DEVELOPMENT OF CATALYSTS FOR (DE)HYDROGENATION REACTIONS

M.Sc. Thesis

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DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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A THESIS

Submitted in partial fulfillment of the
requirements for the award of the degree
of
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by
Pallvi Sharma
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DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF
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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 (De)hydrogenation reactions”** in the partial fulfilment 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 2024** to **May 2025** under the supervision of Prof. Sanjay K. Singh, Department of Chemistry, IIT-Indore.

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

Pallvi sharma
26/05/2025
Pallvi Sharma

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

Signature of the Supervisor of the M.Sc. thesis
(Prof. Sanjay K. Singh)

Pallvi Sharma has successfully given his/her M.Sc. Oral Examination held on **14 May 2025**.

Signature of the Supervisor of the MSc thesis
Prof. Sanjay K. Singh
Date:

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Pallvi Sharma

Abstract

The dehydrogenation of cyclic alcohols represents a promising strategy for the production of value-added chemicals and molecular hydrogen under mild and sustainable conditions. Cyclic alcohol derivatives have diverse applications across industries such as medicine, fuel, and polymers. This thesis focuses on the development of heterogeneous catalysts for the dehydrogenation and hydrogenation reactions. The study aims to achieve high catalytic efficiency at relatively low temperatures using a recyclable and easily separable solid catalyst. The thesis comprises four chapters, structured as follows: The first chapter deals with the general introduction to cyclic alcohols and their dehydrogenated products. The second chapter includes the experimental procedures adopted for catalyst synthesis and the execution of various catalytic reactions. The third chapter includes a detailed discussion of the results obtained from various dehydrogenation experiments. The final chapter presents the conclusion of the thesis, highlighting the major findings. The primary goal of this thesis is to develop an active and efficient heterogeneous catalyst that operates under environmentally benign conditions.

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ACRONYMS

$CDCl_3$	Chloroform-d
CTAB	Cetyltrimethylammonium bromide
H_2	Hydrogen
NMR	Nuclear Magnetic Resonance
NP’S	Nanoparticles
PXRD	Powder X-ray Diffraction
TGA	Thermo-gravimetric Analysis
FTIR	Fourier transform infrared spectroscopy
Ru	Ruthenium
$RuCl_3$. xH_2O	Ruthenium (III) chloride hydrate
SEM	Scanning Electron Microscopy
$NaBH_4$	Sodium borohydride
TMS	Tetramethylsilane
D_2O	Deuterium Oxide

NOMENCLATURE

Conv.	Conversion
°C	Degree Celsius
g	Gram
h	Hour
mL	Milliliter
Min	Minutes
mmol	Millimole
mg	Milligram
pH_2	Pressure of H_2 gas
RB	Round bottom
Ref.	Reference
Sel.	Selectivity
T	Temperature
t	Time

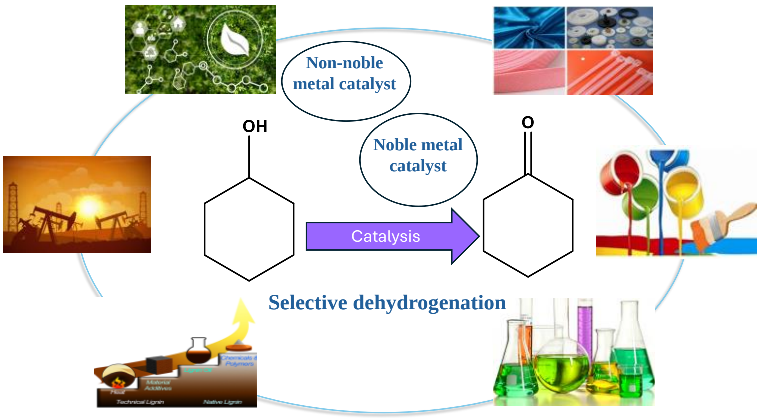
Chapter 1

Introduction

1.1 General introduction

Hydrogenation and dehydrogenation are fundamental chemical processes integral to the synthesis of fuels, chemicals, and pharmaceuticals. Hydrogenation involves the addition of hydrogen (H_2) to a compound, while dehydrogenation is the removal of hydrogen. Hydrogen is widely recognized as a highly promising energy carrier for future energy systems due to its superior energy content per unit mass and its clean combustion profile, producing only water as a by-product when used in fuel cells or combustion engines.[1] As the global energy landscape shifts towards low-carbon solutions, significant efforts are being placed on developing efficient methods for hydrogen generation that yield high-purity hydrogen. The goal is to produce hydrogen without carbon-based contaminants, thus supporting the transition to a net-zero emissions economy. Such clean hydrogen production processes also offer the added benefit of eliminating the need for making the gas readily applicable for direct use in advanced energy technologies.[2] Additionally, cyclohexanol can be synthesized from renewable resources such as biomass or derived as a by-product from industrial processes, enhancing its appeal from both economic and environmental perspectives.

The selective hydrogenation of phenol is particularly significant in the production of valuable intermediates such as cyclohexanone and cyclohexanol, which are essential for various industrial applications.[3] These reactions can be carried out in either liquid-solid or gas-solid phase systems, utilizing a variety of supported metal catalysts, including palladium (Pd)[4], rhodium (Rh)[5], platinum (Pt)[6], ruthenium (Ru)[7], nickel (Ni)[8], and cobalt (Co)[8]. The choice of catalyst is critical, as it significantly influences both the efficiency of the reaction and the selectivity toward desired products. The hydrogenation of phenol to cyclohexanone can follow two primary pathways. The first pathway involves a direct, one-step hydrogenation of phenol to cyclohexanone, typically using metal nano-catalysts, which is often more efficient for cyclohexanone production. The second pathway is a two-step process, beginning with the hydrogenation of phenol to cyclohexanol, usually facilitated by nickel catalysts, followed by the dehydrogenation of cyclohexanol to cyclohexanone.[8] Cyclohexanol and cyclohexanone are essential intermediates for producing caprolactam and adipic acid, which are the primary raw materials for nylon 6 and nylon 66; beyond that, these can be used in polyamide fibres. Cyclohexanone is also a valuable component in the pharmaceutical and fine chemical industries.



Scheme 1: Selective dehydrogenation to cyclohexanone and its applications

Moreover, cyclohexanol dehydrogenation plays a very important role in the industrial synthesis of cyclohexanone. The reaction network is complex, involving various pathways that can produce multiple byproducts. Besides the target reaction, other transformations, such as the dehydration of cyclohexanol to cyclohexene, can occur. Each of these reactions poses distinct challenges regarding selectivity and yield, emphasizing the need for careful optimization of reaction conditions and catalyst design.[9] A wide range of catalysts has been explored for the dehydrogenation of cyclohexanol at high temperatures. The heterogeneous catalytic gas-phase dehydrogenation of cyclohexanol is typically conducted at atmospheric pressure, and it can be characterized as an endothermic process with a reaction enthalpy. This endothermic characteristic requires higher temperatures to proceed with the forward reaction, which also reveals thermodynamic limitations imposed by equilibrium. While increasing temperature can enhance cyclohexanol conversion, it may also promote competing side reactions, such as dehydration and aromatization. This dual effect highlights the critical need for developing catalysts to optimize the yield of cyclohexanone while minimizing undesired byproducts.[10]

This study aims to explore and develop a novel heterogeneous catalytic system that effectively catalyses the hydrogenation and dehydrogenation of cyclic compounds under mild reaction conditions. Our goal is to achieve high conversion rates and selectivity while also facilitating dehydrogenation for the direct production of aromatic compounds. By addressing the challenges associated with existing catalytic systems, this research aspires to contribute significantly to the field of fine chemical synthesis and the advancement of sustainable energy solutions.

1.2 Literature review

The selective hydrogenation and dehydrogenation of phenol and cyclohexanol are crucial processes in industrial chemistry, given their role in synthesizing a range of valuable compounds. Phenol is widely available as a feedstock derived from natural lignin and can be efficiently converted into cyclohexanol using advanced nano-catalysts. Cyclohexanol acts as a precursor for diverse applications in pharmaceuticals, plasticizers, surfactants, paints, and industrial solvents. Additionally, cyclohexanol is increasingly recognized as a promising starting material for sustainable fuel production and acts as a liquid organic hydrogen carrier (LOHC).[11] Recent research has focused on noble metal-based heterogeneous catalysts for the hydrogenation of phenol to cyclohexanol. Catalysts such as Pt/CeO_2,[12] Ni/SiO_2,[13] and Co/CeO_2,[14] have demonstrated significant activity and selectivity. Ruthenium base catalysts offer a more economical alternative[15], though they present challenges in catalyzing this reaction effectively. Recent strategies to enhance the performance of ruthenium include the use of γ-Al_2O_3 as a support, which has employed good conversion rates and selectivity.[16] These systems exploit the unique properties of noble metals, including high dispersion and small particle sizes, to achieve efficient hydrogenation reactions under controlled conditions.

