DEVELOPMENT OF CATALYSTS FOR 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
Master of Science

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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 Hydrogenation reactions”** 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 2023** to **May 2024** 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.

Sneha N. Rathwa

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)

Sneha N. Rathwa has successfully given his/her M.Sc. Oral Examination held on **9th May 2024**.

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Sneha N. Rathwa

Abstract

To synthesize the cyclohexyl derivatives the hydrogenation of substituted aromatic compounds holds significant importance due to their abundance and in nature Also, traditional techniques like aromatic substitutions, condensations, and cross-coupling reactions offer pathways to countless aromatic substrates. So, arene hydrogenation represents the most straightforward, retrosynthetically simple method to access a wide range of cyclic saturated compounds. Cyclohexyl derivatives have diverse applications across industries such as medicine, fuel, and polymers. The hydrogenation of aromatic compounds provides the way for the production of saturated cyclic compounds, opening up new synthetic pathways. This thesis focuses on the development of heterogeneous catalysts for the hydrogenation of aromatic compounds, aiming to convert them into corresponding hydrogenated forms and implement these findings in waste upcycling. This thesis comprises four chapters, structured as follows: The first chapter deals with the general introduction to aromatic compounds and their hydrogenated 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 hydrogenation 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
P-XRD	Powder X-ray Diffraction
TGA	Thermo-gravimetric Analysis
FT-IR	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
Cat.	Catalyst

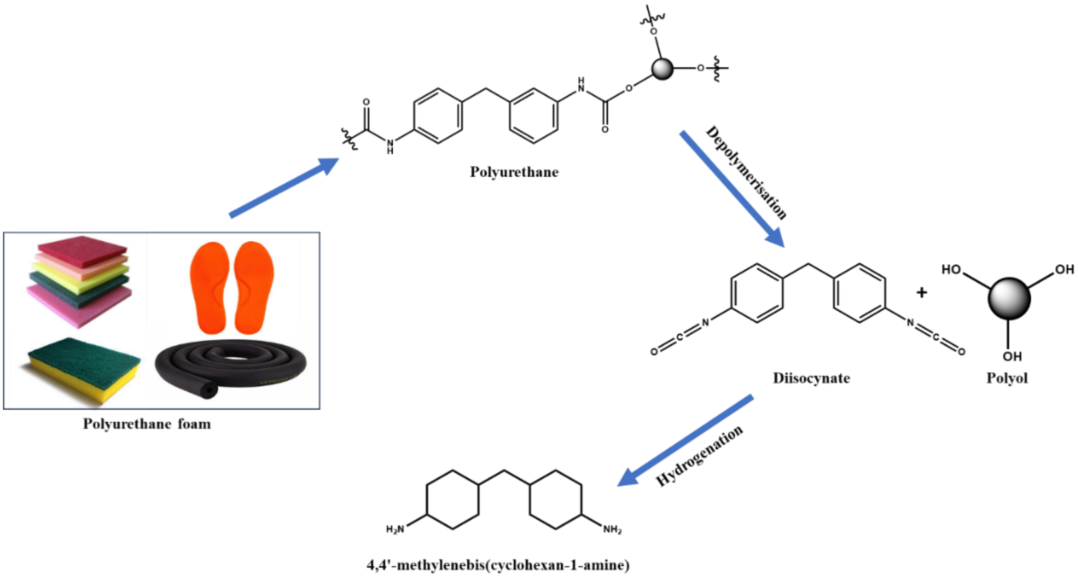
Chapter 1

Introduction

1.1 General introduction

The synthesis of cyclohexane derivatives, vital components in a wide range of organic compounds including pharmaceuticals, presents a significant challenge due to the inherent complexity of modifying cyclohexane rings. Hydrogenation, a fundamental transformation in organic synthesis, isa powerful technique for synthesizing diverse cyclohexane derivatives. While hydrogenation of arenes is a convenient method to access saturated hydrocarbons, it is notably more challenging than nonaromatic substrates due to the presence of resonance stabilization energy.[1] Catalytic hydrogenation of aromatic amine compounds is of significant interest in the chemical industry as this process transforms aromatic amines into hydrogenated forms having various uses. For example, when aniline undergoes hydrogenation, it forms cyclohexylamine (CHA) which has various applications including in the production of dyes, plasticizers, emulsifiers, and rubber additives. Another important compound, bis(4-aminocyclohexyl) methane ($H_{12}MDA$) is obtained from the hydrogenation of 4,4'-methylenedianiline is crucial for producing valuable materials like non-yellowing polyurethane.[2]

