DEVELOPMENT OF CATALYSTS FOR (DE)HYDROGENATION REACTIONS

M.Sc. Thesis

By

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DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE

MAY, 2026

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M.Sc. Thesis

A THESIS

Submitted in partial fulfillment of the requirements

for the award of the degree of

Master of Science

by

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DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE

MAY, 2026

INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the report 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 2025** to **May 2026** 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.

14/05/2026

Signature of the student with date

(Chhagan Lal Meena)

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 M.Sc. thesis

(Prof. Sanjay K. Singh)

Chhagan Lal Meena has successfully given his/her M.Sc. Oral Examination held on **14 May 2026**.

Signature of the Supervisor of the MSc thesis

(Prof. Sanjay K. Singh)

Date: 14.05.2026

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Abstract

Polycarbonates are widely used in engineering thermoplastics known for their high strength, transparency, and thermal resistance. This work presents a cyclic process that involves the dehydrogenation of cyclohexanol to phenol and the hydrogenation of phenol to cyclohexanol. In this approach, waste polycarbonates are employed as a source for phenol production. The phenol obtained is then efficiently converted into cyclohexanol, achieving complete conversion with high selectivity. Aromatic alcohols are valuable chemical intermediates with significant applications in the pharmaceutical and polymer industries. Overall, this study provides a sustainable and cost-effective strategy for transforming polycarbonate waste into useful chemical products. The study aims to use a recyclable, easily separable solid catalyst to achieve high catalytic efficiency at comparatively low temperatures. Four chapters make up the thesis. The first chapter deals with the general introduction to cyclic alcohols and their dehydrogenated products. Chapter second includes the experimental procedures adopted for catalyst synthesis and the execution of various catalyst reactions. Chapter three presents a detailed discussion of the results obtained from various dehydrogenation experiments. Chapter four concludes the thesis by highlighting the major findings. The main target of this thesis is to activate and make a highly efficient heterogeneous catalyst under mild conditions.

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ACRONYMS

$CDCl_3$	Chloroform-d
D_2O	Deuterium Oxide
CD_3OD	Deuterated Methanol
H_2	Hydrogen
NMR	Nuclear Magnetic Resonance
PXRD	Powder X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
PC	Polycarbonate
BPA	Bisphenol A
GHG	Greenhouse gas

NOMENCLATURE

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

Chapter 1

Introduction

1.1 General Introduction

Plastics have become an integral component of modern society. However, the rapid increase in global population has led to a continuous rise in plastic waste, creating significant energy and environmental challenges. Current estimates indicate that worldwide plastic production is approximately 385 million tons annually, with projections suggesting an accumulation of nearly 30,000 million tons by 2050. In 2018, only 9% of plastic waste was recycled, 12% was incinerated, and the remaining 79% was deposited in landfills or released into the environment. This mismanagement has led to the widespread introduction of microplastics into ecosystems, accompanied by substantial greenhouse gas (GHG) emissions, thereby intensifying environmental risks and potential hazards to human health.[1]

Conventional mechanical recycling of plastics is often limited by thermal degradation, which deteriorates the optical, thermal, and mechanical properties of the recovered materials. In contrast, chemical upcycling of plastic waste offers a more sustainable pathway toward a circular, carbon-neutral society.[2] Nevertheless, the absence of highly efficient and scalable technologies highlights the urgent need for the development of advanced recycling and upcycling strategies. Polycarbonate (PC) is a high-performance engineering thermoplastic widely used across sectors such as automotive, construction, safety equipment, electronics, and biomedical applications.[3] Nevertheless, several studies have reported that its monomer, bisphenol A (BPA), can leach from PC-based products such as food containers and infant bottles, raising concerns regarding potential adverse impacts on human health.[4] Despite the continuous increase in global PC production capacity, the sustainable recycling and management of post-consumer PC waste remain imperative. The primary precursor of PC, BPA, is industrially synthesized *via* the acid-catalyzed condensation of phenol

with acetone.[5] Phenol itself is a key commodity chemical, serving as an essential synthetic intermediate in a wide range of industrial manufacturing processes.[6]

Hydrogenation and dehydrogenation are fundamental chemical processes integral to the synthesis of fuels, chemicals, and pharmaceuticals. Hydrogenation involves adding hydrogen to a compound, while dehydrogenation involves removing hydrogen. 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.[7] 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)[8], rhodium (Rh), [9] platinum (Pt),[10] ruthenium (Ru),[11] nickel (Ni),[12] and cobalt (Co).[12] 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 cyclohexanol, typically using metal nano-catalysts, which is often more efficient for cyclohexanol production. The second pathway is a two-step process: hydrogenation of phenol to cyclohexanol, usually catalyzed by nickel, followed by dehydrogenation of cyclohexanol to cyclohexanone.[12] 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 its use in polyamide fibers, cyclohexanone is also a valuable component in the pharmaceutical and fine chemical industries. Moreover, cyclohexanol dehydrogenation is particularly vital 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.[13]

A wide range of catalysts have been explored for dehydrogenation from cyclohexanol at high temperatures. The heterogeneous catalytic gas-phase dehydrogenation of cyclohexanol is typically conducted at atmospheric pressure and is endothermic, with reaction enthalpy. This endothermic characteristic requires elevated temperatures to drive the reaction forward, while also revealing the 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 underscores the critical need to develop catalysts that optimize cyclohexanone yield while minimizing undesired byproducts.[14]

This study aims to explore and develop a novel heterogeneous catalytic system that effectively catalyzes 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 of existing catalytic systems, this research aims to make a significant contribution to the field of fine chemical synthesis and to the advancement of sustainable energy solutions.