Similarly, the catalytic dehydrogenation of cyclohexanol to cyclohexanone or phenol is an equally critical industrial process. Cyclohexanone is a key intermediate in the production of caprolactam and adipic acid, which are essential for manufacturing Nylon 6 and Nylon 66. The increased global demand for nylon materials has fuelled efforts to optimize the dehydrogenation process, making it more efficient and sustainable. This reaction, inherently endothermic, depends on catalytic efficiency to overcome thermodynamic and kinetic barriers.[16] Copper-based catalysts have emerged as the leading choice for cyclohexanol dehydrogenation due to their ability to operate effectively at moderate temperatures. Common systems include Cu/Al_2O_3,[17] Cu-Zn/SiO_2,[18] Co-Al_2O_3,[19] $CuNi$-CeO_2.[20] These catalysts provide impressive activity and selectivity for cyclohexanone. However, by-products such as cyclohexene and condensation products are often generated due to competing side reactions, including dehydration and aromatization. Literature reports highlighted that optimizing copper content enhances catalytic performance, with catalysts containing approximately 26 wt% Cu showing superior activity. This improvement is attributed to enhanced copper dispersion and smaller crystallite sizes, which increase the number of active sites and improve selectivity.[17] Despite the advantages of Cu-based catalysts, they face challenges such as deactivation caused by coking, poisoning, and structural changes during extended use. These limitations have prompted investigations into alternative catalytic systems. Among these, ruthenium (Ru)-based supported catalysts have attracted attention, because of the distinct catalytic properties of ruthenium with support. Hierarchical zeolite 4A (HZ4A) can be a good support for cyclohexanol to phenol conversion with the release of hydrogen due to its acidic and structural characteristics. The Ru/HZ4A system offers the potential for enhanced selectivity and stability, particularly at low operating temperatures. Its performance is influenced by factors such as metallic Ru dispersion, the acid-base nature of the support, and the size of Ru particles. This study explores the use of Ru/HZ4A catalysts for cyclohexanol dehydrogenation, focusing on their activity, selectivity, and stability under varied reaction conditions. By analysing the unique properties of Ru-based catalysts and their interactions with HZ4A supports, we aim to uncover insights that optimize catalyst design for industrial applications. These findings could contribute to more efficient and sustainable processes for producing cyclohexanone, phenol, and related compounds, meeting the growing demands of the chemical industry.

Table 1. Literature reports for hydrogenation and Dehydrogenation Reactions:

Entry	**Substrate**	**Catalyst**	**Temp. (°C)**	**pH_2 (bar)**	**Product**	**Conv. (%)**	**Ref.**
1	Phenol	Pt/CeO_2	100	30	Cyclohexanol	86	12
2	Phenol	Ni/SiO_2	200	10	Cyclohexanol	81	13
3	Phenol	Co/CeO_2	150	30	Cyclohexanol	82	14
4	Cyclohexanol	Cu/Al_2O_3	250	_	Cyclohexanone	81	17
5	Cyclohexanol	$Co\text{-}Al_2O_3$	250	_	Cyclohexanone	60	19
6	Cyclohexanol	$Cu\text{-}Zn/SiO_2$	250	_	Cyclohexanone	91	18
8	Cyclohexanone	Pd/zeolite	250	_	Phenol	46	21
9	Cyclohexanone	Rh/Al_2O_3	250	_	Phenol	59	21

1.3 Objective

- To design and synthesize stable heterogeneous catalysts based on noble/non-noble metals with or without supports.
- To extensively characterize the synthesized catalysts using various techniques like P-XRD (Powder X-ray diffraction), SEM (Scanning Electron Microscope), FTIR (Fourier Transform Infrared spectroscopy), TEM (Transmission Electron Microscope), and XPS (X-ray Photoelectron Spectroscopy).
- To investigate the performance of the synthesized catalysts for the (de)hydrogenation of cyclic alcohol under mild conditions.
- To explore how to make the catalyst more economical and recyclable, making it ideal for large-scale industrial applications.
- To understand and explore the working of equipment like tubular furnace, programmable oven, vacuum oven, high-pressure reactors, and other characterization techniques like P-XRD, GC-MS, and elemental analysis (CHNS). The working principles and handling of these instruments will be learned throughout the year.

CHAPTER 2

Experimental Section

2.1 Material and Instrumentation: All reagents and solvents for the synthesis and analysis were purchased from Merck, Sigma Aldrich, and TCI. Used as received without any further purifications. ^{1}H NMR was recorded in deuterated solvent (D_2O, $CDCl_3$) using Bruker Avance 400 and Bruker Ascend 500. FTIR was conducted in the mid-IR range spanning from 500 to 4000 cm^{-1} using the Brucker VERTEX 70 instrument. The P-XRD was performed in Rigaku Smart Lab, Automated Multipurpose X-ray Diffractometer. The GC-TCD analyses are performed on a Shimadzu GC-2014 system using a Shin Carbon-ST packed column.

2.2 Synthesis of catalysts:

Synthesis of HZ4A: Hierarchical zeolite 4A was synthesised by the previously reported method.[22] Synthesis of hierarchical zeolite 4A by dispersing 1g of pre-heated zeolite 4A in an aqueous urea solution (75 mL distilled water). The mixture was stirred for 20 minutes at room temperature. Then the mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 220 °C for 12 h in a programmable oven. After completion, the autoclave was allowed to cool naturally to room temperature. The solid product was recovered by filtration and washed thoroughly with distilled water until the filtrate reached a neutral pH of 7. The material was then dried and calcined at 350 °C for 12 h using a muffle furnace, with the heating rate set to 5 °C per minute.

Synthesis of Ru nanoparticles: 50 mg CTAB was added to a 5 mL aqueous solution of $RuCl_3.xH_2O$ (0.0104 g). To which aqueous solution of $NaBH_4$ (25 mg in 5 mL H_2O) was subsequently added dropwise under sonication. The contents of the flask were sonicated at room temperature for 30 minutes, resulting in a black coloured suspension of Ru nanoparticles, which were then collected by centrifugation and washed with distilled water for several times, dried under vacuum and then used for catalytic reactions.

Synthesis of ruthenium catalyst: To synthesize ruthenium nanoparticles, (0.05 mmol) ruthenium (III) chloride and (50 mg) CTAB were dissolved in 5 mL of water. Aqueous solution of sodium borohydride (25 mg in 5 mL of water) was added to obtain a black suspension of ruthenium nanoparticles. The suspension was subjected to sonication at room temperature for 20 minutes to ensure uniform dispersion and formation of the catalyst. Ruthenium catalyst was then collected by centrifugation, thoroughly washed multiple times with distilled water to remove impurities and dried under vacuum. The prepared catalyst was stored for subsequent use in catalytic reactions.

Synthesis of ruthenium supported on HZ4A: $RuCl_3.3H_2O$ (0.05 mmol) was dispersed in 5 mL distilled water in the presence of HZ4A (95 mg), followed by stirring for 2 hours. Further, dropwise addition of an aqueous solution of $NaBH_4$ to the above solution, followed by stirring for 20 minutes, resulted in the formation of a black suspension of Ru/HZ4A catalyst. The Ru/HZ4A catalyst was collected by centrifugation, thoroughly washed two times with distilled water, and dried under vacuum. The prepared catalyst was stored for subsequent use in catalytic reactions.

2.3 Catalytic (de)hydrogenation over Ruthenium catalysts:

Catalytic hydrogenation of Phenol over Ru NP catalyst: In a 50 mL round-bottom flask, ruthenium nanoparticles (0.05 mmol) were dissolved in 5 mL of distilled water. After the proper dispersion of the catalyst, phenol (94.1 mg, 1 mmol) was added. The mixture was stirred under a hydrogen balloon at room temperature for 24 h, resulting in a brown-coloured cyclohexanol product. After 24 h, the reaction was monitored with TLC.

Catalytic dehydrogenation of Cyclohexanol over Ru/HZ4A catalyst: In a 10 mL single neck tube, add (0.05 mmol) Ru/HZ4A catalyst and (5 mmol) cyclohexanol. Then, the reaction tube was attached to a condenser (-5 °C) along with a water displacement setup. After three vacuum/argon flash cycles, argon gas was filled in the reaction setup, and the reaction mixture was stirred at 160 °C in an oil bath. The water displacement method was used to estimate the amount of hydrogen gas generated per unit of time. Further, the composition of the released gas was confirmed by GC-TCD analysis.

