Development of Catalysts for Hydrogen Production

M.Sc. Thesis By

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A THESIS

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

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **DEVELOPMENT OF CATALYSTS FOR HYDROGEN PRODUCTION** in the partial fulfillment of the requirements for the award of the degree of **Master of Science** and submitted in the **Department of Chemistry**, **Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2021 to May 2022 under the supervision of Dr. Sanjay K. Singh, Professor, IIT Indore.

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

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

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Signature of PSPC Member #1 Dr. Tridib Kumar Sarma Date: .24-05-2022 Signature of PSPC Member #2 Dr. Satya S. Bulusu Date: 21/.5/.22 Dedicated to my Parents.....

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ABSTRACT

Hydrogen as an energy carrier could be a revolutionary fuel in view of energy sustainable development if we can abstract it from biomass-derived compounds such as biogas, bio-oil, bio-ethanol, bio-butanol, etc. Traditionally, SR, POX, and OSR are the major processes to produce hydrogen from ethanol but it needs a very high temperature. By using catalysts, we can reduce this energy consumption. So, here we performed dehydrogenation of ethanol in presence of in-situ generated ruthenium nanoparticle as a catalyst by using Ru salt as a pre-catalyst in water at low temperature (110 °C). Additionally, optimization of reaction was done by using CTAB and PVP as stabilizing agent and γ -Al₂O₃ as an additive.

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Acronyms

СТАВ	Cetyltrimethylammonium bromide			
GC-TCD	Gas Chromatography			
	-Thermal Conductivity detector			
NMR	Nuclear Magnetic Resonance			
OSR	Oxidative Steam Reforming			
POX	Partial Oxidation			
PVP	Polyvinylpyrrolidone			
SR	Steam Reforming			
TOF	Turnover frequency			
TON	Turnover number			

NOMENCLATURE

°C	Degree Celsius		
equiv.	Equivalent		
Fig.	Figure		
h ⁻¹	per hour		
mg	milligram		
mL	millilitre		
mmol	millimole		
%	Percentage		
Ref.	Reference		
Wt	Weight		

CHAPTER ONE

1. INTRODUCTION

1.1 General Introduction

The importance of hydrogen as an energy carrier is remarkable in view of the environment as well as energy density.^[1] Hydrogen is a clean source of energy, if we can abstract it from water, natural gas, or biomass, can be cast-off to power and heat our homes. There are two core methods used to abstract hydrogen on a large scale: steammethane reforming(gray or blue hydrogen) or electrolysis(green hydrogen).^[2] Electrolysis includes fleeting a high current of electricity over water to isolate the hydrogen and oxygen atoms. It sounds meek sufficient, but this is an expensive process because of the quantity of electricity desirable. And to make the electricity, fossil fuels (e. g. natural gas, oil, or coal) are seared which produces carbon discharges. If the electricity cast-off in electrolysis comes by means of solar panels, wind, or hydropower farms then we can avoid these carbon discharges.^[2-12]

In steam methane reforming there is the unraveling of hydrogen and carbon in methane. Because hydrogen can be taken out in large quantities it is the method used most commonly at the moment, but it results in the releases of carbon monoxide and carbon dioxide.^[13] Both of these gases are harmful to our atmosphere and will contribute to global warming. However, it is possible to capture the carbon emitted throughout the process of producing hydrogen with Carbon Capture Utilization Storage(CCUS) systems which would avoid the carbon from being out into the atmosphere.^[14]

We cannot course out of hydrogen because it is a renewable energy source, at least not on a humanoid timescale. Unlike nuclear energy or natural gas, it doesn't cause damage to human health. Compared to the most fossil-based fuel sources less hydrogen is required to perform the same tasks because it is 3 times more efficient.^[15] That's the reason why hydrogen is used in space exploration to fuel spaceships, airplanes, boats, cars, and fuel cells.