1.2 Literature Survey

Recent research has focused on noble metal-based heterogeneous catalysts for the hydrogenation of phenol to cyclohexanol. Catalysts such as Pd/C,[19] Pt/CeO_2,[20] Ni/SiO_2,[21] Co/CeO_2,[22] have demonstrated significant activity and selectivity. Ruthenium (Ru) offers a more economical alternative,[23] though it presents 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 yielded favorable conversion rates and selectivity. These systems exploit the unique properties of noble metals,

including high dispersion and small particle sizes, to achieve efficient hydrogenation reactions under controlled conditions.

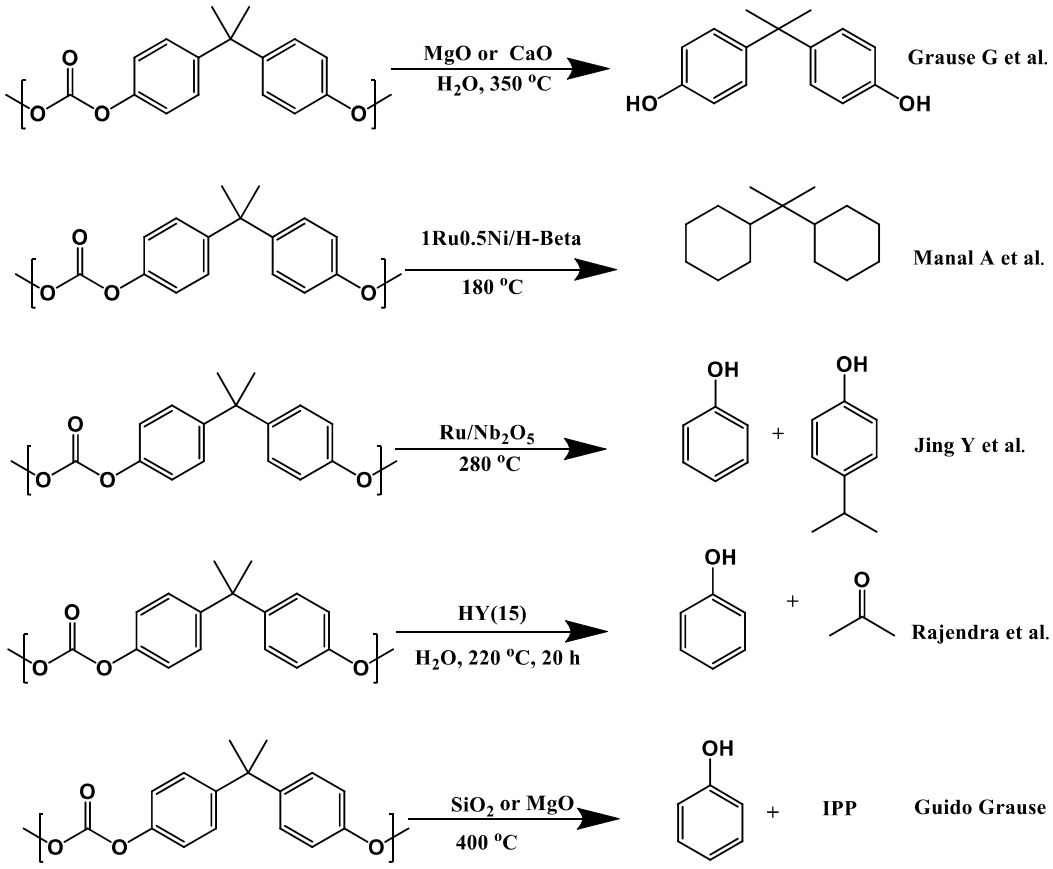
Similarly, the catalytic dehydrogenation of cyclohexanol to cyclohexanone or phenol is an equally critical industrial process. Copper-based catalysts have emerged as the leading choice for cyclohexanol dehydrogenation due to their ability to operate effectively at moderate temperatures. Common systems include, Cu/Al_2O_3,[24] $Cu\text{-}Zn/SiO_2$,[25] $Co\text{-}Al_2O_3$,[26] CuNi-CeO,[27] Cu/ZrO_2,[28] 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. Research has 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.[24] 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. HZ4A can be a good support for cyclohexanol to phenol conversion with the release of hydrogen due to its acidic and structural characteristics.

Table 1. Literature reports for hydrogenation and dehydrogenation reactions

Entry	Substrate	Catalyst	T (°C)	P_{H_2} (bar)	Product	Conv. (%)	References
1	Phenol	Pt/CeO_2	100	30	Cyclohexanol	86	20
2	Phenol	Ni/SiO_2	200	10	Cyclohexanol	81	21
3	Phenol	Co/CeO_2	150	30	Cyclohexanol	82	22
4	Cyclohexanol	Cu/Al_2O_3	250	_	Cyclohexanone	81	25
5	Cyclohexanol	Cu-Zn/SiO_2	250	_	Cyclohexanone	91	26
6	Cyclohexanol	Co-Al_2O_3	250	_	Cyclohexanone	60	27
7	Cyclohexanol	Cu/ZrO_2	250	_	Cyclohexanone	54	28
8	Cyclohexane	Pt/CeO_2	350	_	Benzene	30	30
9	Cyclohexanone	$Pd/(TFA)_2$	80	_	Phenol	64	29
10	Cyclohexanone	Pd/C	90	_	Phenol	99	19

High-density cycloalkanes are typically obtained through methanolysis and hydrodeoxygenation routes.[15] Nevertheless, a sustainable and economically viable pathway for recycling polycarbonate (PC) waste into phenol remains highly attractive for building a circular, resource-efficient economy. Such valorization requires efficient cleavage of the Csp^2–Csp^3 bond, which can be achieved through reductive or oxidative cleavage, de-alkylation, or de-alkenylation. These strategies, however, often demand severe conditions (>400 °C).[16] For example, Grause *et al.* demonstrated catalytic hydrolysis of PC above 350 °C, producing ~90% bisphenol A (BPA) but only 5–7% phenol with Lewis acid–base catalysts.[17] Ikeda *et al.* employed Na_2CO_3 as a homogeneous base, achieving ~50% phenol yield at 250–300 °C.[18] More recently, Jing *et al.* reported selective Csp^2–Csp^3 bond cleavage of PC using Ru/Nb_2O_5 under a hydrogen atmosphere. However, their method required elevated temperatures (270 °C), prolonged reaction time (6 h), pressurized H_2 (0.7 MPa), and a binary solvent system (methanol + hexane), ultimately affording only 20% phenol along with oxygenated by-products, raising both cost and process complexity. Therefore, the development of solid,

inexpensive, and corrosion-resistant catalysts capable of promoting selective phenol formation under mild conditions is essential for designing a more sustainable recycling strategy.