Heterogeneity test

Ru/HZ4A catalyst (100 mg) was stirred with an excess of elemental mercury (Hg^0) at room temperature for 5 hours to poison surface Ru sites. After treatment, 5 mmol of cyclohexanol was added to the reactor fitted with a condenser and gas burette. The system was subjected to three cycles of vacuum and argon flushing. The reaction mixture was stirred at 970 rpm and heated to 160 °C in an oil bath. Hydrogen evolution was measured via water displacement, and the reaction progress was monitored over time (Fig. 7)

CHAPTER 3

Results and Discussions:

3.1 Synthesis and characterisation of the catalyst:

The Ru nanoparticles were characterized using Powder X-ray Diffraction (P-XRD) and Scanning Electron Microscopy (SEM). The XRD pattern exhibited a prominent peak at a 2θ angle of 43°, which can be attributed to the (101) crystallographic plane of hexagonal closed-packed Ru nanoparticles (Figure 1). The presence of broad diffraction peaks in the spectrum suggests the amorphous of synthesized Ru particles

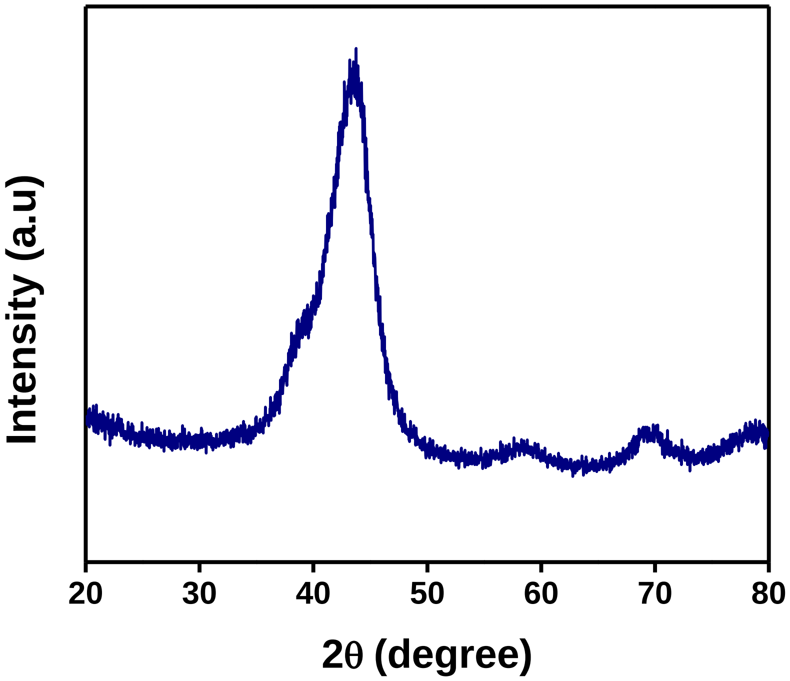


Figure 1. PXRD spectrum of Ru catalyst

To know about the morphology of the catalyst, FE-SEM analysis was carried out. SEM image and corresponding EDS spectra confirmed the presence of Ru (Figure 2).

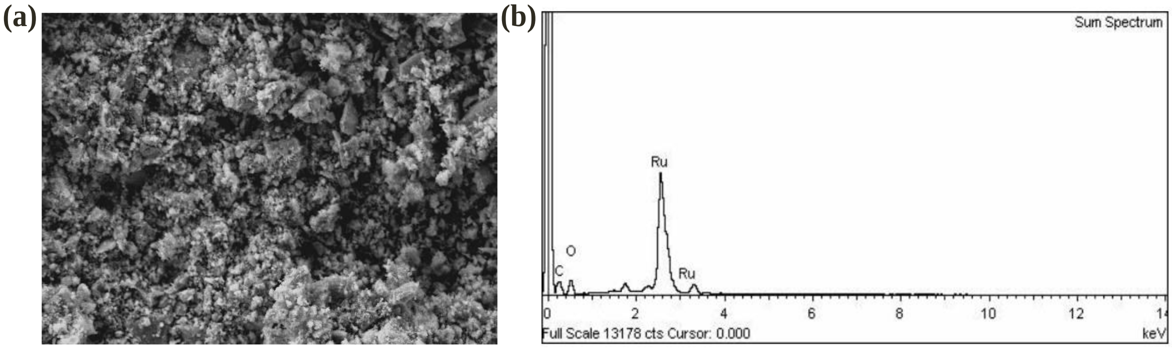


Figure 2. SEM image and corresponding EDS spectra of the Ru catalyst

The Ru/HZ4A (5 wt%) catalyst was analysed using FTIR, P-XRD, and SEM techniques. In the FTIR spectrum of HZ4A, characteristic bands were observed at 466, 534, and 982 cm^{-1}, corresponding to Si-O-Al bending, D4R units, and asymmetric stretching of Si-O-Al in the framework. Following Ru incorporation, these bands showed minor shifts, indicating that the zeolite structure maintained its framework (Figure 3).

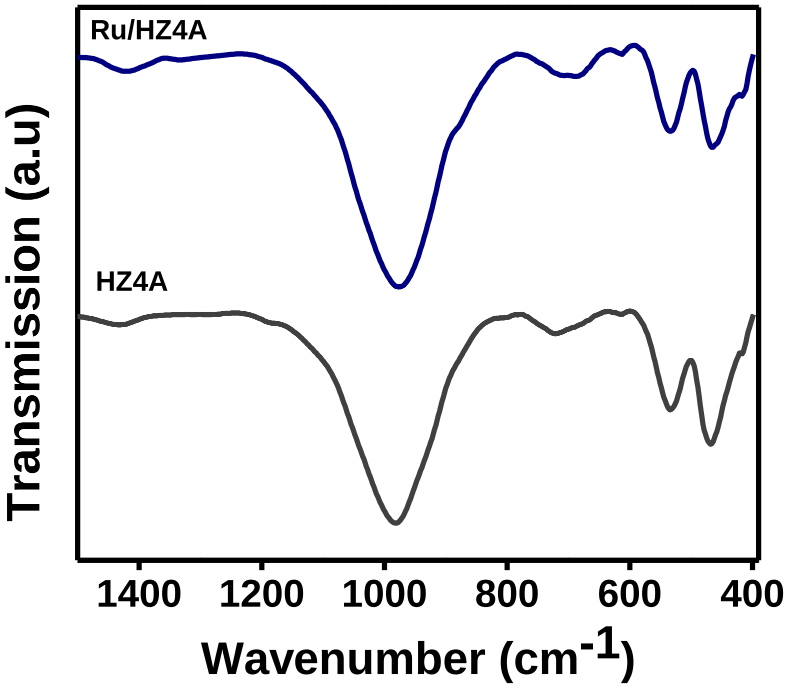


Figure 3. FT-IR spectrum of HZ4A and Ru/HZ4A

P-XRD analysis of HZ4A and Ru/HZ4A showed prominent peaks attributed to the HZ4A framework, confirming its crystalline nature. The absence of Ru-specific peaks indicates high dispersion of Ru nanoparticles on the support (Figure 4).

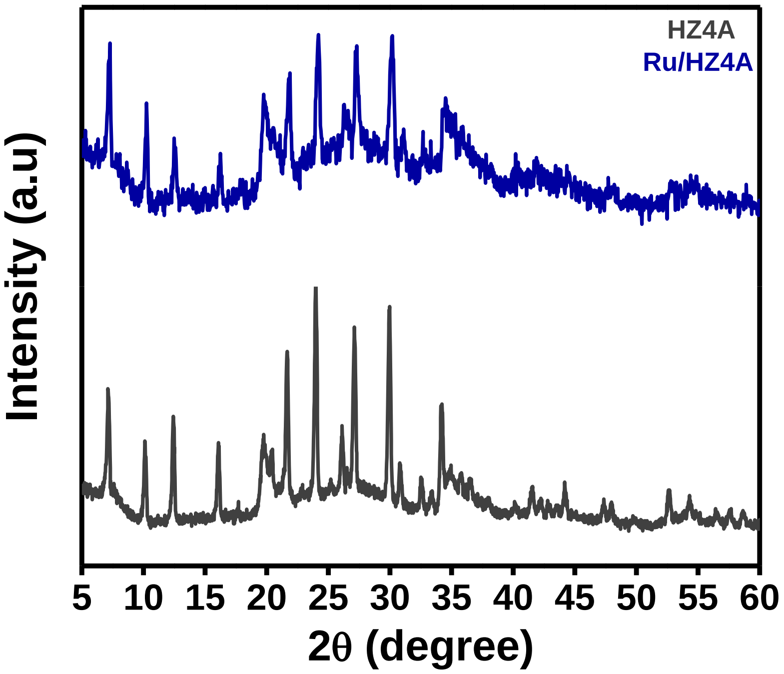


Figure 4. P-XRD data HZ4A and Ru/HZ4A

FE-SEM images of the HZ4A support and Ru/HZ4A catalyst revealed a macro-cavity-like surface morphology, with no distinct Ru nanoparticles visible, likely due to their ultra-small size (Figure 5a, b). EDS confirmed the uniform presence of Ru along with Si, Al, and O within the sample (Figure 5c)