On the other side hydrogen is a volatile and highly flammable matter which makes it a risky fuel to effort with. Also, the processes used to produce it are very expensive. Trials and research are in the course to attempt and notice a low-priced and bearable method to yield sufficient hydrogen without having extra carbon into the atmosphere.^[16]

In the continuation of the same, there are some catalytic reactions to produce hydrogen from different substrates (e. g. alcohols, aldehydes, acids, water, hydrazine, ethylenediamine, ammonia etc.) by using two different types of catalysts namely homogenous catalysts and heterogeneous catalysts.^[17-28]

When a catalyst and reactant are in the same phase then that catalyst is known as a homogeneous catalyst whereas when a catalyst and reactants are in a different phase then the catalyst is known as a heterogeneous catalyst. In heterogeneous catalysis, at active sites of the catalyst, one or more of the reactants are adsorbed. Because of the interaction between the surface of the catalyst and the reactant molecules, the reactant becomes more reactive and a reaction happens. And desorption of product takes place. A decent catalyst wishes not to adsorb more or less permanently to the surface but adsorb the reactant molecules sturdily enough for them to react. Like, reactant molecule can't add-on sturdily to the silver because of which it is not a decent catalyst. Conversely, Tungsten adsorbs too sturdily that's why it isn't a good catalyst.

Platinum and nickel adsorb sturdily to clasp and activate the reactants but not so sturdily that the products can't break down away that's why they make good catalysts.

1.2 Review of Past Work and Problem Formulation

Different substrates have different content of hydrogen among which some of them have been shown here in the following table.

Table 1 Some hydrogen storage materials with their stoichiometric hydrogen yield

Hydrogen storage materials	Stoichiometric H ₂ Yield			
	moles	%		
		(By wt)		
Methane	2	25.14		
Methanol	3	12.5		
Ethanol	6	12.5		
Formic acid	1	4.35		
Hydrazine Hydrate	2	7.9		
Glycerol	1	2.17		
Formaldehyde	2	8.4		

Among all the above several renewable feedstock alternatives, because of its availability, relatively high hydrogen content, storage or handling ease, non-toxicity, and safety, ethanol has been regarded as an attractive feedstock. In past years, the major processes for hydrogen production from ethanol are steam reforming (SR), partial oxidation (POX), and oxidative steam reforming (OSR).

$CH_3CH_2OH + 3H_2O \longrightarrow 6H_2 + 2CO_2$	(SR)
$CO + H_2O \longrightarrow H_2 + CO_2$ (Water-Gas shift r	eaction)
$CH_3CH_2OH + 1.5O_2 \longrightarrow 3H_2 + 2CO_2$	(POX)
$CH_3CH_2OH + 1.8H_2O + 0.6O_2 \longrightarrow 4.8H_2 + 2CO_2$	(OSR)

There is a vital part of catalysts in terms of whole ethanol transformation and making the most of hydrogen. Non-noble metals like Ni, Co and noble metals like Ru, Rh, Pd, Pt, and Ir metal possess high C-C bond cleavage capacity that has been widely investigated. ^[29-35] The catalyst activity can be influenced by support which interacts with ethanol and accelerates its transformation.^{[36],[37]}

Table 2 Comparative chart of product variety for ethanol OSR on M/Al_2O_3 (M = Rh, Pd, Ag, Au, Pt) under the following catalytic conditions: $H_2O/ethanol = 3$ and $O_2/ethanol = 0.3$ at 600 °C.^[38]

Catalyst	Y _{H2}	S _{CH3} сно	SC2H4	S _{CH4}	Sco	S _{CO2}
	(%)	(%)	(%)	(%)	(%)	(%)
Rh (1.6 wt%)	94	0	0	18	41	41
Ag (1.4 wt%)	14	58	3	11	0	24
Au (1.6 wt%)	18	53	5	13	3	26
Pd (1.3 wt%)	22	17	28	13	12	28
Pt (1.5 wt%)	29	17	24	18	11	29

 $X_{C_2H_6O}(\%) = [(moles of fed ethanol - moles of exited)]$

ethanol)/(moles of fed ethanol)] \times 100%.

