermore, the ethanol and *n*-propanol were also investigated under catalytic reaction conditions and the results showed that the studied **Ru/L9** catalysts can also efficiently generate hydrogen gas along with value-added products such as acetic acid (Table 5.1, entries 12, 13, and Figure 5.9).



Figure 5.9. Hydrogen production using different alcohols (methanol, ethanol and n-propanol) over Ru/L9 catalyst. Reaction condition: alcohol (16.08 mmol), Ru/L9 catalyst (0.625 mol%, n([Ru]-1)/n(L9) = 1:2), KOH (1.2 equiv.), water (1 equiv.), 110 °C, Argon.

The activity of the catalyst slightly decreased with subsequent catalytic runs, attributed to the surface oxide coating of the Ru catalyst, as also confirmed by XPS analysis (Figure 5.10). Though the turnover number was relatively low for the studied **Ru/L9** catalyst, it is evident that **Ru/L9** catalysts exhibited the generation of higher equivalents of hydrogen gas per moles of methanol ($n(H_2)/n(MeOH)$ 1.42) as compared to the earlier reported catalysts. Moreover, in the studied catalytic system, formate/formic acid is obtained as a worthful byproduct. Advantageously, this resulted in the generation of hydrogen gas in high purity from methanol. Therefore, the studied **Ru/L9** catalytic system could be a promising candidate for low-temperature bulk hydrogen production from methanol.



Figure 5.10. XPS spectra corresponding to (a) $Ru \ 3p_{3/2}$ (b) $Ru \ 3d_{5/2}$ and (c) N 1s core for ruthenium catalyst obtained in the absence of ligand L9.

To obtain insights into the structural and chemical nature of the *in-situ* generated **Ru/L9** catalyst, we employed several characterization methods. Powder X-ray diffraction of Ru nanoparticles obtained after the catalytic reaction showed a broad peak at 25-45°, suggesting the highly dispersed small Ru nanoparticles over the carbon support.^[44] Transition electron microscopy (TEM) images confirm the existence of homogenous dispersion of Ru nanoparticles of particle size *ca.* 1.5 nm on the carbon support (Figure 5.11a). Furthermore, the dispersion of *in-situ* generated ruthenium nanoparticles in the presence of **L9** ligand was also estimated as 86%, as calculated from the generalized equations using mean particle size (d_{TEM}) as obtained from the TEM by considering ~110 particles.^[45-46] In sharp contrast, without ligand, the Ru nanoparticles have an average particle size of *ca.* 18.7 nm with poor dispersion (Figure 5.11). High angle annular darkfield (HAADF) scanning transmission electron microscopy (STEM) images and energy-dispersive X-ray spectroscopic (EDS) analysis inferred the presence of Ru element (Figure 5.11b-d). Moreover, the EDS line scan also confirmed the even distribution of Ru nanoparticles over the carbon support (Figure 5.11d).



Figure 5.11 (a) TEM image (inset particle size distribution), (b) EDS point analysis, and (c) HAADF image and the corresponding (d) EDS line scan analyses for Ru/L9 catalyst.

Thermogravimetric analysis of the *in-situ* generated **Ru/L9** catalyst inferred the presence of large organic content (~30% more) as compared to the Ru nanoparticles obtained in the absence of the ligand **L9**. Further, the presence of 0.74% nitrogen content observed for **Ru/L9** in the elemental analysis, further suggesting the presence of the ligand **L9** in the catalyst. Such behavior is consistent with the stabilization of smaller Ru nanoparticles with 2-hydroxypyridine ligand (**L9**). This phenomenon was also revealed earlier where Ru nanoparticles were stabilized by small ligands.^[47-48] In addition, the binding energy of **Ru/L9** as obtained from X-ray photoelectron spectroscopy (XPS) experiment for both Ru(3d) and Ru(3p) core levels are assigned to the oxidation state of Ru in the catalyst using CuO as a standard (Cu²⁺3p_{3/2} 933.5 eV in CuO). In the XPS spectra of **Ru/L9** catalyst, peak maxima observed at the binding energy values of 461.7 eV (Ru 3p_{3/2}) and 279.8 eV (Ru 3d_{5/2}) are assigned to the metallic ruthenium (Figure 5.12 and Figure 5.10). Moreover, the low-intensity XPS peak at 399.07 eV corresponding to N 1s for the XPS of **Ru/L9** catalyst, manifested the presence of the ligand over the ruthenium nanoparticles (Figure 5.12).



*Figure 5.12. XPS spectra corresponding to the (a) Ru 3p*_{3/2} *(b) Ru 3d*_{5/2} *and (c) N 1s core levels of Ru/L9 catalyst.*

Notably, XPS of the Ru nanoparticles obtained in the absence of ligand L9 inferred the higher content of ruthenium oxide (Figure 5.10), further suggesting that the presence of ligand L9 over the Ru nanoparticles prevented the facile oxidation of the surface in **Ru/L9** catalyst. Hence, the observed enhanced catalytic performance of the **Ru/L9** catalyst can be attributed to the smaller particle size ruthenium nanoparticles and the ligand L9.

5.3. Concusions

We developed an efficient new **Ru/L9** catalyst comprises of ligand capped ruthenium nanoparticles homogeneously dispersed over the carbon support, *in-situ* generated from the ruthenium arene precursor and 2-hydroxypyridine (**L9**) ligand. The **Ru/L9** catalytic system displayed excellent catalytic activity for CO₂ free hydrogen production from methanol (1.43 mol of H₂ per mol of methanol) at low temperature (110 – 130 °C). This process also generated formic acid as a byproduct. The studied catalyst exhibited outstanding long-term stability to generate 186 L of H₂ gas per gram of Ru. This catalytic system may encourage the search of an efficient industrially viable process for the low-temperature transformation of methanol to hydrogen gas and formic acid.