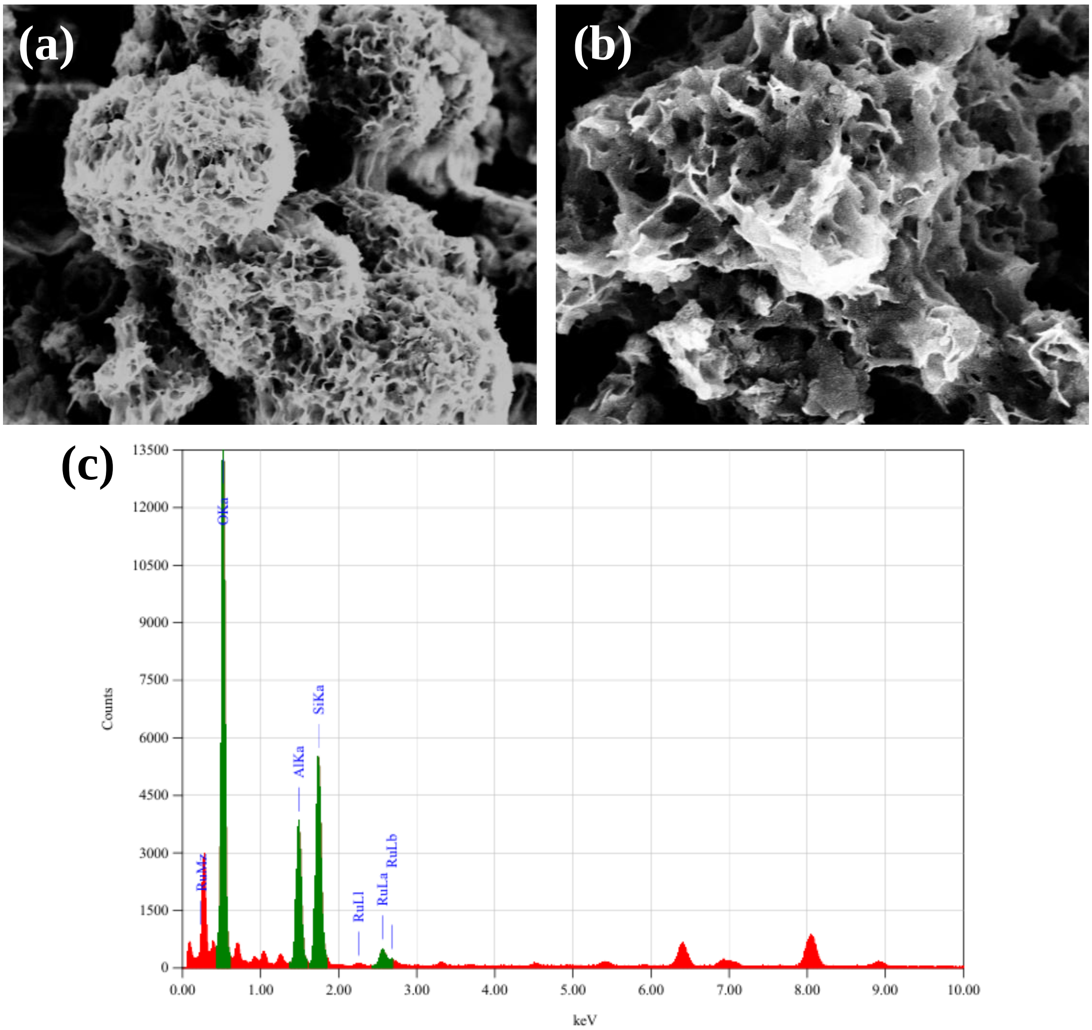


Figure 5. SEM images of (a) HZ4A, (b) Ru/HZ4A, and EDS data of (c) Ru/HZ4A

3.2 Catalytic activity for the dehydrogenation of cyclohexanol

After successful synthesis of catalysts, we optimised the catalytic activity of various ruthenium-based systems and assessed them for the dehydrogenation of cyclohexanol under different thermal and reaction conditions, as summarised in Table 2. Initially, Ru nanoparticles (Ru NP) were tested in aqueous KOH medium at 130 °C and 140 °C (Table 2, entries 1-2), but no conversion or hydrogen gas evolution was observed, suggesting that these conditions were insufficient to activate the catalyst. In the absence of a solvent (Table 2, entry 3), the system also remained inactive. However, a notable change occurred in (Table 2, entry 4) when KOH was retained and the solvent removed; the conversion reached 8%, with >99% selectivity for cyclohexanone and 10 mL of gas evolved. After an elevated temperature of 160 °C (Table 2, entry 5), Ru NP still showed no activity in aqueous KOH, implying that solvent presence may suppress catalytic sites or alter reaction dynamics unfavourably. Interestingly, under solvent- and base-free conditions for an extended reaction time of 10 h (Table 2, entry 6), the catalyst exhibited a significant conversion of 51%, with 96% selectivity to cyclohexanone and 4% to phenol, alongside 76 mL of H_2 gas evolution. This demonstrates that thermal activation and longer residence time are key drivers for efficient hydrogen evolution, even in the absence of additives. The catalytic efficiency improved substantially upon employing Ru supported on HZ4A zeolite (Ru/HZ4A). The reaction at 140 °C for 8 h (Table 2, entry 7) without solvent or base showed no evolution of H_2 gas. Increase in temperature to 160 °C and reduction in reaction time to 4 h (Table 2, entry 8) resulted in 84% conversion with 97% cyclohexanone selectivity, 3% phenol formation, and 112 mL of H_2 evolution. These results highlight the enhanced activity of the Ru/HZ4A system under optimal thermal conditions, likely due to the synergistic interaction between Ru species and acidic zeolite sites. In the presence of KOH (Table 2, entry 9), although the conversion decreased to 4%, the selectivity to cyclohexanone remained >99%, and gas evolution was very less (6 mL). The Ru/HZ4A catalyst, particularly under base-free and high-temperature conditions, demonstrated superior performance, making it a promising candidate for efficient hydrogen production and selective cyclohexanone synthesis.

Table 2. Optimization of reaction conditions for the cyclohexanol dehydrogenation

Entry	**Catalyst**	**Solvent (mL)**	**Base (equiv.)**	**Time (h)**	**Temp. (°C)**	**Conv. (%)**	**Selectivity (%)**		**H_2 gas (mL)**
							Cyclohexanone	**Phenol**	
1	Ru NP	H_2O	KOH	8	130	_	_	-	_
2	Ru NP	H_2O	KOH	8	140	_	_	-	_
3	Ru NP	H_2O	KOH	8	160	_	_	_	_
4	Ru NP	_	_	8	140	_	_	_	_
5	Ru NP	_	KOH	8	140	8	>99	_	10
6	Ru NP	_	_	10	160	51	96	4	76
7	Ru/HZ4A	_	_	8	140	_	_	_	_
8	Ru/HZ4A	_	_	4	160	84	97	3	112
9	Ru/HZ4A	_	KOH	8	160	4	>99	_	6
Reaction condition: Substrate (5 mmol), Catalyst (0.05 mmol), and 160 °C.									

Moreover, we further screened the various catalysts for the dehydrogenation of cyclohexanol was conducted at a constant temperature of 160 °C, and the results are summarised in Table 3. Among all the catalysts tested, Ru/HZ4A exhibited the highest catalytic performance, achieving 84% conversion within just 4 h. This catalyst also showed excellent selectivity, with 97% of the product being cyclohexanone and a minor formation of phenol (3%). Additionally, it facilitated the highest H_2 gas evolution (112 mL), indicating its superior dehydrogenation efficiency (Table 3, entry 1). In contrast, catalysts such as Ru/CeO_2 and Ru/H-Silica demonstrated moderate activity, with conversions of 20% and 23%, respectively, over a longer duration of 8 h. Both catalysts, however, maintained high selectivity toward cyclohexanone (> 99%) and produced lower H_2 volumes (26 mL and 30 mL, respectively) (Table 3, entries 2-3). The Cu/HZ4A catalyst showed very low activity, yielding only 6% conversion and 8 mL of hydrogen gas, despite maintaining high selectivity (Table 3, entry 4). In the case of Co/HZ4A, exhibited negligible activity under the same conditions, with no measurable conversion or hydrogen production (Table 3, entry 5). The bare HZ4A support also showed no activity under the same conditions (Table 3, entry 6). Interestingly, a nanocomposite catalyst comprising Ru nanoparticles supported on HZ4A (RuNP+HZ4A) achieved 33% conversion and generated 44 mL of H_2 gas, demonstrating a significant improvement over the support alone and indicating the important role of nanoscale metal dispersion. Overall, Ru-based catalysts, particularly Ru/HZ4A, were found to be highly effective for cyclohexanol dehydrogenation, both in terms of conversion and hydrogen evolution, underscoring their potential in hydrogen storage and release applications.