 $S_{H_2}(\%) = \{ (moles of produced H_2) / [3 \times (moles of fed ethanol] \} \times 100\%.$

 $S_X(\%) = [(moles of carbon in product X)/(total moles of carbon in products)] \times 100\%.$

Table 3 Comparison of alumina-supported noble metal catalystsperformance in ethanol reforming.

Active	Support	Т	C ₂ H ₆ O/H ₂ O	X _{C2} H ₆ O	S _{H2}	Ref.
Metal		(°C)	(molar ratio)	(%)	(%)	
Rh (1 wt%)	Al ₂ O ₃	700	1/3	100	72	39
Ru (0.6wt%)	Al ₂ O ₃	700	1/3	100	46	39
Pd (0.8 wt%)	Al ₂ O ₃	700	1/3	100	55	39
Pt (1 wt%)	Al ₂ O ₃	700	1/3	100	38	39
Rh (1 wt%)	Al ₂ O ₃	750	1/3	79	90	40
Ru (1wt%)	Al ₂ O ₃	750	1/3	18	52	40
Pd (1wt%)	Al ₂ O ₃	750	1/3	25	45	40
Pt (1wt%)	Al ₂ O ₃	750	1/3	32	63	40

 $X_{C_2H_6O}(\%) = [(moles of fed ethanol - moles of exited)]$

ethanol)/(moles of fed ethanol)] \times 100%.

 S_{H_2} (%) = {(moles of produced H₂)/ [3 × (moles of fed ethanol]} × 100%.

All the data given in the above table suggested that for the production of hydrogen from ethanol we need a very high temperature. Also, to be specific, for non-noble metal catalytic reactions we need a high content of water. So, we need to develop a method that can efficiently produce hydrogen from ethanol at low temperatures and by using less amount of water.

1.2 The Aim and Strategy of our work

The aim of our work is to synthesize a highly effective catalyst to produce hydrogen from ethanol at low temperatures. The strategy of our work is to use metal nanoparticles as a catalyst in the basic medium for dehydrogenation of ethanol with water and produce hydrogen from it. And also optimize the reaction by changing the reaction conditions or providing appropriate support to the catalyst to get the most effective results.



Scheme 1: Ethanol dehydrogenation in the presence of catalyst and base

CHAPTER TWO

2. EXPERIMENTAL SECTION

2.1 Materials and Instrumentation

Sigma-Aldrich, Alfa Aesar and Merck are the ones from where all metal salts and chemicals were purchased and used with no more purification. Using a Rigaku SmartLab, Automated Multipurpose X-ray diffractometer at 40 kV and 30 mA using Cu K α radiation (λ = 1.5418 Å Powder X-ray diffraction (PXRD) measurements were performed on the dried particles. Scanning electron microscopic (SEM) images, elemental mapping, energy dispersive X-ray spectroscopy (EDS) analyses, and elemental mapping were carried out with a Supra55 Zeiss (operating voltage 5 kV) equipped with an Oxford instrument EDS X-ray spectrometer. ¹H NMR (400 MHz) were recorded in D₂O on a Bruker Avance 400 spectrometer at 298 K using tetramethylsilane (TMS) as an external standard. Chemical shifts were reported in ppm relative to the center of the singlet at 4.75 ppm for D₂O in ¹H NMR.

2.4 Catalytic hydrogen production from ethanol

A suitable amount of RuCl₃.3H₂O (0.1 mmol) and support (50mg) in ethanol-water solution ($n(C_2H_5OH)/n(H_2O) = 1:1$) was taken in a 10 mL test tube reaction vessel and a suitable base (1.1 equiv. with respect to ethanol) was added. After de-aerating, the reaction vessel was flushed with N₂ where the reaction vessel was equipped with a condenser (-10 °C) and water displacement setup. By using the water displacement method, the amount of gas generated per unit time was quantified, and by using GC-TCD the content of the released gas was confirmed. By using the formula $[n(H_2)/n(catalyst)]$, the turnover number (TON) was calculated. The turnover frequency (TOF) was calculated as TON/time. After the catalytic reaction, by using centrifugation the

supported ruthenium nanoparticles were collected and dried in a vacuum oven which can be used for the further catalytic cycles.