Note: The content of this chapter is published as Awasthi et al., Catal. Sci. Technol., 2021, 11, 136-142 (DOI: 10.1039/D0CY01470B) and reproduced here with the permission of Royal Society of Chemistry.

5.5. References

- Schlapbach L., Züttel A. (2001), *Nature*, Hydrogen-storage materials for mobile applications, 414, 353–358 (DOI: 10.1038/35104634).
- Orimo S., Nakamori Y., Eliseo J. R., Züttel A., Jensen C. M. (2007), Complex Hydrides for Hydrogen Storage, *Chem. Rev.*, 107, 4111–4132 (DOI: 10.1021/cr0501846).
- Eberle U., Felderhoff M., Schuth F. (2009), Chemical and Physical Solutions for Hydrogen Storage, *Angew. Chem., Int. Ed.*, 48, 6608–6630 (DOI: 10.1002/anie.200806293).
- Yang J., Sudik A., Wolverton C., Siegel D. J. (2010), High capacity hydrogenstorage materials: attributes for automotive applications and techniques for materials discovery, *Chem. Soc. Rev.*, 39, 656–675 (DOI: 10.1039/B802882F).
- Singh S. K., Xu Q. (2013), Nanocatalysts for hydrogen generation from hydrazine, *Catal. Sci. Technol.*, 3, 1889-1900 (DOI: 10.1039/C3CY00101F).
- Singh S. K., Singh A. K., Aranishi K., Xu Q. (2011), Noble-Metal-Free Bimetallic Nanoparticle-Catalyzed Selective Hydrogen Generation from Hydrous Hydrazine for Chemical Hydrogen Storage, *J. Am. Chem. Soc.*, 133, 19638-19641 (DOI: 10.1021/ja208475y).
- Singh S. K., Xu Q. (2009), Complete Conversion of Hydrous Hydrazine to Hydrogen at Room Temperature for Chemical Hydrogen Storage, *J. Am. Chem. Soc.*, 131, 18032-18033 (DOI: 10.1021/ja908037t).
- Singh S. K., Zhang X.-B., Xu Q. (2009), Room-Temperature Hydrogen Generation from Hydrous Hydrazine for Chemical Hydrogen Storage, *J. Am. Chem. Soc.*, 131, 9894-9895 (DOI: 10.1021/ja903869y).
- Patra S., Singh S. K. (2020), Hydrogen Production from Formic Acid and Formaldehyde over Ruthenium Catalysts in Water, *Inorg. Chem.*, 59, 4234–4243 (DOI: 10.1021/acs.inorgchem.9b02882).

- Heim L. E., Schlorer N. E., Choi J.-H., Prechtl M. H. G., (2014), Selective and mild hydrogen production using water and formaldehyde, *Nat. Commun.*, 5, 3621 (DOI: 10.1038/ncomms4621).
- Trincado M., Sinha V., Rodriguez-Lugo R. E., Pribanic B., Bruin B. D., Grutzmacher, H. (2017), Homogeneously catalysed conversion of aqueous formaldehyde to H₂ and carbonate, *Nat. Commun.*, 8, 14990 (DOI: 10.1038/ncomms14990).
- Trincado M., Grützmacher H., Prechtl M. H. G. (2018), CO₂-based hydrogen storage – Hydrogen generation from formaldehyde/water, *Phys. Sci. Rev.*, 3, 20170013 (DOI: 10.1515/psr-2017-0013).
- Heim L. E., Thiel D., Gedig C., Deska J., Prechtl M. H. G. (2015), Bioinduced Room-Temperature Methanol Reforming, *Angew. Chem., Int. Ed.*, 54, 10308– 10312 (DOI: 10.1002/anie.201503737).
- van de Watering F. F., Lutz M., Dzik W. I., de Bruin B., Reek J. N. H. (2016), Reactivity of a Ruthenium–Carbonyl Complex in the Methanol Dehydrogenation Reaction, *ChemCatChem*, 8, 2752-2756 (DOI: 10.1002/cctc.201600709).
- Cheng W. H., Kung H. H. (1994), Methanol production and use, Kung H. H and Cheng W.-H., Marcel Dekker, New York, (ISBN: 0824792238).
- Dina I. U., Shaharunb M. S., Alotaibia M. A., Alharthia A. I., Naeem A. (2019), Recent developments on heterogeneous catalytic CO₂ reduction to methanol, *J. CO₂ Util.*, 34, 20–33 (DOI: 10.1016/j.jcou.2019.05.036).
- Jadhava S. G., Vaidyaa P. D., Bhanageb B. M., Joshi J. B. (2014), Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies, *Chem. Eng. Res. Des.*, 92, 2557–2567.
- Alberico E., Nielsen M. (2015), Towards a methanol economy based on homogeneous catalysis: methanol to H₂ and CO₂ to methanol, *Chem. Commun.*, 51, 6714–6725 (DOI: 10.1039/C4CC09471A).