Polyurethane (PU) foam is a versatile class of plastics which is prevalent in everyday consumer items like furniture, footwear, and household sponges and could be depolymerized to give diisocynate and polyols (scheme 1).[3] No wonder the worldwide consumption of polyurethane has grown as the market volume for PU which was nearly about 24 MMt in 2020, is likely to increase to 27.6 Mmt by the year 2026.[4] Unfortunately, efficient and sustainable recycling strategies still need to be effectively implemented, resulting in a huge portion of PU based plastic waste going into landfills, negatively impacting the climate and soil health.[5]



Scheme 1. Schematic representation of polyurethane upgradation into value-added chemicals

Herein, we aim to develop catalyst for the hydrogenation of aromatic compounds active under mild reaction conditions with high conversion rate and selectivity and to implement the same catalytic system for the upcycling of waste materials via depolymerization of polyurethane foam into its constituent diisocynates along with polyols. These aniline fractions could be further hydrogenated to value-added chemicals.

1.2 Literature review and problem formulation

The catalytic hydrogenation of aromatics to form valuable cyclohexane derivatives is crucial for the production of fine chemicals and to address various environmental and health concerns.[6] Hydrogenation/dehydrogenation process also aids energy storage, with cyclohexane derivatives acting as efficient hydrogen gas storage materials, advancing renewable energy. Additionally, it purifies fuels by removing aromatic compounds that hinder combustion efficiency, enhancing both performance and environmental friendliness. Also, arene hydrogenation for cyclohexyl derivatives offers multifaceted solutions to environmental, health, and energy challenges.[7] To expedite the hydrogenation process, the development of innovative catalytic techniques allows reaction at milder condition by reducing the activation energy and modifying the reaction kinetics.

To facilitate the process of hydrogenation, catalyst plays an important role by regulating the product activity and selectivity. There exist two categories of catalysts: homogeneous and heterogeneous catalysts. Homogeneous catalysts generally exhibit superior performance with higher selectivity at milder conditions compared to heterogeneous catalysts. However, main disadvantage with homogeneous catalysts lies with their poor recyclability and recovery. Thus, for hydrogenation the heterogeneous catalysts are well-suited in terms of thermal stability and facile recyclability. This is because separating the catalyst from reaction mixture through filtration or centrifugation is easier. Additionally, heterogeneous catalysts can be employed in continuous flow processes, facilitating the industrial-scale operations of hydrogenation and dehydrogenation for the uptake and release of hydrogen.[8]