CHAPTER THREE

3. RESULTS AND DISCUSSION

3.1 Characterisation of *in-situ* generated Ru nanoparticle

Ruthenium nanoparticles were synthesized in-situ and CTAB, PVP, and γ -Al₂O₃ were added as an additive in the reaction. A 20 value of 43° in the powder X-ray diffractogram (PXRD) (Figure 1) shows the presence of (101) lattice plane. PXRD analysis also suggests a hexagonal closed packed (hcp) structure of the nanoparticles. The PXRD analysis of the nanoparticles shows the characteristic peaks for the Ru. Also, the Scanning Electron Microscope (SEM) images tell the presence of ruthenium nanoparticles (Fig. 2a). This is also supported by Energy Dispersive X-ray Spectroscopy (EDS) where the corresponding peak with respect to ruthenium was observed (Fig. 2b).



Fig. 1 PXRD of in-situ generated ruthenium nanoparticles



Fig. 2 (a)SEM image and (b)EDS analysis of in-situ generated ruthenium nanoparticles



Fig. 3 Elemental mapping of in-situ generated ruthenium nanoparticles

3.2 Catalytic dehydrogenation reaction

The catalytic dehydrogenation of ethanol was carried out over in-situ generated Ru nanoparticles to produce hydrogen at a very low temperature. For that, first, we have taken RuCl₃.3H₂O as a pre-catalyst in the presence of 1.1 Equiv. KOH and ethanol (1:1 molar ratio of C₂H₅OH: H₂O) at 110 °C, where the release of 48 mol gas per mol of Ru was observed (Initial TOF 14 h⁻¹) (Table 3, entry 1,

Fig 4). The evolved gases were identified as hydrogen and methane by GC-TCD (Fig 10).

Also, when we do an NMR study of the reaction aliquot after the reaction, we got peaks corresponding to acetic acid and formic acid (Fig 6). On basis of GC-TCD and NMR data, we can say that probably there are two reactions happening simultaneously in the reaction mixture. At the very first dehydrogenation of ethanol to acetic acid and hydrogen occurs then the cleavage of C-C bond occurs in the presence of hydrogen produced in the first reaction to give methane and formic acid (Scheme 2).

 $CH_3CH_2OH \longrightarrow CH_3COOH + 2H_2$ (1)

 $CH_3COOH + H_2 \longrightarrow CH_4 + HCOOH$ (2)

Scheme 2: Plausible pathway of the reaction

From the past studies, it is observed that the size of the generated ruthenium nanoparticle can also alter the reaction.^{[42], [43]} So, we tried CTAB and PVP as stabilizing agents separately with RuCl₃.3H₂O to know about the effect of the size of the particle generated in the reaction (Table 3, entry 2, 3, and Fig. 4). We observed that in the case of CTAB stabilized particles it releases 0.24 mol gas per mol of ethanol (TON 39 mol gas per mol of Ru) whereas PVP st abilized particles releases 0.36 mol gas per mol of ethanol (TON 58 mol gas per mol of Ru).

An important role in the stability and activity of the catalyst has frequently been shown by the supports.^[43] Therefore, we investigated γ -Al₂O₃ as a support not only for the finest metallic distribution and thermal stability on the metal phase but also to contribute straight in the catalytic course. When we use γ -Al₂O₃ as the support, there is a decrease in the gas released to 0.32 mol of H₂ per mol of ethanol.