Table 3. Screening of different metal catalysts for the cyclohexanol dehydrogenation

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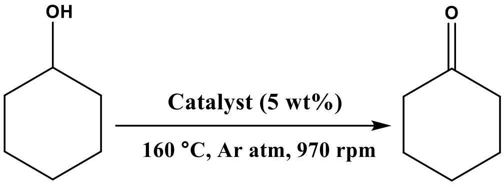
<tr><td colspan="8">
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<tr><th rowspan="2">Entry</th><th rowspan="2">Catalyst</th><th rowspan="2">Temp. (°C)</th><th rowspan="2">Time (h)</th><th rowspan="2">Conv. (%)</th><th colspan="2">Selectivity (%)</th><th rowspan="2">H_2 gas (mL)</th></tr>
<tr><th>Cyclohexanone</th><th>Phenol</th></tr>
<tr><td>1</td><td>Ru/HZ4A</td><td>160</td><td>4</td><td>84</td><td>97</td><td>3</td><td>112</td></tr>
<tr><td>2</td><td>Ru/CeO_2</td><td>160</td><td>8</td><td>20</td><td>>99</td><td>_</td><td>26</td></tr>
<tr><td>3</td><td>Ru/H-Silica</td><td>160</td><td>8</td><td>23</td><td>>99</td><td>-</td><td>30</td></tr>
<tr><td>4</td><td>Cu/HZ4A</td><td>160</td><td>8</td><td>6</td><td>>99</td><td>_</td><td>8</td></tr>
<tr><td>5</td><td>Co/HZ4A</td><td>160</td><td>8</td><td>–</td><td>–</td><td>–</td><td>–</td></tr>
<tr><td>6</td><td>HZ4A</td><td>160</td><td>8</td><td>–</td><td>–</td><td>–</td><td>–</td></tr>
<tr><td>7</td><td>RuNP+HZ4A</td><td>160</td><td>8</td><td>33</td><td>>99</td><td>_</td><td>44</td></tr>
<tr><td colspan="8">Reaction condition: Cyclohexanol (5 mmol), Catalyst (100 mg), 160 °C, and 970 rpm.</td></tr>
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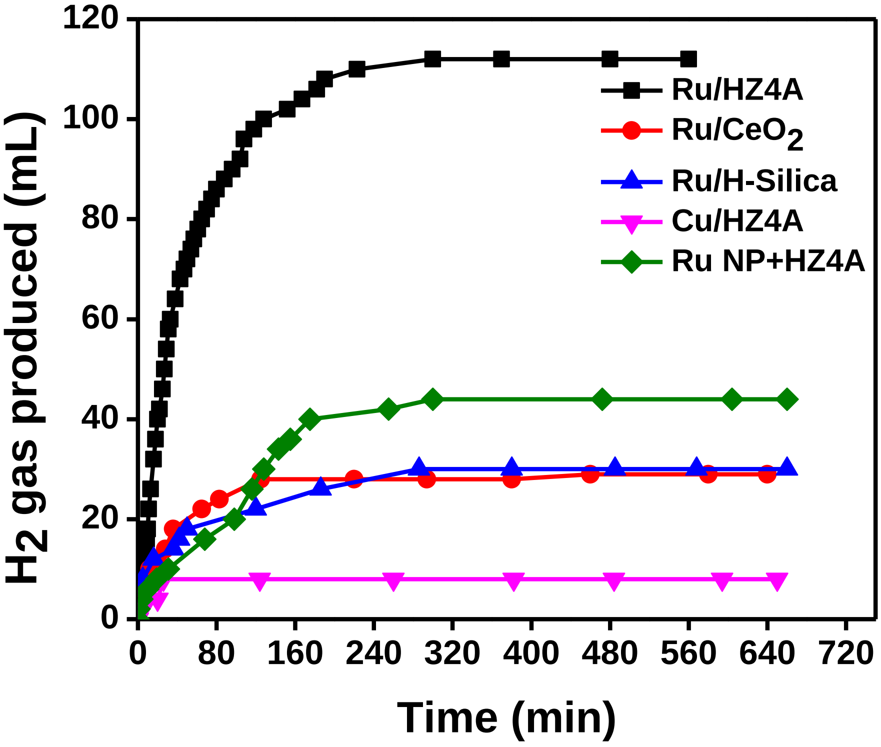

Figure 6. Time course plot of hydrogen production from cyclohexanol over the catalysts

3.3 Substrates Scope for dehydrogenation reaction with Ru/HZ4A catalyst

The catalytic activity of Ru/HZ4A was evaluated for the dehydrogenation of various alcohol substrates under identical reaction conditions. Among all, cyclohexanol exhibited the highest reactivity, with 84% conversion achieved in 4 hours, accompanied by the evolution of 112 mL of hydrogen gas. This result highlights the favourable interaction between the cyclic structure of cyclohexanol and the Ru/HZ4A catalyst. In contrast, linear alcohols such as 1-butanol and primary aromatic alcohols like benzyl alcohol showed significantly lower activity. Specifically, 1-butanol resulted in only 4% conversion and 6 mL of hydrogen gas after 6 hours (Table 4, entry 2), while benzyl alcohol yielded just 2% conversion and 4 mL of hydrogen. Notably, substrates such as propanol and 2-phenylethanol did not show any measurable conversion or hydrogen evolution under the same conditions (Table 4, entries 1-4). The poor performance of linear and aromatic alcohols may be attributed to steric hindrance or reduced adsorption affinity on the catalytic surface.

Overall, the results indicate that Ru/HZ4A is highly effective for the dehydrogenation of cyclohexanol, but its activity significantly diminishes with other alcohol substrates under identical reaction conditions.

Table 4. Substrates Scope for dehydrogenation reaction with Ru/HZ4A catalyst

Entry	**Substrate**	**Catalyst**	**Temp. (°C)**	**Time (h)**	**Conv. (%)**	**H_2 gas (mL)**
1	Propanol	Ru/HZ4A	160	6	_	_
2	1-Butanol	Ru/HZ4A	160	6	4	6
3	Benzyl alcohol	Ru/HZ4A	160	6	2	4
4	2-Phenylethanol	Ru/HZ4A	160	6	_	_
5	Cyclohexanol	Ru/HZ4A	160	4	84	112
Reaction condition: Substrate (5 mmol), Catalyst (0.05 mmol), and 160 °C.						

Further, the Ru/HZ4A catalyst lost activity in the presence of Hg(0), confirming the heterogeneous nature of the catalyst.

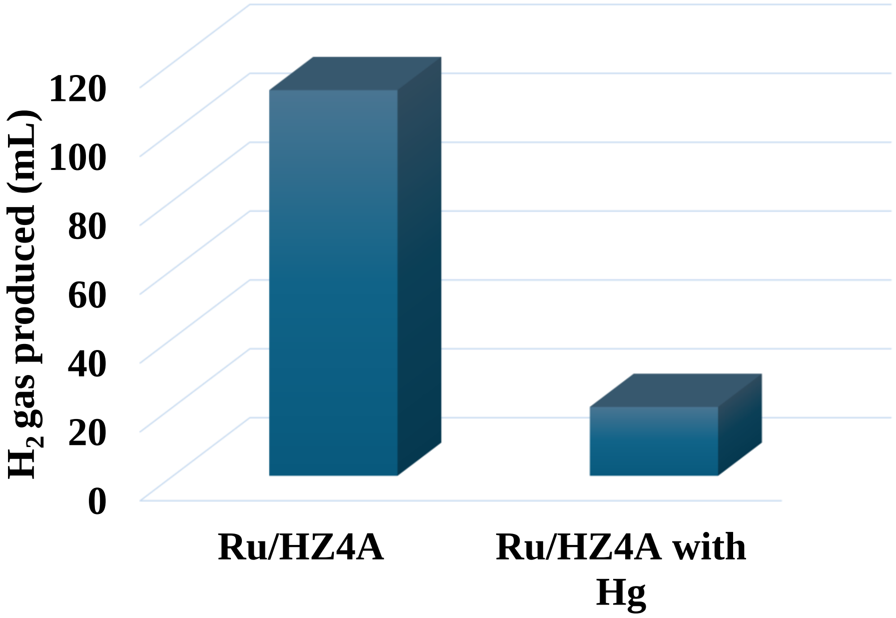

Figure 7. Heterogeneity test using an Hg(0) poisoning experiment for catalytic hydrogen production from cyclohexanol over the Ru/HZ4A catalyst

3.4 Mechanistic investigations:

. Infrared spectroscopy was employed to study the adsorption behaviour of cyclohexanol and cyclohexanone on HZ4A and Ru/HZ4A catalysts. On HZ4A, only characteristic cyclohexanol bands were observed at 25 °C, after heating to 160 °C. A slight decrease in band intensity at elevated temperature indicated partial desorption. However, the absence of new absorptions suggested no conversion to ketones. This suggests that HZ4A does not possess the active sites required to facilitate the dehydrogenation of cyclohexanol (Figure 8a).