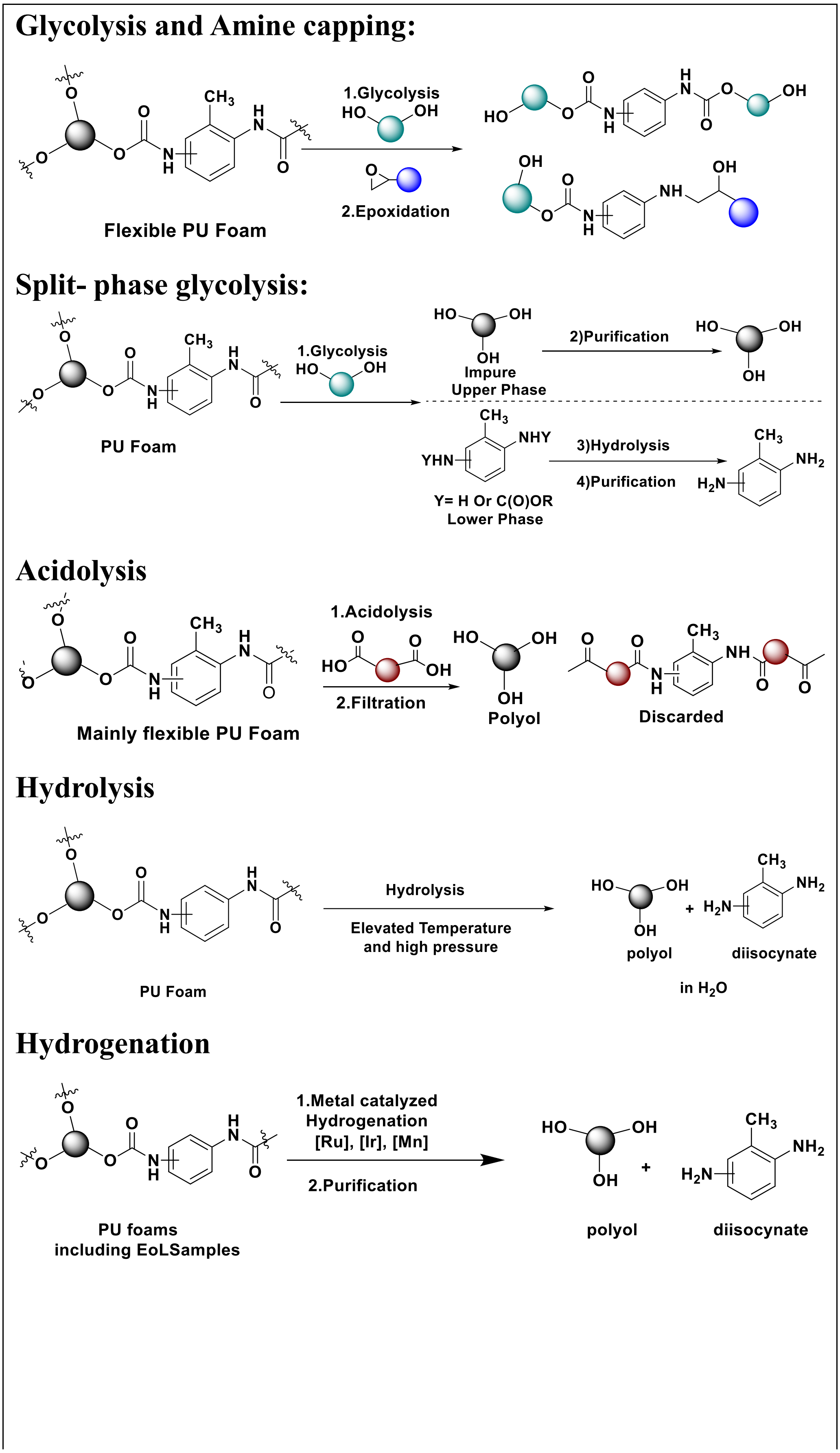
Table 1. Literature reports for hydrogenation of arenes.