- Sordakis K., Tang C., Vogt L. K., Junge H., Dyson P. J., Beller M., Laurenczy G. (2018), Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols, *Chem. Rev.*, 118, 372-433 (DOI: 10.1021/acs.chemrev.7b00182).
- Crabtree R. H. (2017), Homogeneous Transition Metal Catalysis of Acceptorless Dehydrogenative Alcohol Oxidation: Applications in Hydrogen Storage and to Heterocycle Synthesis, *Chem. Rev.*, 117, 9228–9246 (DOI: 10.1021/acs.chemrev.6b00556).
- Rodriguez-Lugo R. E., Trincado M., Vogt M., Tewes F., Santiso- Quinones G., Grutzmacher H. (2013), A homogeneous transition metal complex for clean hydrogen production from methanol–water mixtures, *Nat. Chem.*, 5, 342–347 (DOI: 10.1038/nchem.1595).
- 22. Sá S., Silva H., Brandão L., Sousa J. M., Mendes A. (2010), Catalysts for methanol steam reforming—A review, *Appl. Catal. B*, 99, 43–57 (DOI: 10.1016/j.apcatb.2010.06.015).
- Setthapun W., Bej S. K., Thompson L. T. (2008), Carbide and Nitride Supported Methanol Steam Reforming Catalysts: Parallel Synthesis and High Throughput Screening, *Top. Catal.*, 49, 73–80 (DOI: 10.1007/s11244-008-9070-7).
- Palo D. R., (2007), Methanol Steam Reforming for Hydrogen Production, *Chem. Rev.*, 107, 3992-4021 (DOI: 10.1021/cr050198b).
- Nielsen M., Alberico E., Baumann W., Drexler H.-J., Junge H., Gladiali S., Beller M. (2013), Low-temperature aqueous-phase methanol dehydrogenation to hydrogen and carbon dioxide, *Nature*, 495, 85–89 (DOI: 10.1038/nature11891).
- 26. Hu P., Diskin-Posner Y., Ben-David Y., Milstein D. (2014), Reusable Homogeneous Catalytic System for Hydrogen Production from Methanol and Water, ACS Catal., 4, 2649–2652 (DOI: 10.1021/cs500937f).
- Bielinski E. A., Forster M., Zhang Y., Bernskoetter W. H., Hazari N., Holthausen M. C. (2015), Base-Free Methanol Dehydrogenation Using a Pincer-Supported

Iron Compound and Lewis Acid Co-catalyst, *ACS Catal.*, 5, 2404–2415 (DOI: 10.1021/acscatal.5b00137).

- Prichatz C., Alberico E., Baumann W., Junge H., Beller M. (2017), Iridium–PNP Pincer Complexes for Methanol Dehydrogenation at Low Base Concentration, *ChemCatChem*, 9, 1891–1896 (DOI: 10.1002/cctc.2017S00015).
- Campos J., Sharninghausen L. S., Manas M. G., Crabtree R. H. (2015), Methanol Dehydrogenation by Iridium N-Heterocyclic Carbene Complexes, *Inorg. Chem.*, 54, 5079–5084 (DOI: 10.1021/ic502521c).
- 30. Anderez-Fernandez M., Vogt L. K., Fischer S., Zhou W., Jiao H., Garbe M., Elangovan S., Junge K., Junge H., Ludwig R., Beller M. (2017), A Stable Manganese Pincer Catalyst for the Selective Dehydrogenation of Methanol, *Angew. Chem., Int. Ed.*, 56, 559–562 (DOI: 10.1002/anie.201610182).
- Lee J. K., Ko J. B., Kim D. H. (2004), Methanol steam reforming over Cu/ZnO/Al₂O₃ catalyst: kinetics and effectiveness factor, *Appl. Catal. A Gen.*, 278, 25–35 (DOI: 10.1016/j.apcata.2004.09.022).
- Zhao M., Zhang H., Li X., Chen Y. (2014), Co-modified Pd/CeO₂-ZrO₂ catalysts for methanol decomposition, *J. Energ. Chem.*, 23, 755–760 (DOI: 10.1016/S2095-4956(14)60209-6).
- 33. Du P., Wu P., Cai C. (2017), Mechanism of Methanol Decomposition on the Pt₃Ni(111) Surface: DFT Study, *J. Phys. Chem. C*, 121, 9348–9360 (DOI: 10.1021/acs.jpcc.7b01114).
- Mitani H., Xu Y., Hirano T., Demura M., Tamura R. (2017), Catalytic properties of Ni-Fe-Mg alloy nanoparticle catalysts for methanol decomposition, *Catal. Today*, 281, 669–676 (DOI: 10.1016/j.cattod.2016.10.036).
- 35. Lin L., Zhou W., Gao R., Yao S., Zhang X., Xu W., Zheng S., Jiang Z., Yu Q., Li Y.-W., Shi C., Wen X.-D., Ma D. (2017), Low-temperature hydrogen production from water and methanol using Pt/α-MoC catalysts, *Nature*, 544, 80-83 (DOI: 10.1038/nature21672).