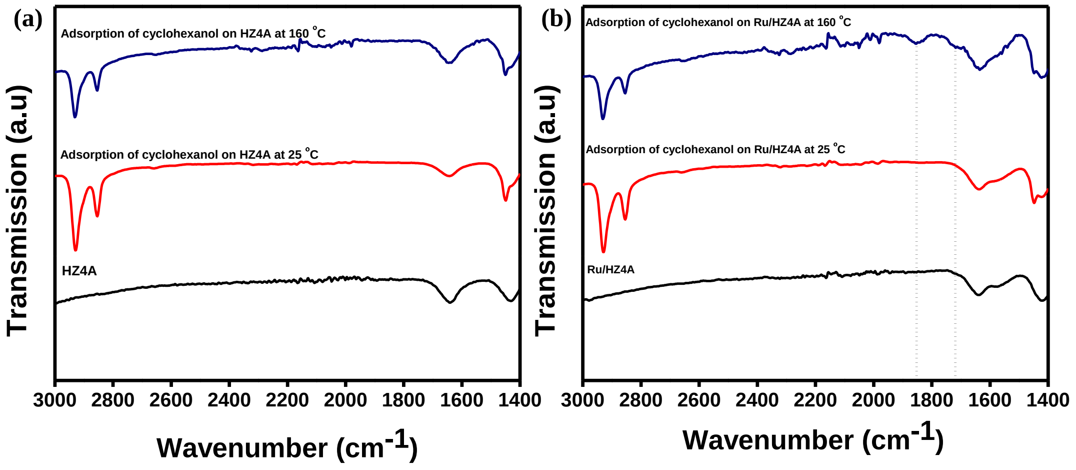

Figure 8. IR spectra of (a) HZ4A, showing the adsorption of cyclohexanol at 25 °C and 160 °C on the surface of the HZ4A support. (b) IR spectra of Ru/HZ4A, detailing the adsorption of cyclohexanol at 25 °C and 160 °C on the surface of the Ru/HZ4A catalyst.

The Ru/HZ4A catalyst showed distinct behaviour with cyclohexanol, displaying only physical adsorption at 25 °C. Upon heating to 160 °C, new IR bands at 1859 cm^{-1} and 1700 cm^{-1} appeared, indicating the formation of cyclohexanone via dehydrogenation. The 1859 cm^{-1} band corresponds to surface-bound carbonyl species. These results highlight the crucial role of Ru sites in activating O-H and C-H bonds for the dehydrogenation reaction (Figure 8 b).

The adsorption of cyclohexanone on HZ4A showed a carbonyl band near 1700 cm^{-1} at 25 °C, indicating intact adsorption. Heating to 160 °C led to reduced band intensity, suggesting partial desorption. No new IR features appeared in the 1700–1900 cm^{-1} region, indicating no transformation of the carbonyl group. This highlights the inert nature of HZ4A toward cyclohexanone activation under these conditions. (Figure 9a).

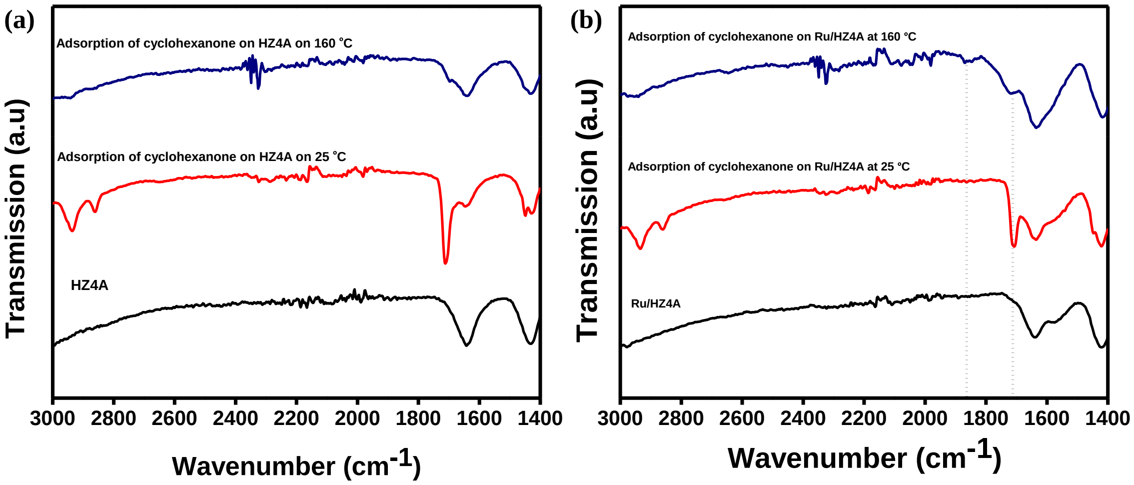

Figure 9. IR spectra of (a) HZ4A show cyclohexanone adsorption at 25 °C and 160 °C on the surface of the HZ4A support. (b) IR spectra of Ru/HZ4A, detailing the adsorption of cyclohexanone at 25 °C and 160 °C on the surface of the Ru/HZ4A catalyst.

Cyclohexanone adsorption on Ru/HZ4A showed a C=O stretching band at 1700 cm^{-1} at 25 °C. Upon heating to 160 °C, this band weakened and a new broad band near 1859 cm^{-1} appeared, indicating interaction of the carbonyl group with Ru sites. These results confirm Ru's role in facilitating both dehydrogenation and hydrogenation via bond activation through surface coordination (Figure 9b).

3.4 Catalytic (De)hydrogenation Reactions Results:

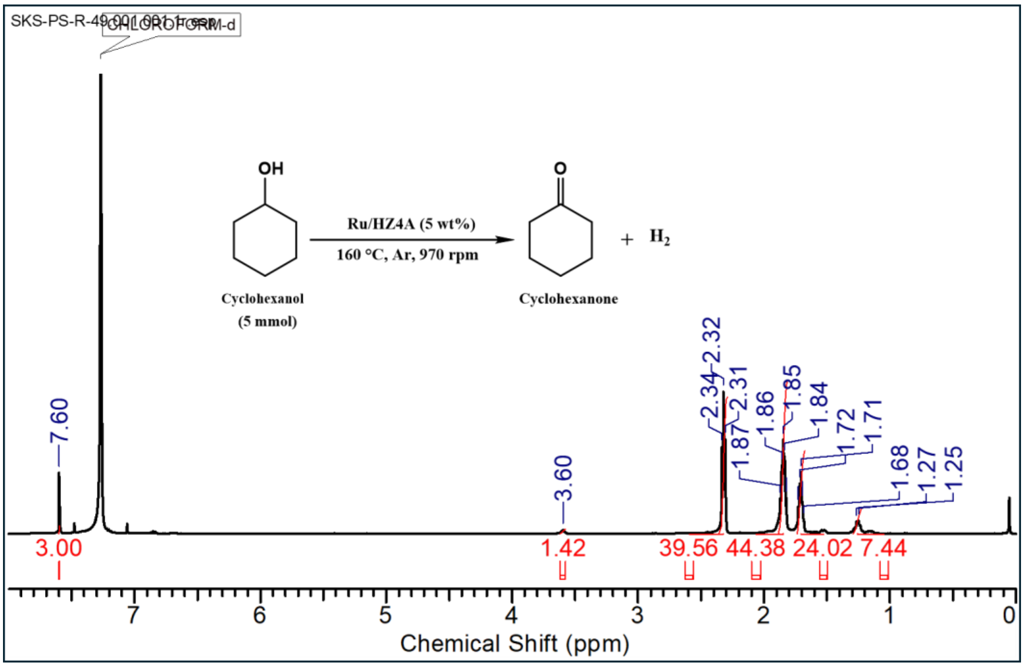

Figure 10. ^{1}H NMR spectra of catalytic dehydrogenation of cyclohexanol over the Ru/HZ4A catalyst