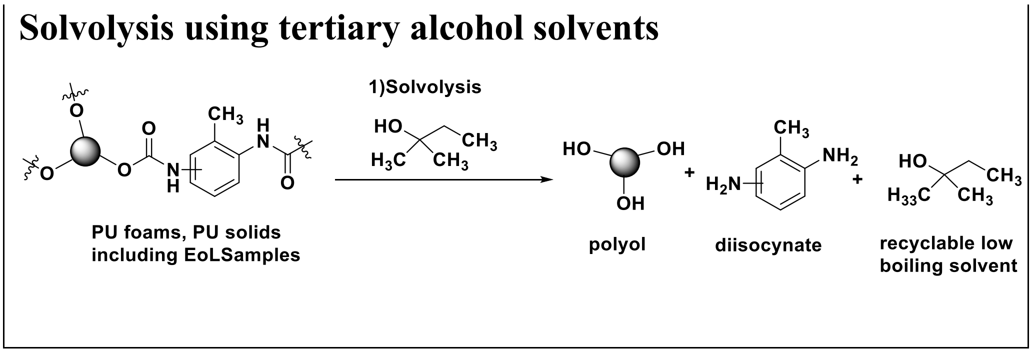
Sr. No.	Substrate	Catalyst	Conditions	Product	Conv. /yield (%)	Ref.
1	Phenol	Ru/HNT-C_{18}	80 °C, 30 bar H_2, 3 h, water	Cyclo hexanol	63/59	8
2.	2,4-toluene diamine	Rh/CNT	130 °C, 100 bar H_2, 4 h, THF	2-Methyl-1,3-cyclohexanediamine	>99/54	9
3.	*p*-toluidine	Rh/CNT	130 °C, 100 bar H_2, 6 h, THF	4-methylcyclohexan-1-amine	89/80	9
4.	Toluene	Pd-Ni/ SiO_2	150 °C, 70 bar H_2, 6 h, neat	Cyclohexylmethane	98/73	10
5.	Toluene	Pt-Ru/ SiAlTUD-1	25 °C, 1 bar H_2, 4 h, water	Cyclohexylmethane	78/68	11
6.	Toluene	Ru-Ni-Co/ C	60 °C, 45 bar H_2, 1 h, neat	Cyclohexylmethane	>99/90	12
7.	Naphthalene	Rh/Fe_2O_3-TiO_2	290 °C, 68 bar H_2, 2 h, water	Decalin	100/>99	13
8.	Methylene dianline	Ru/CeO_2	190 °C, 180 bar H_2, 4 h, 1,4-dioxane	bis(4-aminocyclohexyl)methane	>99/70	2
9.	Naphthalene	Pt/ HZSM-5-25	210 °C, 45 bar H_2, 1 h, water	Tetralin	97/89	14
10	Tetralin	Pt/ MCM-41 (Al/Pt = 10)	280 °C, 50 bar H_2, 0.5 h, neat	Decalin	86/79	15
11	Quinoline	Pd/ GS1000	60 °C, 1 bar H_2, 4 h, acetonitrile	Decahydroquinoline	100/>99	16

12	Diphenyl methane	Rh/C	80 °C, 5 bar H_2, 1 h, water	Dicyclohexyl methane	100/ 57	17
HNT= Halloysite nanotubes, SiAlTUD-1= aluminosilicate, CNT= carbon nanotubes, HZSM-5-25= Mesoporous ZSM-5 zeolite MCM-41= Mobil Composition of Matter No. 41, GS1000= guanine sulfate						

In recent years, various noble metal based heterogeneous catalysts such as Ru/HNT-C_{18},[8] Rh/C,[17] Pt/HZSM-5-25,[14] and Rh/Fe_2O_3-TiO_2,[13] Pd/GS1000[16] have been studied for the hydrogenation of arenes (table 1). These catalytic systems were studied at various temperatures ranging from 25 °C - 290 °C and H_2 pressure (1 bar-180 bar). Among these Pd/GS1000, stands out for its remarkable ability to completely hydrogenate quinoline. This catalyst is particularly effective achieving full conversion under mild conditions, especially at lower temperatures (60 °C) and hydrogen pressure of merely 1 bar. This achievement is a significant advancement in the field of arene hydrogenation, offering great potential for various industrial applications that require precise control over hydrogenation processes. Thus, active metals are crucial for selective hydrogenation reactions. They help in adsorption and cleavage of H_2 molecule, as well as in the adsorption of reactant molecules. These actions directly affect the reaction rates as well as product selectivity. [18] Though, Pd and other noble metals such as Pt, Rh and Ir, are readily active for arene hydrogenation but high cost associated with them makes their usage unsuitable for large scale applications.[19]

In this direction, Ru being more cost effective than other transition metals makes it a suitable choice for many catalytic reactions.[20] Therefore, in this work, we also used Ru catalyst for the hydrogenation of diphenylmethane which was used as a model substrate because of it's structural similarity with dianilines which are monomer precursors of polyurethane foams at room temperature and 1 bar H_2 pressure at 1000 rpm and got good yields for hydrogenated product.