Scheme 1. Strategies used for the upcycling of polycarbonate waste for the production of different value-added chemicals.[16]

1.3 Objective

- To design and synthesize stable heterogeneous catalysts based on 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 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

2. Experimental Section

2.1 Material and Instrumentation:

All chemicals and solvents used for synthesis and analysis were purchased from Sigma-Aldrich and TCI. Used as received, with no further purifications. Bruker Avance 400 and Ascend 500 were used to record ^{1}H NMR in deuterated solvents (D_2O, $CDCl_3$, $CDCl_3$). The Brucker VERTEX 70 device was used to perform FTIR in the mid-IR band (500 to 4000 cm-1). The P-XRD was carried out on a Rigaku Smart 16 Lab, Automated Multipurpose X-ray Diffractometer.

2.2 Synthesis of catalysts:

Synthesis of HZ4A: Took a 100 mL round-bottom flask, zeolite 4A (1 g), and aqueous urea (0.333 g in 75 mL distilled water). Stir the mixture at room temperature for 20 minutes. Transferred the mixture into a 100 mL Teflon-lined autoclave. Carried out hydrothermal treatment at 220 °C for 12 h in a programmable oven. Allowed the autoclave to cool naturally to room temperature. Recovered the solid product by filtration and washed thoroughly with distilled water. Dried the product at 80 °C for 12 h. Calcined the dried sample at 350 °C for 12 h in a muffle furnace, with a heating rate of 5 °C/min.

Synthesis of palladium supported on HZ4A: Took a 50 mL round-bottom flask and added palladium tetrachloropalladate (0.05 mmol) and HZ4A (95 mg) into 5 mL of distilled water. Stir the mixture for 20 h at room temperature. Added an aqueous solution of $NaBH_4$ dropwise to the above mixture. Continued stirring for 3 h, which resulted in the formation of a block suspension of Pd/HZ4A catalyst. Collected the catalyst by

centrifugation. Washed the obtained solid twice with distilled water. Dried the Pd/HZ4A catalyst under vacuum.

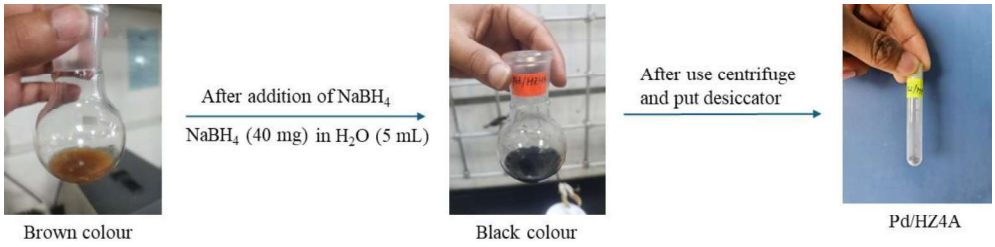


Fig. 1 Schematic diagram for the synthesis of Pd/HZ4A

2.3 Catalytic hydrogenation of phenol over Pd/HZ4A catalyst: In a 10 mL single-neck tube, add (0.5 mmol) palladium catalyst and 470.5 mg (5 mmol) of phenol. Then, the catalyst was properly dispersed, and phenol (470.5 mg, 5 mmol) was added. The reaction tube was attached to a condenser (-5 °C). After purging with hydrogen gas, the hydrogen balloon was placed, and the reaction vessel was dipped in the oil bath at 60 °C for 24 h and 970 rpm. The reaction was monitored with TLC, and the product was analyzed with ^{1}H NMR.

2.4 Catalytic dehydrogenation of cyclohexanol over Pd/HZ4A catalyst: In a 10 mL single-neck tube, add (0.5 mmol) palladium catalyst and 5 mmol of 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 introduced into 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 time.

2.5 Extraction of phenol from polycarbonates with HZ4A:

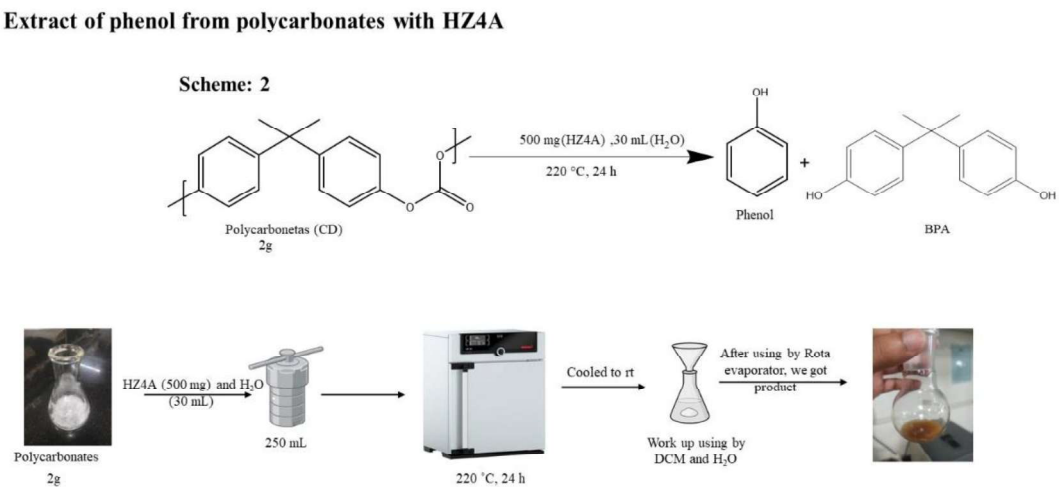


Fig. 2 Schematic diagram for the extraction of phenol

Procedure:

The waste polycarbonate (2.0 g) and distilled water (30 mL) were charged into a hydrothermal reactor. The reaction was conducted at 220 °C for 24 h. After completion, the reaction mixture was cooled to room temperature, followed by separation of the solid catalyst through centrifugation. The recovered solid was washed with distilled water and dried. The liquid fraction was extracted using dichloromethane (DCM). The organic phase was concentrated by rotary evaporation to afford the desired product.

CHAPTER 3

Results and Discussions:

3.1 Characterization of the HZ4A:

3.1.1 The P-XRD pattern of HZ4A shows many sharp peaks especially between 10° and 30° (2θ). These strong peaks indicate that the material has a well-organized crystalline structure. The large number of peaks suggests that HZ4A contains a typical silica/aluminosilicate framework. After 30°, the peak intensity gradually decreases, which means that a small amount of amorphous (less ordered) phase may also be present.

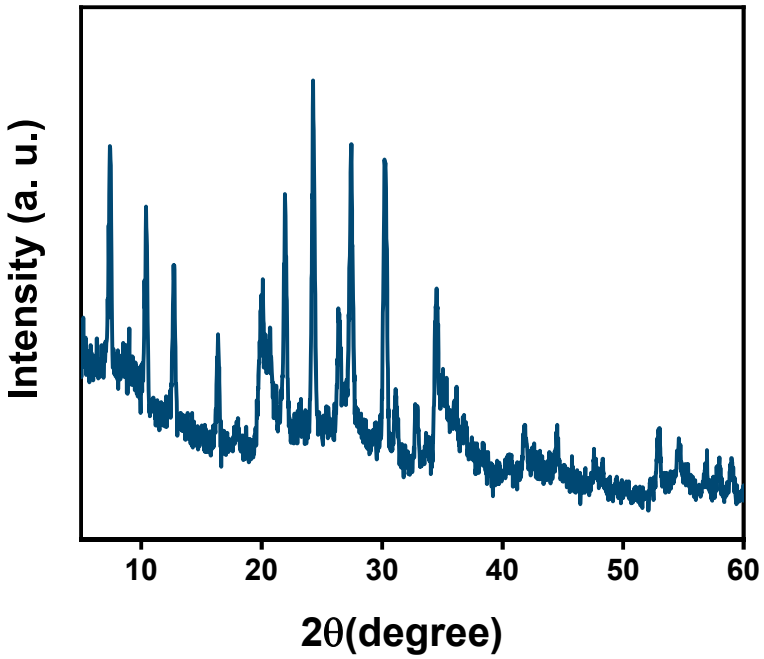


Fig. 3 P-XRD of HZ4A

3.1.2 FTIR spectra of HZ4A and Pd/HZ4A:

The FTIR spectra of HZ4A and Pd/HZ4A show identical characteristic framework vibrations, demonstrating that the zeolite structure is still intact following Pd loading. Both samples exhibit the bands about ~810, ~610, ~540, and ~450 cm^{-1}, which correspond to typical framework vibrations. Pd/HZ4A, on the other hand, shows small shifts and variations in band intensity, indicating interaction between Pd species and the zeolite framework. Overall, there is no discernible structural collapse, indicating that Pd was successfully incorporated without changing the core framework.

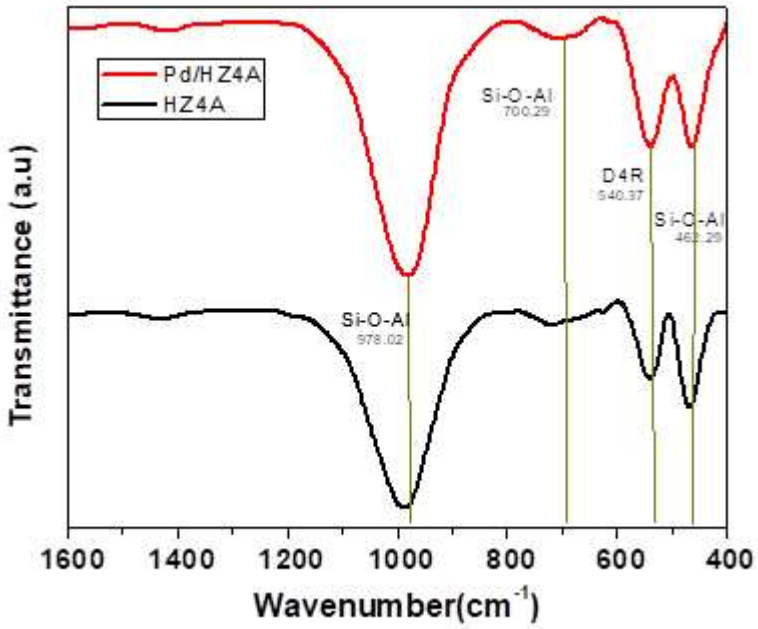
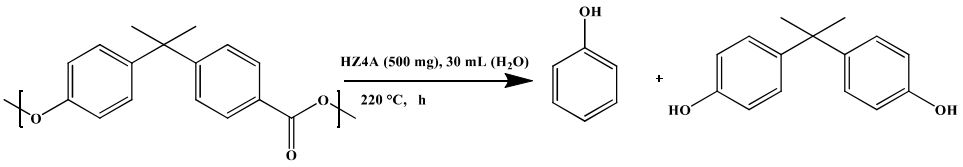