- 36. Wang P., Verma P., Xia G., Shi J., Qiao J. X., Tao S., Cheng P. T. W., Poss M. A., Farmer M. E., Yeung K.-S., Yu J.-Q. (2017), Ligand-accelerated non-directed C–H functionalization of arenes, *Nature*, 551, 489–494 (DOI: 10.1038/nature24632).
- Binnani C., Rai R. K., Tyagi D., Mobin S. M., Singh S. K. (2018), Ligand-Tuned C–H Bond Activation/Arylation of 2-Arylpyridines over Pyridine-Based N,O/N,N Ligated Ruthenium–Arene Complexes, *Eur. J. Inorg. Chem.*, 1435–1445 (DOI: 10.1002/ejic.201701446).
- 38. Wakizaka M., Matsumoto T., Tanaka R., Chang H.-C., Dehydrogenation of anhydrous methanol at room temperature by *o*-aminophenol-based photocatalysts, *Nat. Commun.* 2016, 7, 12333 (DOI: 10.1038/ncomms12333).
- 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).
- 40. Widegren J. A., Bennett M. A., Finke R. G. (2003), Is It Homogeneous or Heterogeneous Catalysis? Identification of Bulk Ruthenium Metal as the True Catalyst in Benzene Hydrogenations Starting with the Monometallic Precursor, Ru(II)(η⁶-C₆Me₆)(OAc)₂, Plus Kinetic Characterization of the Heterogeneous Nucleation, Then Autocatalytic Surface-Growth Mechanism of Metal Film Formation, J. Am. Chem. Soc., 125, 10301-10310 (DOI: 10.1021/ja021436c).
- Crabtree R. H., (2012), Resolving Heterogeneity Problems and Impurity Artifacts in Operationally Homogeneous Transition Metal Catalysts, *Chem. Rev.*, 112, 1536–1554 (DOI: 10.1021/cr2002905).
- Philippot K., Lignier P., Chaudret B. (2014), Organometallic Ruthenium Nanoparticles and Catalysis, *Top Organomet Chem.*, 48, 319–370 (DOI: 10.1007/3418_2014_83).
- 43. Martínez-Prieto L. M., Chaudret B. (2018), Organometallic Ruthenium Nanoparticles: Synthesis, Surface Chemistry, and Insights into Ligand

Coordination, *Acc. Chem. Res.*, 51, 376–384 (DOI: 10.1021/acs.accounts.7b00378).

- 44. Ohyama J., Kumada D., Satsuma A. (2016), Improved hydrogen oxidation reaction under alkaline conditions by ruthenium–iridium alloyed nanoparticles, J. Mater. Chem. A, 4, 15980–15985 (DOI: 10.1039/c6ta05517f).
- 45. Gallezot P., Bergeret G. (2008), in Handbook of Heterogeneous Catalysis, 738–765 (ISBN: 978-3-527-31241-2).
- 46. Borodzinski A., Bonarowska M. (1997), Relation between Crystallite Size and Dispersion on Supported Metal Catalysts, *Langmuir*, 13, 5613-5620 (DOI: 10.1021/la962103u).
- 47. Creus J., Drouet S., Suriñach S., Lecante P., Collière V., Poteau R., Philippot K., García-Antón J., Sala X. (2018), Ligand-Capped Ru Nanoparticles as Efficient Electrocatalyst for the Hydrogen Evolution Reaction, ACS Catal., 8, 11094–11102 (DOI: 10.1021/acscatal.8b03053).
- 48. García-Antón J., Axet M. R., Jansat S., Philippot K., Chaudret B., Pery T., Buntkowsky G., Limbach H. H. (2008), Reactions of Olefins with Ruthenium Hydride Nanoparticles: NMR Characterization, Hydride Titration, and Room-Temperature C-C Bond Activation, *Angew. Chem., Int. Ed.*, 47, 2074–2078 (DOI: 10.1002/anie.200704763).

Chapter 6

Summary and Future Scope

6.1 Summary of the PhD thesis work

Indeed using hydrogen gas as the energy carrier is a more sustainable and environmental friendly way to meet the global energy demand. Hydrogen can be produced by water electrolysis, gasification of biomass, reforming of hydrocarbons and methanol, and so on. Process such as gasification and reforming needs high temperature and pressure to produce hydrogen. However, contamination of the produced hydrogen gas with CO, CO₂ and other harmful gases are the major drawback with the reforming and gasification processes. On the other hand, water electrolysis is an energy-intensive process, which also suffers from low efficiency. Therefore, it is the need of the hour to explore and develop low-temperature hydrogen production techniques for the selective production of hydrogen. Apart from the hydrogen production processes, the easy and safe storage and transportation of hydrogen gas are one of the major challenges in realizing the Hydrogen Economy. Due to some physical and chemical properties of hydrogen, the storage of large content of hydrogen in high-pressure cylinders is difficult and challenging. Therefore, conventionally hydrogen is being stored in the form of liquid for hydrogen supply under on-board or off-board usage. However liquid hydrogen or hydrogen stored under high pressure, which both have 100 wt% of hydrogen have several drawbacks such as in the case of liquid hydrogen, its needs -252.87 °C temperature and 1.013 bar pressure to liquefy hydrogen. Further heat flow takes place from the environment to the container leads to the evaporation of hydrogen and due to that the pressure inside the container increase and after some time its needs to vent in the environment to maintain the inside pressure. In this process, even in an ideal parking state, the hydrogen loss to the environment is called boil off the gas. Furthermore, in the case of hydrogen stored under high pressure needs 35-70 MPa pressure. However above this pressure, deviations from the ideal gas behavior are too large, and lowering the pressure decreases the energy content. On the other hand, the liquid

hydrogen carriers, offers several advantages as these are liquid at room temperature and hence can be easily and safely stored and transported and also that these liquid hydrogen carriers contains high hydrogen content which can be generated with the intervention of a suitable catalyst under moderate conditions. Notably, efforts are being made to develop efficient, additive-free and low-temperature processes for hydrogen production from these liquid hydrogen carriers for the onboard/offboard production of hydrogen. An intensive literature study of liquid hydrogen storage sources evidenced some open questions for the hydrogen production from various liquid hydrogen storage sources such as hydrazine, methanol, formaldehyde and aromatic alcohols.

For hydrazine dehydrogenation, most of the literature reports are based on heterogeneous catalysts, while homogeneous metal complexes-based catalysts are not extensively explored for hydrazine dehydrogenation. Though the complexation of hydrazine with metal complexes are studied well, insitu identification of important intermediates and the detailed investigation of the mechanistic pathway for hydrogen production from hydrazine over homogeneous catalysts need to be explored.