Glycolysis and Amine capping:
CH$_3$
Flexible PU Foam
1.Glycolysis
HO
OH
2.Epoxidation
NH
Split- phase glycolysis:
PU Foam
Impure
Upper Phase
2)Purification
YHN
NHY
Y= H Or C(O)OR
Lower Phase
3)Hydrolysis
4)Purification
H$_2$N
NH$_2$
Acidolysis
Mainly flexible PU Foam
1.Acidolysis
2.Filtration
Polyol
Discarded
Hydrolysis
PU Foam
Hydrolysis
Elevated Temperature
and high pressure
polyol
diisocynate
in H$_2$O
Hydrogenation
PU foams
including EoLSamples
1.Metal catalyzed
Hydrogenation
[Ru], [Ir], [Mn]
2.Purification
polyol
diisocynate


Solvolysis using tertiary alcohol solvents

Scheme 2. Literature reports on Chemical upcycling technologies for depolymerization of polyurethane foam materials. Reproduced with the permission from ref. 9. Copyright 2022 American Chemical Society.

Further, we also performed the depolymerization of flexible and rigid foams via hydrolysis process. Various other processes for the foam depolymerization includes acidolysis, aminolysis, alcoholysis, and glycolysis, yield diisocyanate precursors and polyols as major components (table 2).[9] But, these reported methods of depolymerization of polyurethane face several limitations. For example, glycolysis and acidolysis methods result in the loss of valuable dianilines as polyol is the only targeted fraction and thereby in many cases capped with an epoxide or a cyclic carbonate to convert the amines into non-virgin polyols. On the other hand, transition metal-catalysed hydrogenation, though a promising technique but relies on expensive catalysts and ligands, potentially limiting its cost-effectiveness. Traditional methods like glycolysis involve the use of high-boiling glycol solvents, while acidolysis leads to the removal of aromatic compounds, impacting the properties of recycled materials. Additionally, split-phase glycolysis and acidolysis require further refinement for isolating dianilines or filtering off solid waste, adding complexity. Proper disposal or recycling of waste streams containing aromatic core structures is necessary, posing environmental concerns. Dependence on specific catalysts in transition metal-catalysed hydrogenation may limit efficiency across different PU materials. Also, the reported hydrolysis requires high energy input due to the need for temperatures exceeding 300 °C and high pressure, hindering its industrial scalability. In our work, we performed hydrolysis of rigid refrigerator foam and flexible blue foam with 74 and 62 wt% recovery, respectively with the waste polyurethane foam to yield its monomeric precursors polyol and dianilines fractions. The diisocyanate precursor has a structural similarity with diphenylmethane. The aim of this work is to explore transformation of waste PU foam into valuable products via hydrogenation of diisocyanate fractions over the heterogeneous catalyst.

1.3 Objectives of the Project

- To design and synthesize a stable ruthenium based heterogeneous catalysts.
- To extensively characterize the synthesised catalysts using various techniques like P-XRD, SEM, TGA and UV-Vis.
- To investigate the performance of the synthesised catalysts under milder reaction conditions for the hydrogenation of aromatic compounds and to implement the findings for the upcycling of waste materials.
- To explore the ways to make the catalyst more economical and recyclable making it ideal for large scale industrial applications.

CHAPTER 2

Experimental section

2.1 Materials and instrumentation

All chemicals and metal salts were purchased from Alfa-Aesar, Sigma-Aldrich and Spectrochem which were used without any further purification. Foams used for hydrolysis are collected from yellow household kitchen sponge (scratch brand), blue household foam and refrigerator door foam. UV-Visible spectra were recorded in the wavelength range of 200-800 nm by Agilent UV Cary-60 Spectrophotometer. Thermogravimetric analysis was carried out using Mettler Toledo TGA/DSC 1 STARe System. The 1H NMR (400 MHz and 500 MHz), 13C NMR (100 MHz and 125 MHz) spectra are recorded using $CDCl_3$ as the solvent on a Bruker Advance 400 and Bruker Ascend 500 spectrometer. Chemical shifts were referenced to the internal solvent resonances and reported relative to TMS. Powder X-ray diffraction (P-XRD) measurements were performed using Rigaku Smart Lab, Automated Multipurpose X-ray diffractometer at 40 KV and 30 mA (Cuα $\lambda = 1.5418$ A). SEM was performed using JSM-7610FPlus.