Fig. 4 FT-IR data of HZ4A and Pd/HZ4A

Table 2. Optimization table for the extraction of phenol from PC over HZ4A

Scheme:3



ENTRY	CATALYST (500 mg)	TIME (h)	TOTAL PRODUCT (g)	TOTAL PRODUCT (g)		SELECTIVITY (%)		YIELD (%)		CONVERSION (%)
				PHENOL	BPA	PHENOL	BPA	PHENOL	BPA	
1	HZ4A	16	1.23 g	1.077	0.152	87.6	12.39	72.77	8.49	>99%
2	HZ4A	20	1.31	1.215	0.095	92.77	7.22	82.09	5.30	>99%
3	HZ4A	24	1.57	1.47	0.102	93.51	6.49	99.3	5.6	>99%
4	HZ4A	30	1.18	1.12	0.05	94.92	5.07	75.7	3.35	>99%
5	HZ4A	40	1.19	1.17	0.011	99.1	0.99	80.40	0.61	>99%
6	HZ4A	46	1.4	1.386	0.014	99	1	99	0.78	>99%

Reaction condition: Reactant 2 g (PC), solvent 30 mL (H_2O), catalyst 500 mg (HZ4A), reaction temperature (220 ˚C), 250 mL autoclave reactor.

Phenol was obtained from the depolymerization of polycarbonate (2 g) using HZ4A (500 mg) in 30 mL of water at 220 °C, producing both phenol and bisphenol A (BPA). The influence of reaction time was studied over a range of 16 to 46 hours. At 16 hours, phenol selectivity was about 70%, indicating partial conversion. As the reaction time increased, phenol selectivity steadily improved, while BPA selectivity decreased, suggesting that BPA acts as an intermediate that further converts into phenol. At longer reaction times of 40 and 46 hours, phenol selectivity exceeded 99%, with complete (>99%) polycarbonate conversion. These results confirm that extended reaction time promotes the transformation of BPA into phenol, thereby enhancing phenol selectivity.

3.1.3 Selectivity of phenol and BPA

Selectivity is determined by reaction time. With time, phenol selectivity increases while BPA selectivity decreases. At 40 and 46 hours, phenol selectivity stays practically constant, at around 99%.

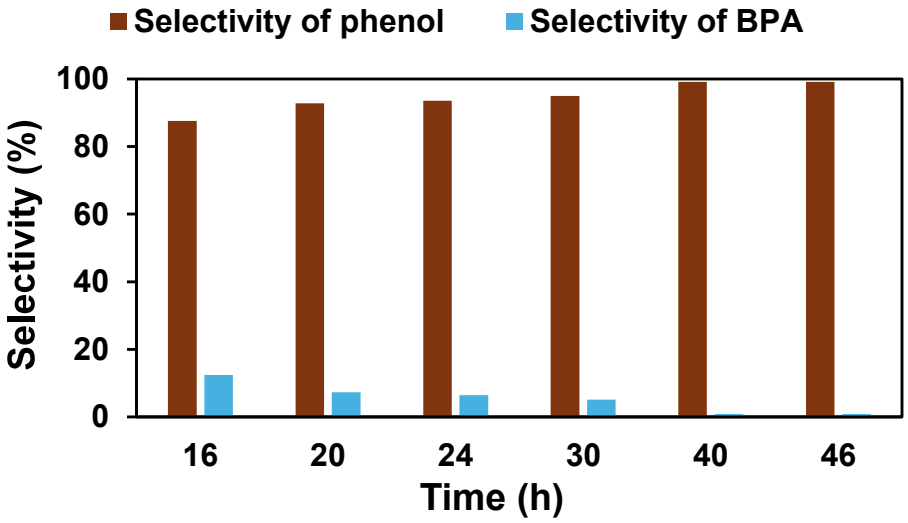


Fig.5 Selectivity data of phenol and BPA

3.1.4 SEM images of HZ4A and Pd/HZ4A

FE-SEM images of the HZ4A support and Ru/HZ4A catalyst presented a surface shape similar to a macrocavity. with no visible nanoparticles, possibly because of their small size (Fig. 6a, b). Pd, Si, Al, Na, and O were all uniformly present in the sample, based on EDS (Fig. 6c).