Further low-temperature, additive-free hydrazine dehydrogenation also needs to be explored using metal complexes. Moreover, acceptorless dehydrogenation of alcohols can produce hydrogen along with the value-added chemicals is an atom economic process. In this regard, acceptorless dehydrogenation of alcohols has been explored using the various homogeneous complexes, but the activity of the studied complexes needs to be improved. Particularly, the reaction needs to be performed and designed to produce hydrogen gas with high turnover at low temperature and with green solvents under additive-free conditions. Furthermore, few recent reports using ruthenium-based complexes for hydrogen production from formaldehyde has been explored at a temperature <100 °C, but still, efforts need to be made to develop more robust catalysts for hydrogen production from formaldehyde at low temperature/room temperature in water. Further, detailed mechanistic investigations to study the role of the catalyst in hydrogen production from formaldehyde is also required.

Apart from higher alcohols, methanol also contains a high weight percentage of

hydrogen, however, the production of hydrogen from methanol is performed at a high-temperature reforming process (>200 °C), which suffers from several drawbacks including contamination of hydrogen produced. Therefore, considering the importance of this process, efforts need to be made for the selective production of hydrogen gas from methanol at low temperature using suitable catalysts. Therefore, to address these research gaps and the limitations with the existing process for hydrogen production from liquid hydrogen carries, in this PhD work several low-temperature hydrogen production techniques are developed by utilizing a wide range of ruthenium-based catalysts to efficiently and selectively produce hydrogen gas from liquid hydrogen carriers such as hydrazine, methanol, formaldehyde and aromatic alcohols under moderate reaction condition.

For the hydrogen production from hydrazine, several arene-ruthenium based molecular catalysts containing N-substituted imino-pyridine ligands were employed at 80 °C in ethanol and THF-methanol in the presence of a suitable base. Experimental findings inferred the crucial role of the ligand in tuning the catalytic efficacy, where N-hydroxyiminopyridine ligated ruthenium-arene catalyst exhibited the highest catalytic activity over others mechanistic investigations inferred the coordination of hydrazine with ruthenium center and subsequent weakening of the N-H bond of hydrazine is the key to achieve efficient transformation of hydrazine to hydrogen gas. After achieving hydrogen production from hydrazine over iminopyridine-arene-ruthenium complexes, the pyridylamine ligated arene-Ru complexes are employed for the catalytic acceptorless dehydrogenation of primary aromatic alcohols to the corresponding carboxylic acids in toluene with the production of H₂ gas. The well-characterized complexes also efficiently transform a wide range of other primary alcohols to the corresponding carboxylic acids in good yields (up to 86%) with the production of hydrogen gas. Results clearly inferred that determining role of the pyridylamine ligands over the hydrogen production process, where the steric bulkiness and the electron density over the amine are crucial factors. Among the studied catalysts, the arene-Ru-pyridylamine catalyst displayed superior catalytic behavior to achieve the turnover of 1378 for the bulk reaction of hydrogen gas from benzyl alcohol. The detailed mechanistic investigations resulted in the

identification of several important catalytic intermediates, including aldehyde and diol-coordinated Ru species, under catalytic and controlled reaction conditions. Further, a range of ligands are explored to in situ generate active arene-ruthenium catalyst for hydrogen production from formaldehyde in water. Screening of various ligands inferred that the in situ arene-ruthenium catalyst generated in the presence of imidazole ligand outperformed other for the production of hydrogen gas from formaldehyde and paraformaldehyde in water under moderate reaction conditions. Moreover, the L/Ru ratio also found to be a crucial factor to achieve high catalytic turnover, where L/Ru ratio of 1:1 was found to be optimal. The identity of the in situ synthesized catalytic species was confirmed by mass, and further its active role in the catalytic reaction was established by the ex-situ synthesis of the arene-rutheniumimidazole complex. The ex-situ synthesized complex exhibited analogous catalytic behaviour as observed with the in situ condition further evidenced the involvement of the arene-ruthenium-imidazole (L/Ru = 1:1) in the catalytic hydrogen production from formaldehyde in water. Advantageously, the studied catalytic system produces hydrogen from formaldehyde without the use of any external base and works effectively at 95 °C in water. Moreover, an appreciably higher turnover number $(>12\,000)$ and appreciably good TOF (5175 h^{-1}) was also achieved during long-term bulk hydrogen production from a paraformaldehyde-water solution over the areneruthenium-imidazole catalyst.

In the last project, the in situ generated arene-ruthenium complex in the presence of 2-hydroxypyridine was employed for the synthesis of ruthenium nanoparticles **Ru/L9** catalyst that comprises ligand capped ruthenium nanoparticles homogeneously dispersed over the carbon support. The **Ru/L9** catalytic system displayed excellent catalytic activity for CO₂ free hydrogen production from methanol (1.43 mol H₂ per mol methanol) at low temperature (110–130 °C). This process also generated formic acid as a by-product. The studied catalyst exhibited outstanding long-term stability and generated 186 L of H₂ gas per gram of Ru. This catalytic system may encourage the search for an efficient industrially viable process for the low-temperature transformation of methanol into hydrogen gas and formic acid. Overall, a wide range of ruthenium catalysts was developed and employed for

hydrogen production from several liquid hydrogen carriers based on hydrazine, aromatic alcohols, formaldehyde, and methanol, and with the help of extensive mechanistic investigations, the plausible role of the synthesized ruthenium catalysts in the hydrogen production process was deduced. Through this work, the role of ligand-to-metal interactions, metal-to-hydrogen carriers interactions, and the ligand-to-hydrogen carriers interactions in the hydrogen production process was studied, and therefore it may also be useful to further design the new and efficient catalysts for such reactions.