2.2 Synthesis of ruthenium catalyst

50 mg CTAB was added to 5 mL aqueous solution of $RuCl_3.3H_2O$ (0.0104 g). To this, aqueous solution of $NaBH_4$ (25 mg in 5 mL H_2O) was added dropwise under sonication. The contents of the round bottom flask were sonicated at room temperature for 30 minutes resulting into black coloured suspension of Ru nanoparticles, which were then collected by centrifugation and washed with distilled water several times, dried under vacuum and then used for catalytic reactions.

2.3 Depolymerization reactions

2.3.1. Depolymerization of polyurethane foam

Firstly, 100 mg of polyurethane foam was shredded into small pieces and placed in a thermal autoclave. Then, aq. KOH (1 M, 10 mL) was added to the autoclave of a high-pressure reactor, the reactor was tightened by using hex key and kept in a preheated oven at 180 °C, reaction was carried out for 24 h.

After this period, the reaction mixture was allowed to cool down to room temperature. The aqueous layer was first acidified using concentrated HCl and extracted using dichloromethane (3 × 15 mL) and further same aqueous layer was basified using KOH and extracted using dichloromethane (3 × 15 mL). After both acidic and basic workups, combined organic layers were dried over anhydrous Na_2SO_4, filtered, and solvent was evaporated under reduced pressure, and products were analysed using ^{1}H NMR.

2.3.2 Gram scale reactions for depolymerization of polyurethane foam

Firstly, 5 g of polyurethane foam was shredded into small pieces and placed in a thermal autoclave. Then, aq. KOH (1 M, 50 mL) was added to the autoclave of a high-pressure reactor, the reactor was tightened by using hex key and kept in a preheated oven at 180 °C, reaction was carried out for 24 h. After this period, the reaction mixture was allowed to cool down to room temperature. The aqueous layer was first acidified using concentrated HCl and extracted with dichloromethane (3 × 60 mL) and further same aqueous layer was basified using KOH and extracted using dichloromethane (3 × 60 mL). After both acidic and basic workups, combined organic layers were dried over anhydrous Na_2SO_4, filtered, and solvent was evaporated under reduced pressure, and products were analysed using ^{1}H NMR.

2.4 Catalytic hydrogenation reactions

2.4.1 Catalytic hydrogenation reactions of diphenylmethane

The diphenylmethane (1 mmol) was taken in a 50 mL round bottom flask. Then a suspension of 4 mol% Ru catalyst in 10 mL solvent was added to it. The reaction vessel was equipped with H_2 balloon and stirred at 600 rpm for 24 h at room temperature. After the completion of reaction, catalyst was recovered by centrifugation and the product was extracted with dichloromethane (5x10 mL). Organic layer was dried over anhydrous Na_2SO_4 using rotatory evaporator. Conversion and selectivity were calculated from ^{1}H NMR using benzaldehyde as an internal standard.

Bulk Scale and recyclability experiment: In a 100 mL high-pressure autoclave reactor, the diphenylmethane (6 mmol) and an aqueous suspension of 0.67 mol % Ru catalyst (15 mL) were added. The reactor was flushed three times with H_2 gas to eliminate any air and then pressurized with H_2 gas (1 bar). The reaction progress was monitored periodically using TLC and the reaction was completed after 72 h. After the completion of the reaction, catalyst was recovered by centrifugation, the aqueous layer was extracted with dichloromethane (6 × 15 mL). After workup, the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and solvent was evaporated under reduced pressure

2.4.2 Catalytic hydrogenation reactions of aniline

In a 50 mL high-pressure autoclave reactor, aniline (1 mmol) and an aqueous suspension of 4 mol% Ru catalyst (20 mL) were added. The reactor was flushed three times with H_2 gas to eliminate any air and then pressurized with H_2 gas (5 bar) and the reactor was heated to desired temperature. After the completion of the reaction, the reactor was brought to room temperature and catalyst was recovered by centrifugation, the aqueous layer was extracted with dichloromethane (6 × 15 mL). After workup, the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and solvent was evaporated under reduced pressure.