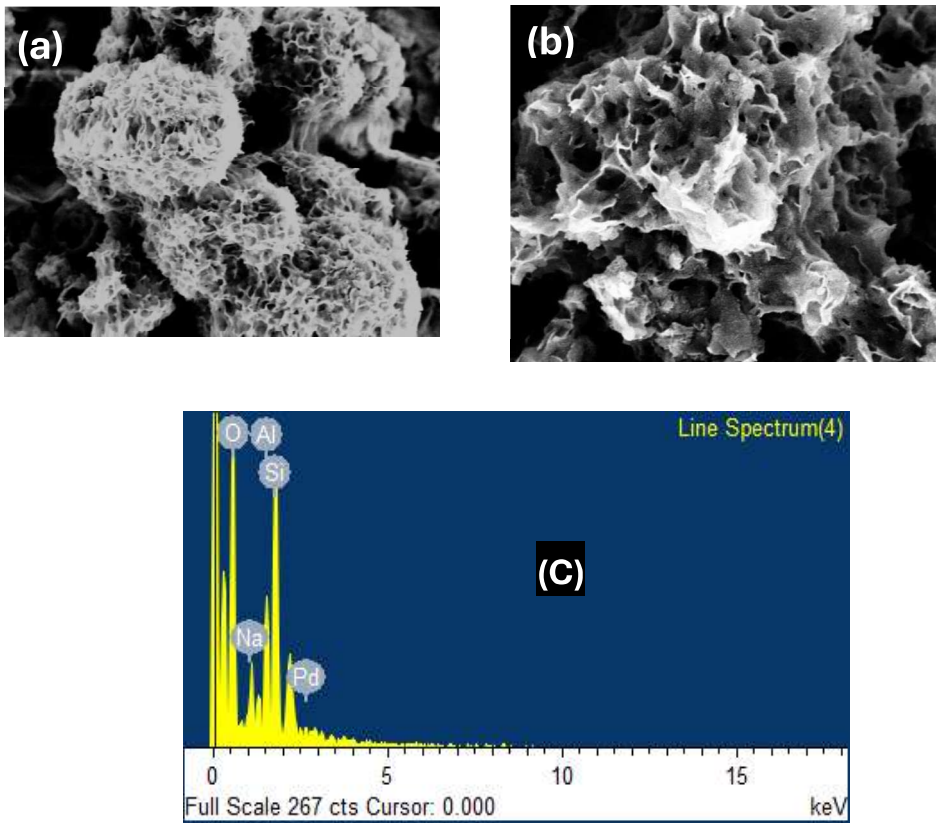
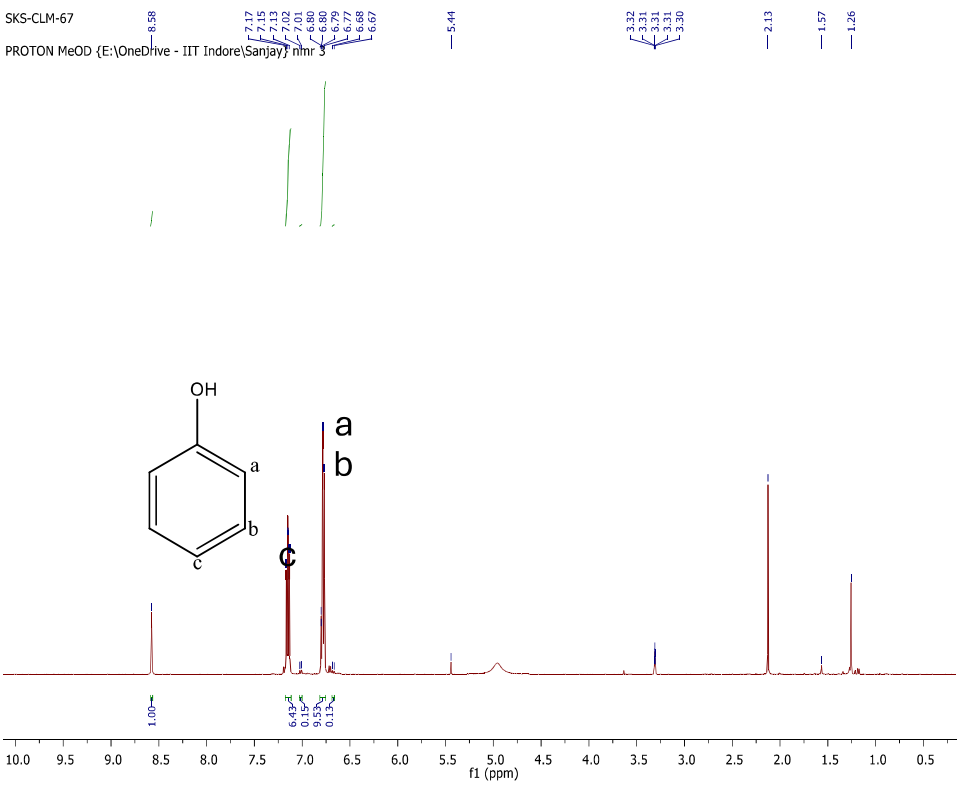


Fig 6. SEM images of (a) HZ4A, (b) Pd/HZ4A, and (c) EDS of Pd/HZ4A.

3.1.5 ^{1}H NMR of extracted phenol from polycarbonates



Chemical shift (ppm)

Fig 7. ^{1}H NMR of phenol extracted from polycarbonates.