6.2. Future Scope

The use of hydrogen as an energy carrier to produce clean fuel is the need of the hour for current society due to the depletion of fossil fuels and increasing pollution due to the burn of fossil fuels. Therefore, searching for new and efficient catalysts for hydrogen generation from various liquid hydrogen carriers is highly desirable. In the recent past, various researchers have extensively investigated the hydrogen production process by hydrocarbon reforming, water splitting, methanol-reforming and others over a wide range of efficient homogeneous and heterogeneous catalysts. However, still, efforts need to be made to achieve high productivity for the hydrogen production process at low temperature with high efficiency and robustness of the catalysts. Systematic studies in the area of heterogeneous catalysts for hydrogen production reactions can revolutionize the field in various aspects. Further using various supported heterogeneous catalysts with the high surface area can be explored to achieve better efficiency in for hydrogen production process. This will also prevent the leaching of the metal catalyst during the reaction and hence will increase the chances of the recovery of active catalysts. Despite rapid advancement in the field, the development of a robust catalytic system for hydrogen production is still the top-most requirement to escalate the laboratory scale results to an industrial scale. Analogously the development of homogeneous catalysts based on air-stable and inexpensive metals for the hydrogen production from various liquid hydrogen carriers is also underexplored.

For instance, hydrazine dehydrogenation is very well explored over heterogeneous catalysts, whereas homogenous catalysts for the same are still only a few. Efforts

need to be made to develop homogeneous catalysts for low-temperature hydrogen production from hydrazine. Through, interaction of hydrazine with metal complexes have been studied in detail, but these results need to be explored with respect to the application of the same for hydrazine activation reaction. Through our work on arene-ruthenium complexes from hydrogen production from aromatic alcohols, we tried to provide an alternative process for low-temperature hydrogen production. However, there are still several challenges that need to be addressed such as using green solvents, less basic or without base, low-temperature, and use of non-noble base metals complexes. We also explored the formaldehyde dehydrogenation over in situ generated ruthenium complexes and achieved appreciably good TON and TOF at 90 °C. However, there are still a demand to search for an efficient and highly active catalytic system to produce hydrogen from formaldehyde solution at room temperature with high TON and TOF value under base free condition. Using methanol (12.5wt% of hydrogen content) as a hydrogen source has several advantages as compared to other liquid hydrogen carriers. We achieved good conversion of methanol to pure hydrogen at <150 °C by an in situ generated Ru nanoparticles-based catalyst under alkaline condition. However, efforts need to be made to develop catalysts that can work efficiently even at low temperature for hydrogen production from methanol. Further efforts can be towards stabilizing active metal nanoparticle catalyst over the support material, which may result in enhancing the catalytic activity to achieve high productivity for hydrogen production from methanol.

Hence, lots needs to be done to realize the hydrogen economy, where the role of the catalysts is crucial to achieve high productivity for hydrogen generation from a wide range of promising liquid hydrogen carriers.

APPENDIX – I

(Rights and Permissions)

C	CC		
Ric	hts	Lin	ĸ

ACS Publications



侖

Home

?

Help v

1

Live Chat

2

Mahendra Awasthi 🗸

Copyright © 2013, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.

If figures and/or tables were requested, they may be adapted or used in part.

Please print this page for your records and send a copy of it to your publisher/graduate school.

- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate

information in place of the capitalized words.

- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

			1
н	0		ĸ
-		~	••

CLOSE WINDOW

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com

CC ghtsLink	A Home	? Help ∨	R Live Chat	Lange Mahendra Awasthi		
	The Mechanism of Acceptorles by N,N,N-Amide Ruthenium(II) Experimental and Computation	s Amine I Hydrides nal Study	Double Del : A Combir	hydrogenation ned		
ACS Publications	Author: Lillian V. A. Hale, Tanmay Malakar, Kuei-Nin T. Tseng, et al Publication: ACS Catalysis Publisher: American Chemical Society					
	Date: Aug 1, 2016 Copyright © 2016, American Chemical Society					
ERMISSION/LICENSE IS his type of permission/licen harged for your order. Pleas	GRANTED FOR YOUR ORDER AT NO (se, instead of the standard Terms and Con se note the following:	CHARGE ditions, is se	nt to you beca	ause no fee is being		
Dermission is granted for up	our request in both print and electronic for	mats, and tra	anslations.			