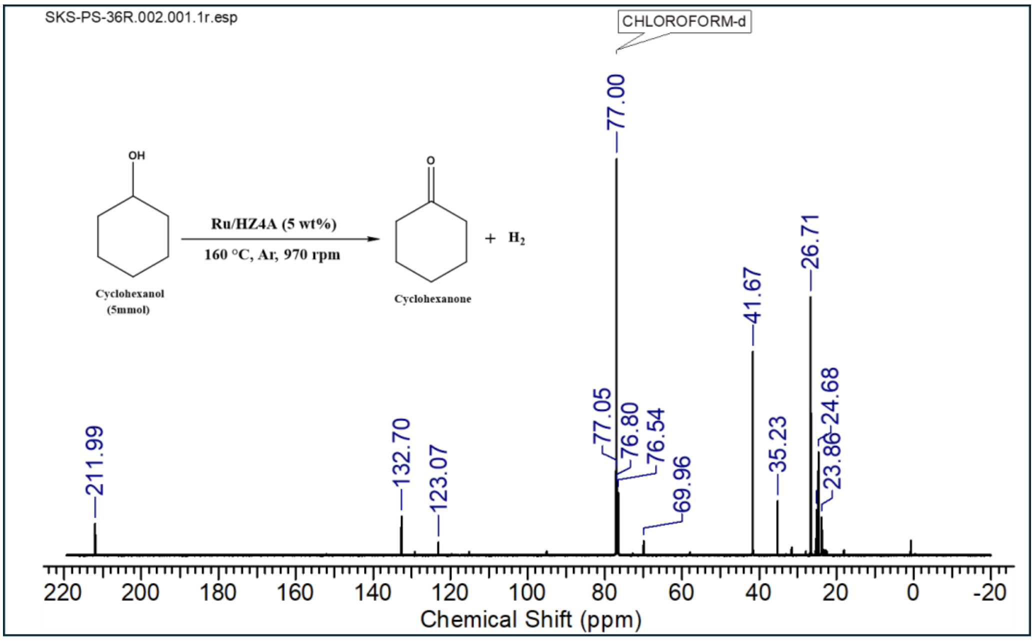

Figure 11. ^{13}C NMR spectra of catalytic dehydrogenation of cyclohexanol over the Ru/HZ4A catalyst

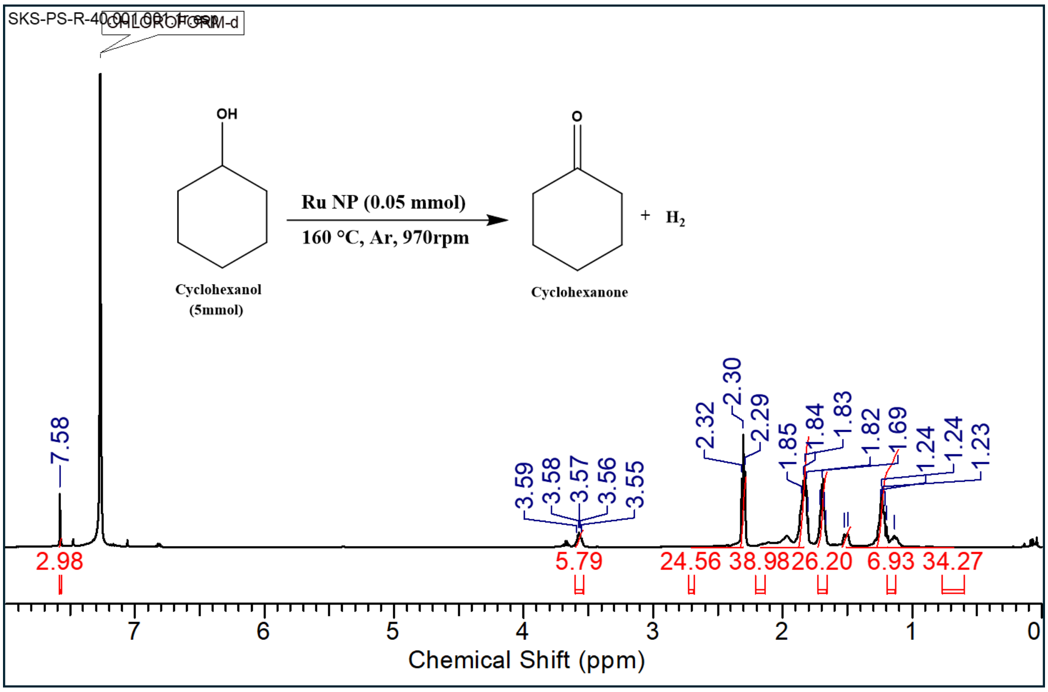

Figure 12. ^{1}H NMR spectra of the catalytic dehydrogenation of cyclohexanol over the Ru NP catalyst

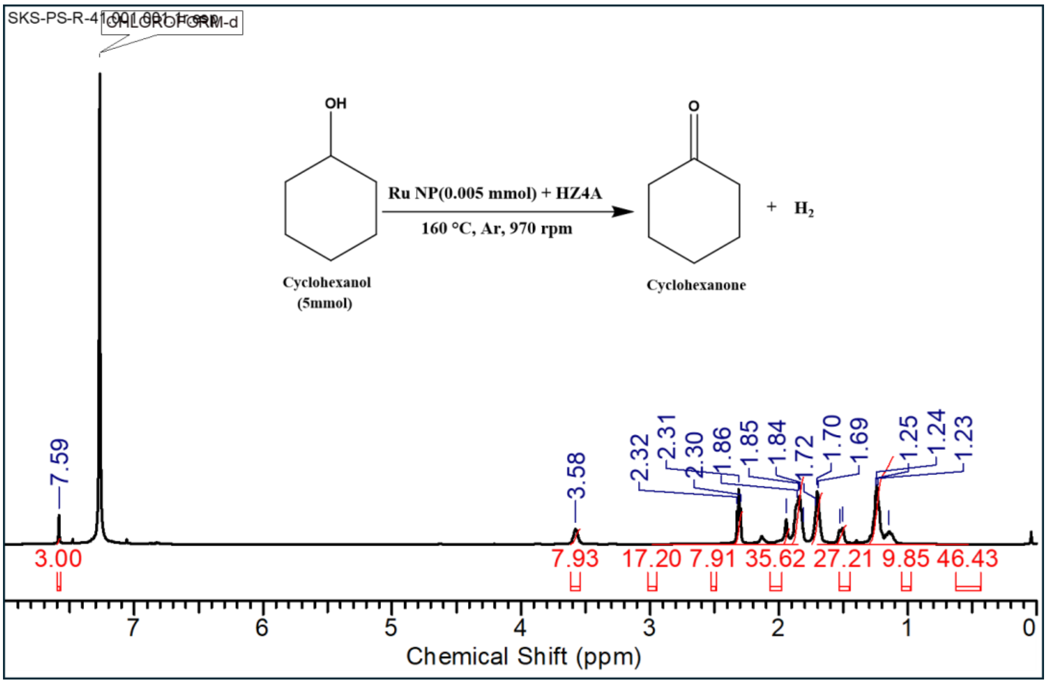

Figure 13. ^{1}H NMR spectra of the catalytic dehydrogenation of cyclohexanol over the Ru NP catalyst

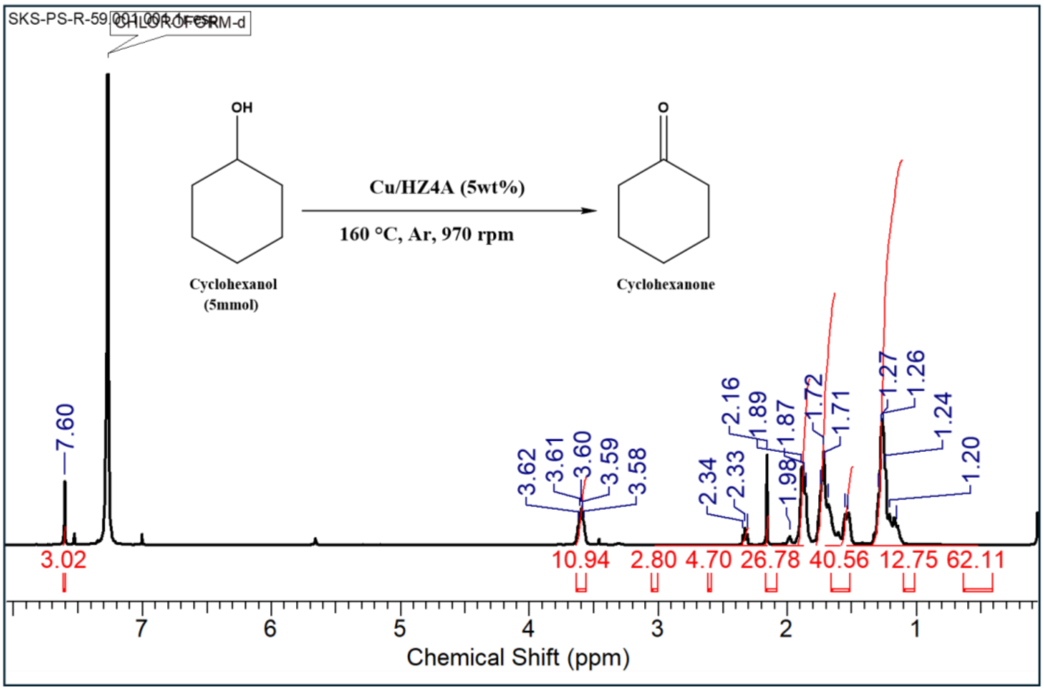

Figure 14. ^{1}H NMR spectra of the catalytic dehydrogenation of cyclohexanol over the Cu/HZ4A catalyst