Entry	Cat.	Additive	n(alc.)/	Т	КОН	n(gas)/	n(gas)/	TOF*
			n(H ₂ O)	(°C)	(equiv.)	n(ethanol)	n(cat.)	(h-1)
1	Ru	-	1:1	110	1.1	0.30	48	14
2	Ru	СТАВ	1:1	110	1.1	0.24	39	12
3	Ru	PVP	1:1	110	1.1	0.36	58	15
4	Ru	γ-Al ₂ O ₃	1:1	110	1.1	0.32	52	14

Table 3 Screening of catalyst with various additives to produce hydrogen from ethanol

Reaction condition: Ethanol (16.08), Ru catalyst (0.628mol%), additive 50 mg, KOH (1.1 equiv.), 10h, Nitrogen. *Initial average Turnover frequency at 1h.



Fig. 4 Effect of Additive on in-situ generated Ru catalyst for hydrogen production from ethanol at 110 °C. (Reaction condition:

ethanol (16.08 mmol), additive(50mg), Ru catalyst (0.625mol%), KOH (1.1 equiv.) and ethanol to water molar ratio (1:1), nitrogen)

Further, ¹H NMR of the reaction aliquot after the completion of the catalytic reaction inferred the presence of acetic acid and formic acid. In GC-TCD analysis, there is no peak corresponding to CO or CO₂ suggesting the breakdown of formic acid does not take place.



Fig. 5. Effect of stabilizing agent on the dehydrogenation of ethanol. (Reaction conditions: ethanol (16.08 mmol), Ru catalyst (0.625mol%), CTAB (50 mg), KOH (1.1 equiv.), 72h, and ethanol to water molar ratio (1:1), Nitrogen)

The literature tells those reactions performed under reducing conditions may come with the transformation of Ru salt to Ru (0) nanoparticles.^[44]

Furthermore, in the considered catalytic system, acetate/acetic acid and formate/formic acid is found to be a worthful side product. These results inferred that using PVP as a stabilizing agent with Ru salt can produce a little bit higher content of hydrogen gas from ethanol. Therefore, by changing the size and morphology, and stabilization of the catalyst we can get good results as shown here by taking different stabilizing agents and additives.

APPENDIX A.



Fig.7 ¹H NMR spectrum of the reaction mixture obtained after the reaction. Reaction condition: ethanol (16.08 mmol), Ru catalyst (0.625 mol%), KOH (1.1 equiv.), water (1 equiv.), 110 °C, Nitrogen (Table 3, entry 1).



Fig. 8 ¹H NMR spectrum of the reaction mixture obtained after the reaction. Reaction condition: ethanol (16.08 mmol), Ru catalyst (0.625 mol%, 50mg CTAB), KOH (1.1 equiv.), water (1 equiv.), 110 °C, Nitrogen (Table 3, entry 2).



Fig. 9 ¹H NMR spectrum of the reaction mixture obtained after the reaction, yield was determined using the maleic acid (1 mmol) as internal standard. Reaction condition: ethanol (16.08 mmol), Ru catalyst (0.625 mol%, 50mg PVP), KOH (1.1 equiv.), water (1 equiv.), 110 °C, Nitrogen (Table 3, entry 3).



Fig. 10 ¹H NMR spectrum of the reaction mixture obtained after the reaction, yield was determined using the maleic acid (1 mmol) as internal standard. Reaction condition: ethanol (16.08 mmol), Ru catalyst (0.625 mol%,), γ - Al₂O₃(50mg), KOH (1.1 equiv.), water (1 equiv.), 110 °C, Nitrogen (Table 3, entry 4).



Fig. 11 GC-TCD of gas evolved from the reaction mixture (using Argon as carrier gas). Reaction condition: ethanol (16.08 mmol), Ru catalyst (0.625 mol%,), KOH (1.1 equiv.), water (1 equiv.), Nitrogen (Table 3, entry 1).



Fig. 12 GC-TCD of gas evolved from the reaction mixture (using Argon as carrier gas). Reaction condition: ethanol (16.08 mmol), Ru catalyst (0.625 mol%,), CTAB (50mg), KOH (1.1 equiv.), water (1 equiv.), Nitrogen (Table 3, entry 2).

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