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

BACK

CLOSE WINDOW

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com

htsl ink		Home Help v	Live Chat Mahendra Awasthi
IIISLIIK	low-temperature agu	eous-phase meth	and dehydrogenation to
	hydrogen and carbon	dioxide	anor denjar ogenador to
	Author: Martin Nielsen et al		
SPRINGER NATURE	Publication: Nature		
A RINGER MATORE	Publisher: Springer Nature		
	Date: Feb 27, 2013		
	Copyright © 2013, Nature Publish Reserved.	ing Group, a division of Mac	millan Publishers Limited, All Rights
Order Completed			
Thank you for your order			
This Agreement between license details and the te	Mr. Mahendra Awasthi ("You") an rms and conditions provided by S	d Springer Nature ("Spring pringer Nature and Copyri	ger Nature") consists of your ght Clearance Center.
Your confirmation email v	vill contain your order number f	for future reference.	
License Number	5140171393825		Printable Details
License date	Sep 01, 2021		
Licensed Content		Order Details	
Licensed Content Publisher	Springer Nature	Type of Use Requestor type	Thesis/Dissertation
Licensed Content	Nature	Format	print and electronic
Publication	reactine .	Portion	figures/tables/illustrations
	Low-temperature aqueous- phase methanol	Number of	
Licensed Content Title	dehydrogenation to hydrogen	figures/tables /illustrations	2
Licensed Content	and carbon dioxide	High-res required	no
Author	Martin Nielsen et al	Will you be	no
Licensed Content	Feb 27, 2013	Circulation/distribution	1 - 29
Date		Author of this	
		Springer Nature content	no
About Your Work		Search Additional Data	
	Design and Development of	Portions	figure 1 and 3
Title	Efficient Catalysts for		
	Indian Institute of Technology		
Institution name	Indore		
Expected presentation date	Dec 2021		
Requestor Location		Tax Details	
	Mr. Mahendra Awasthi		
	Indian Institute of Technology		
	MP		
Requestor Location	India Indore India 452552		
	India		
	Attn: Mr. Mahendra Awasthi		
\$ Price			
Total	0.00 USD		
			Total Contract
			Total: 0.00 USD

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com

uhtsl ink		Home	Help 🗸	Live Chat	Mahendra Awast
SPRINGER NATURE	Catalytic transformation of alcohols to carboxylic acid salts and H2 using water as the oxygen atom source Author: Ekambaram Balaraman et al Publication: Nature Chemistry Publisher: Springer Nature Date: Jan 6, 2013				
	copyright & 2013, hatare Paolos	ining Group			
Order Completed					
Thank you for your order This Agreement between license details and the te	r. Mr. Mahendra Awasthi ("You") a rms and conditions provided by !	nd Springer Na Springer Natur	ature ("Spring e and Copyrig	er Nature") co ght Clearance	nsists of your Center.
Your confirmation email v	vill contain your order number	for future rel	erence.		Printable Details
License date	Sep 01, 2021			2	
Licensed Content		💼 Order (Details		
icensed Content	Springer Nature	Type of Use		Thesis/Dis	sertation
icensed Content Publication	Nature Chemistry	Format Portion	уре	print and figures/ta	electronic bles/illustrations
icensed Content Title	alcohols to carboxylic acid salts and H2 using water as the oxygen atom source	Number of figures/tabl /illustration	es s	2	
Licensed Content Author	Ekambaram Balaraman et al	High-res rec Will you be	uired	no	
Licensed Content Date	Jan 6, 2013	translating? Circulation/ Author of th Springer Na content	distribution his ture	1 - 29 no	
About Your Work		🏷 Additi	onal Data		
Title	Design and Development of Efficient Catalysts for Hydrogen Production	Portions		Figure 1 a	nd 3
nstitution name	Indian Institute of Technology Indore				
Expected presentation date	Dec 2021				
Requestor Location		🛢 Tax Det	tails		
Requestor Location	Mr. Mahendra Awasthi Indian Institute of Technology Indore MP India Indore, India 453552 India Attn: Mr. Mahendra Awasthi				
\$ Price					
Total	0.00 USD				
				То	otal: 0.00 USD





Please print this page for your records and send a copy of it to your publisher/graduate school.

- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate

information in place of the capitalized words.