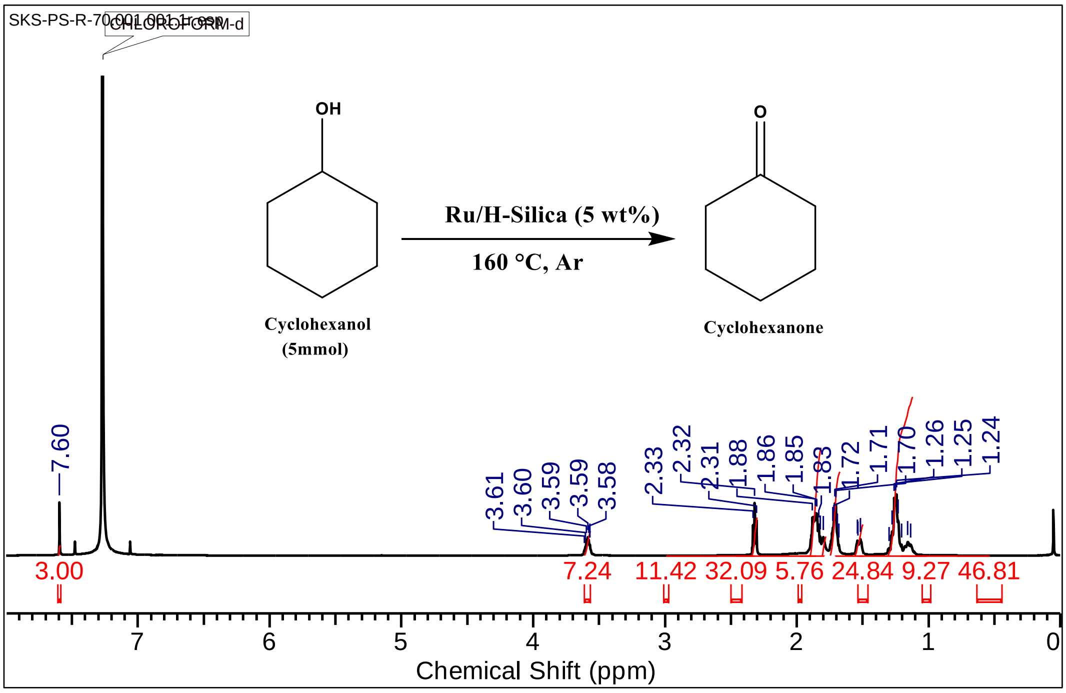

Figure 15. ^{1}H NMR spectra of the catalytic dehydrogenation of cyclohexanol over the Ru/H-Silica catalyst

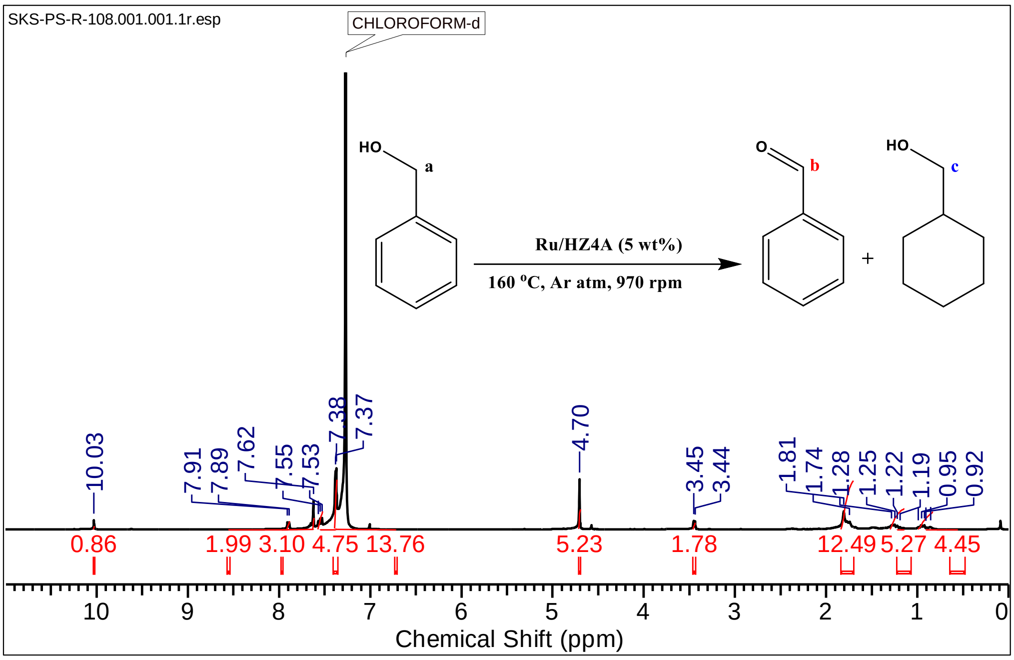

Figure 16. ^{1}H NMR spectra of the catalytic dehydrogenation of benzyl alcohol over the Ru/HZ4A catalyst

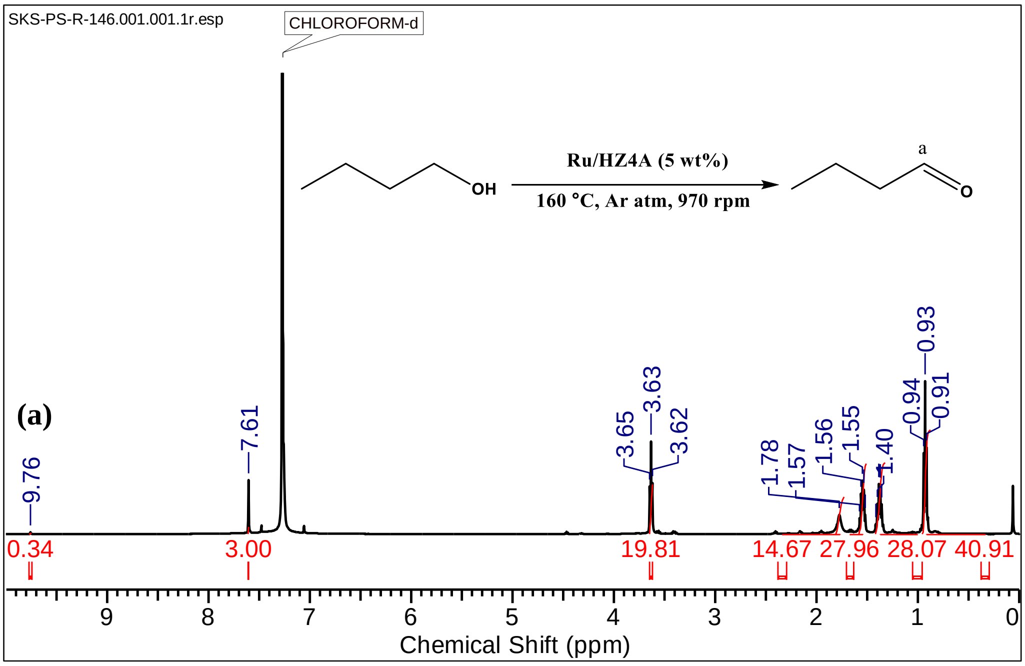

Figure 17. ^{1}H NMR spectra of the catalytic dehydrogenation of butanol over the Ru/HZ4A catalyst

4. Conclusion and Future Plan of Work

We successfully synthesized the Ru nanoparticles, Ru/HZ4A catalyst characterized by Powder X-ray Diffraction (P-XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDS). Furthermore, the process involves the use of a heterogeneous catalyst that is easy to separate and reuse. So, we found an efficient way to dehydrogenate the model compounds, which are value-added chemicals, achieving good conversions under mild reaction conditions. GC-TCD analysis confirmed the evolution of hydrogen gas during the reaction. The Ru/HZ4A catalyst demonstrated superior activity specifically for cyclohexanol. Additionally, a series of control experiments was performed using different catalysts. Further, we have performed some controlled experiments to explore the mechanistic aspects of the dehydrogenation reaction, providing deeper insights into the reaction pathways and the role of the Ru/HZ4A catalyst. To understand the scope of the catalyst, investigation of structurally diverse alcohols, including polyols and biomass-derived feedstocks, can help in broadening the application of this catalytic system for green chemical synthesis. Long-term catalytic stability, recyclability tests, and leaching studies should be performed to assess the durability and commercial feasibility of Ru/HZ4A in repeated cycles.

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