3.1.6 Catalytic hydrogenation reaction of after 6h:

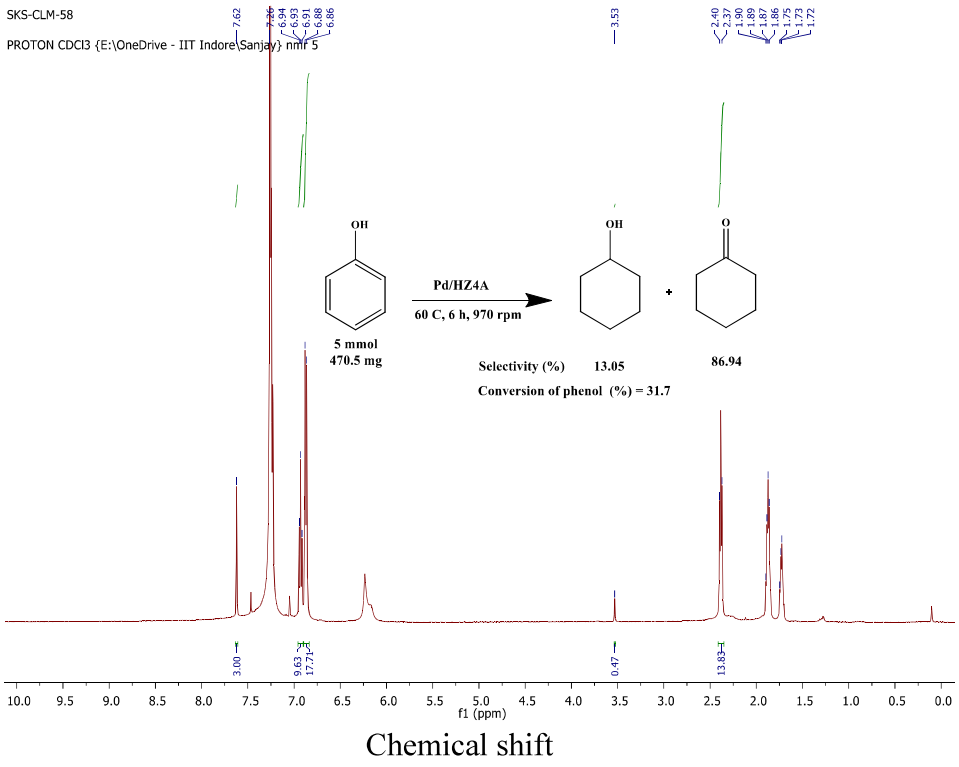


Fig. 8 ^{1}H NMR spectra of catalytic hydrogenation of phenol over the Pd/HZ4A catalyst.

3.1.7 Catalytic hydrogenation reaction of after 24 h results:

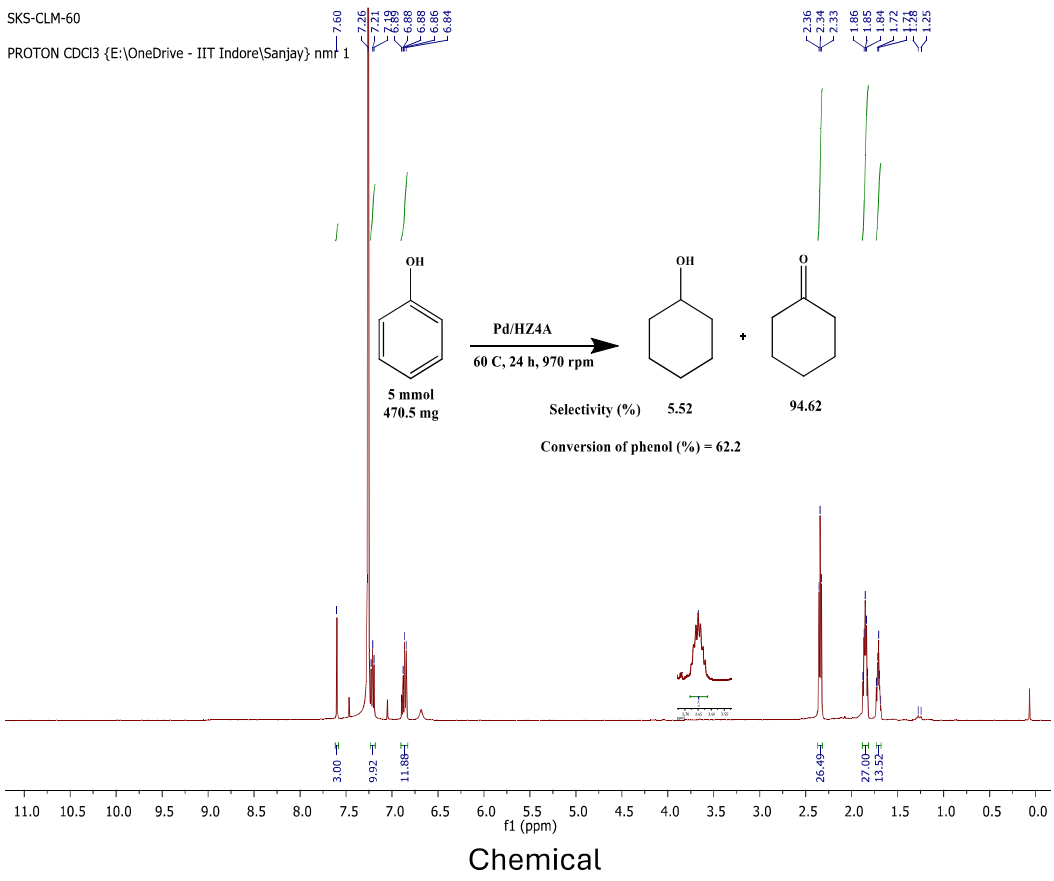


Fig. 9 ^{1}H NMR spectra of catalytic hydrogenation of phenol over the Pd/HZ4A catalyst.

3.1.8 The spectrum of substrates for the Pd/HZ4A catalyst dehydrogenation reaction

Pd/HZ4A catalytic activity was determined for the dehydrogenation of cyclohexanol with 74% conversion in 10 h and the evolution of 188 mL of hydrogen gas. Both phenol and cyclohexanone are produced by the process. However, the catalyst showed more selectivity towards phenol (55 %).