One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

-		~	
_	<i>.</i>		v
-		-	

CLOSE WINDOW

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com

Image: Second
Ruthenium Complexes for Catalytic Dehydrogenation of Hydrazine and Transfer Hydrogenation Reactions Author: Sanjay Kumar Singh, Shaikh M. Mobin, Rohit Kumar Rai, et al Publication: Chemistry - An Asian Journal Publisher: John Wiley and Sons Date: May 9, 2018 • 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim • 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim • 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim • 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim • 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim • 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim • 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim • 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim • 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim • 2018 Wiley and Sons Unit State
Order Completed Thank you for your order. This Agreement between Mr. Mahendra Awasthi ('You') and John Wiley and Sons ('John Wiley and Sons') consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center. Your confirmation email will contain your order number for future reference. Jicense Number 5142420996057 Licensed date Sep 05, 2021 Licensed Content John Wiley and Sons John Wiley and Sons Type of use Dissertation/Thesis Ruthenium Complexes for Catalytic Dehydrogenation of Hydrazine and Transfer Hydrogenation Reactions Jicensed Content Jicensed Content Jicensed Content Jicensed Content Jicensed Content Wilford Reactions Sanjay Kumar Singh, Shakh M. Mobin, Rohit Kumar Rai, et al Jicensed Content May 9, 2018 Jicensed Content Jicensed Content May 9, 2018 Jicensed Content
Thank you for your order. This Agreement between Mr. Mahendra Awasthi ('You'') and John Wiley and Sons ('John Wiley and Sons') consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center. Your confirmation email will contain your order number for future reference. Jacense Number 5142420996057 Licensed Content Sep 05, 2021 Licensed Content John Wiley and Sons Jacense Content John Wiley and Sons Licensed Content Chemistry - An Asian Journal Ruthenium Complexes for Catalytic Dehydrogenation of Hydrazine and Transfer Hydrazine and Transfer Will you be Transfer Will you be Transfer May 9, 2018 Licensed Content May 9, 2018 Licensed Content May 9, 2018
This Agreement between Mr. Mahendra Awasthi ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center. Afour confirmation email will contain your order number for future reference. License Number 5142420996057 Licensed date Sep 05, 2021 Licensed Content John Wiley and Sons Licensed Content John Wiley and Sons Licensed Content Licensed Content Title Licensed Content Title Licensed Content Title Licensed Content Licensed Content May 9, 2018 Licensed Content Licensed Content Licensed Content May 9, 2018 Licensed Content Licensed Content Licensed Content Licensed Content Licensed Content May 9, 2018 Licensed Content Licensed Content
Your confirmation email will contain your order number for future reference. License Number 5142420996057
Joense Number 5142420996057 License date Sep 05, 2021 Licensed Content John Wiley and Sons Licensed Content John Wiley and Sons Licensed Content John Wiley and Sons Licensed Content Chemistry - An Asian Journal Ruthenium Complexes for Catalytic Dehydrogenation of Hydrazine and Transfer Hydrogenation Reactions Type of use Requestor type Dissertation/Thesis Requestor type Licensed Content Sanjay Kumar Singh, Shaikh M. Mobin, Rohit Kumar Rai, et al Sanjay Kumar Singh, Shaikh M. Mobin, Rohit Kumar Rai, et al No Licensed Content May 9, 2018 Ja Licensed Content 13
Joense date Sep 05, 2021 Licensed Content John Wiley and Sons Image: Content Publisher Other Wiley and Sons Jubisher John Wiley and Sons Type of use Dissertation/Thesis Subisher Chemistry - An Asian Journal Requestor type Author of this Wiley article Publication Chemistry - An Asian Journal Format Print and electronic Jubisher Chemistry - An Asian Journal Will you ube Format Hydrazine and Transfer Ywill you ube Format Print and electronic Jubersed Content Sanjay Kumar Singh, Shaikh Will you ube Format Jicensed Content May 9, 2018 Jubersed Content Ja Jicensed Content 13 Jubersed Content Ja
Licensed Content John Wiley and Sons Type of use Requestor type Dissertation/Thesis Requestor type Jubinsher John Wiley and Sons Type of use Requestor type Dissertation/Thesis Requestor type Jubinsher Chemistry - An Aslan Journal Ruthenium Complexes for Catalytic Dehydrogenation of Hydrazine and Transfer Hydrogenation Reactions Format Portion Print and electronic Jubinsher Sanjay Kumar Singh, Shaikh M. Mobin, Rohit Kumar Rai, et al Sanjay Kumar Singh, Shaikh M. Mobin, Rohit Kumar Rai, et al No Jubersed Content May 9, 2018 Jubersed Content Jubersed Content Jubersed Content 13 Jubersed Content
Joensed Content Vublisher John Wiley and Sons Type of use Requestor type Dissertation/Thesis Joensed Content Vublication Chemistry - An Asian Journal Ruthenium Complexes for Catalytic Dehydrogenation of Hydrogenation Reactions Format Portion Print and electronic Joensed Content Title Ruthenium Complexes for Catalytic Dehydrogenation of Hydrogenation Reactions Will you be translating? No Jicensed Content Sanjay Kumar Singh, Shaikh Muthor May 9, 2018 Joensed Content al Joensed Content Jicensed Content Olume 13 Joensed Content Joensed Content
Licensed Content Title Ruthenium Complexes for Hydragenation of Hydragenation of Hydragenation Reactions Licensed Content Lic
Licensed Content Sanjay Kumar Singh, Shaikh M. Mobin, Rohit Kumar Rai, et al Licensed Content May 9, 2018 Jicensed Content 13 Licensed Content Lisensed Co
Jcensed Content May 9, 2018 Jate Content 13 Jeensed Content 4
Joensed Content /olume 13 Joensed Content
licensed Content
ssue
Licensed Content 8
🕯 About Your Work 🛸 Additional Data
Design and Development of Title Efficient Catalysts for Hydrogen Production
nstitution name Indian Institute of Technology Indore
Expected Dec 2021 presentation date
Requestor Location
Mr. Mahendra Awasthi Publisher Tax ID EU826007151 Indian Institute of Technology Indore MP India India Indore, india 453552 India Attn: Mr. Mahendra Awasthi
Price
otal 0.00 USD
Would you like to purchase the full text of this article? If so, please continue on to the content ordering system located here: Purchase PDF If you click on the buttons below or close this window, you will not be able to return to the content ordering system.
Total: 0.00 USD
CLOSE WINDOW ORDER MORE

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com

CCC RightsLink		A Home	? Help ∨	R Live Chat	Aahendra Awasthi 🗸	
	Ruthenium Catalyzed Mechanistic Study	d Dehydro	genation	of Alcohol	s and	
ACS Publications	Author: Mahendra K. Awasthi, Sanjay K. Singh					
Weit Tusted, Mart Chel, Nert Real,	Publisher: American Chemi	cal Society				
	Date: Nov 1, 2019	cursocicity				
	Convright @ 2019. American Chi	emical Society				
PERMISSION/LICENSE IS This type of permission/licen- charged for your order. Pleas Permission is granted for you If figures and/or tables were Please print this page for you Appropriate credit for the re from (COMPLETE REFRENCE) Information in place of the ca Const time permission is regression.	GRANTED FOR YOUR ORL se, instead of the standard Te ie note the following: Nur request in both print and 4 requested, they may be ada iur records and send a copy o equested material should be g CITATION). Copyright (YEAR) apitalized words.	electronic for pted or used i f it to your pu given as follow American Ch	LHAKGE ditions, is see mats, and tra in part. blisher/grad vs: "Reprinte vemical Socie	nt to you beca inslations. luate school. d (adapted) w ty." Insert app	use no fee is being ith permission propriate	
(such as derivative works or o	other editions). For any uses, p	please submit	a new reque	est.	iai uses are granteu	
If credit is given to another so from that source.	surce for the material you req	juested from	RightsLink, p	ermission mu	ist be obtained	

BACK

CLOSE WINDOW

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com