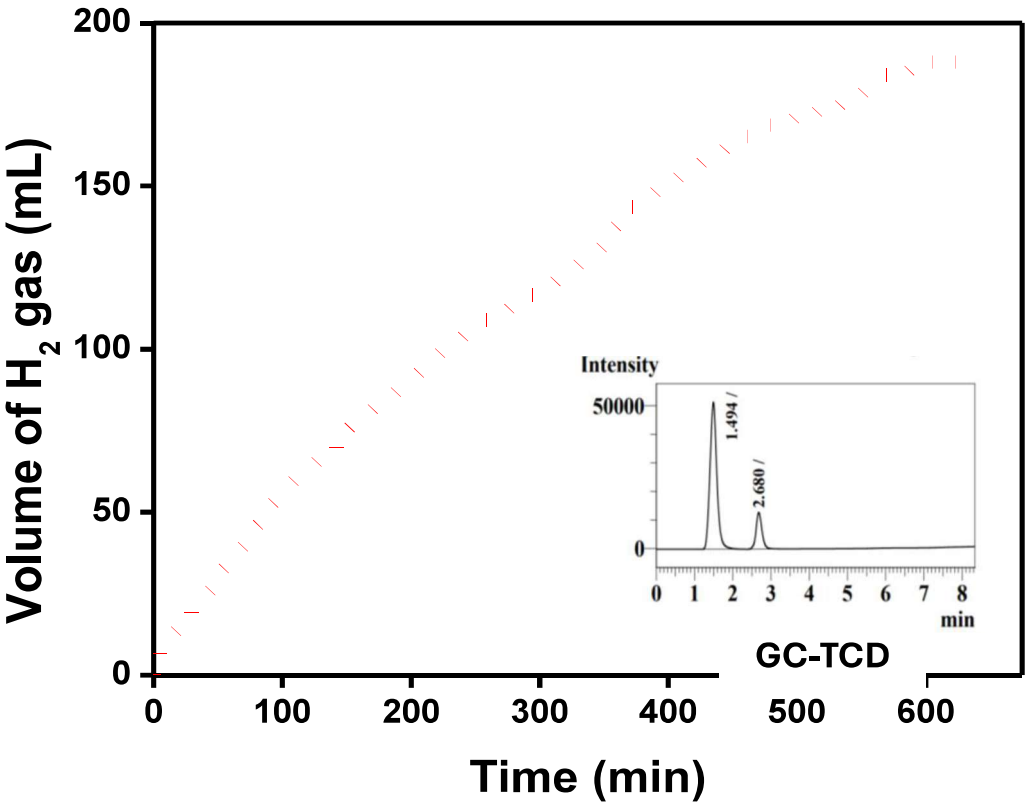


Fig 10. Time course plot of hydrogen production from cyclohexanol over the Pd/HZ4A catalyst.

3.1.9 Catalytic dehydrogenation reactions results:

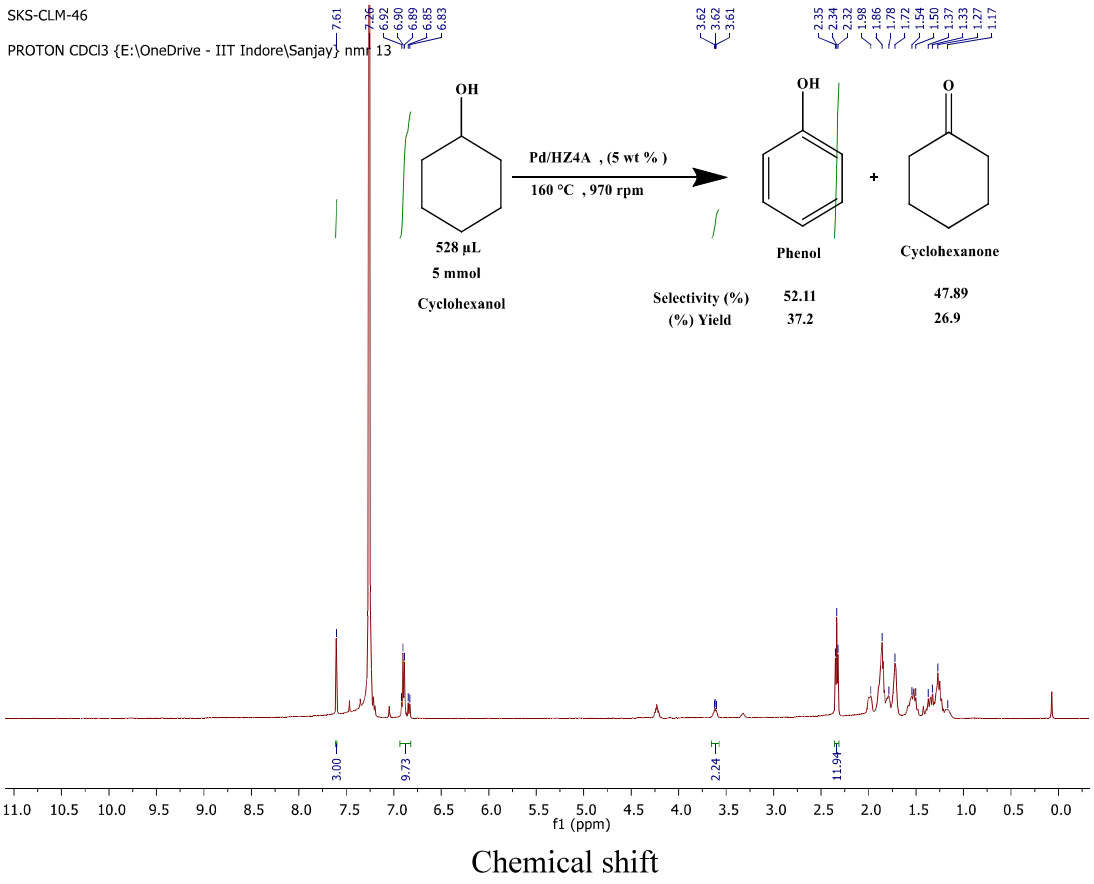


Fig. 11 ^{1}H NMR spectra of catalytic dehydrogenation of cyclohexanol over the Pd/HZ4A catalyst.

Chapter 4

Conclusion

We efficiently synthesized Pd/HZ4A catalyst, which was characterized using Powder X-ray diffraction (P-XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDS). Furthermore, the technique makes use of a heterogeneous catalyst that can be easily separated and reused. So, we discovered an effective method for dehydrogenating the model compounds, which are value-added chemicals, resulting in good conversions under mild reaction conditions. The GC-TCD analysis confirmed the evolution of hydrogen gas during the process. The Pd/HZ4A catalyst showed greater activity for cyclohexanol. The HZ4A catalyst was used to successfully extract phenol from polycarbonates, resulting in a 100% conversion with 99% selectivity. Moreover, phenol hydrogenation was effectively carried out at a low temperature of 60 °C, resulting in 65% conversion and the primary products being cyclohexanol and cyclohexanone.

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