2.4.3 Catalytic hydrogenation reactions of aniline fractions obtained from depolymerization of polyurethane foams

In a 50 mL high-pressure autoclave reactor, the substrate (1 mmol) and an aqueous solution 0.4 mol% Ru catalyst (20 mL) were added. The reactor was flushed three times with H_2 gas to eliminate any air and then pressurized with H_2 gas (5 bar) and the reactor was heated to 100 °C temperature. After the completion of the reaction, the reactor was brought to room temperature and catalyst was recovered by centrifugation, the aqueous layer was extracted with dichloromethane (6 × 15 mL). After workup, the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and solvent was evaporated under reduced pressure.

CHAPTER 3

Results and discussion

3.1 Synthesis and characterization of the Ru catalyst

The synthesized Ru nanoparticles were characterized by UV-vis spectra. From Figure 1 the formation of Ru nanoparticles could be confirmed when the UV-vis absorption band at ~309 nm disappeared, indicating that the reduction of Ru^{3+} salt to Ru^0 was complete.

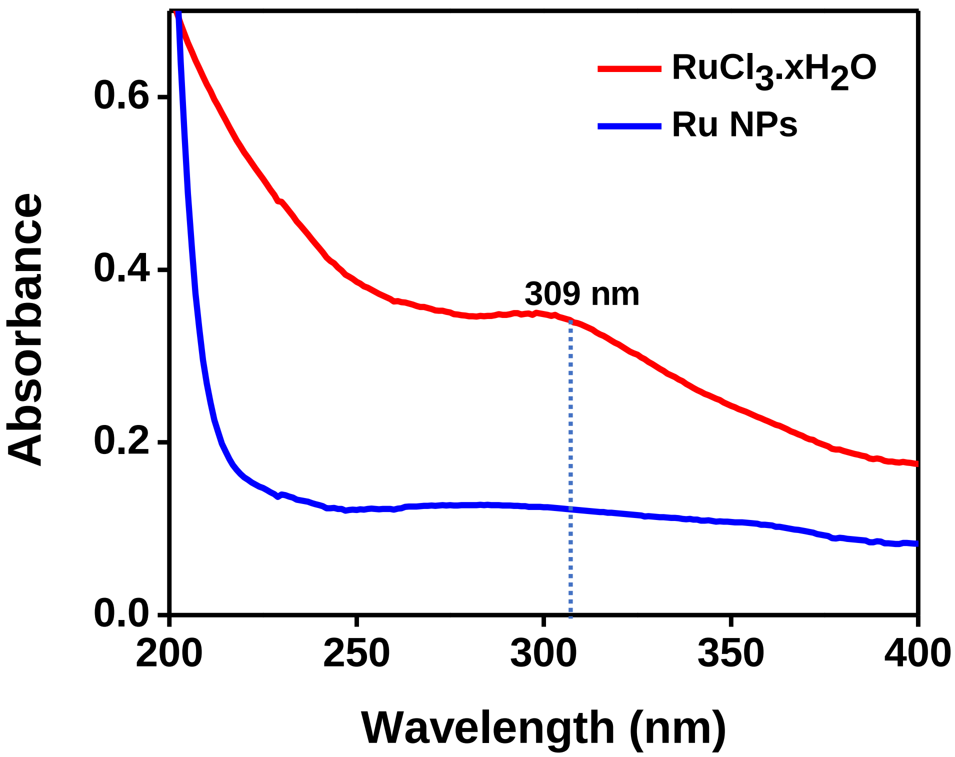


Figure 1. UV-visible absorption spectra of synthesized Ru nanoparticles

Ru nanoparticles catalyst was characterized by P-XRD and SEM. Powder X-ray diffractogram of Ru nanoparticles shows a peak at 2θ~43° which corresponds to (101) plane of hexagonal closed packed Ru nanoparticles (Figure 2). Further, P-XRD spectrum showing the broad peaks which are indicating the amorphous nature and small size of Ru nanoparticles.

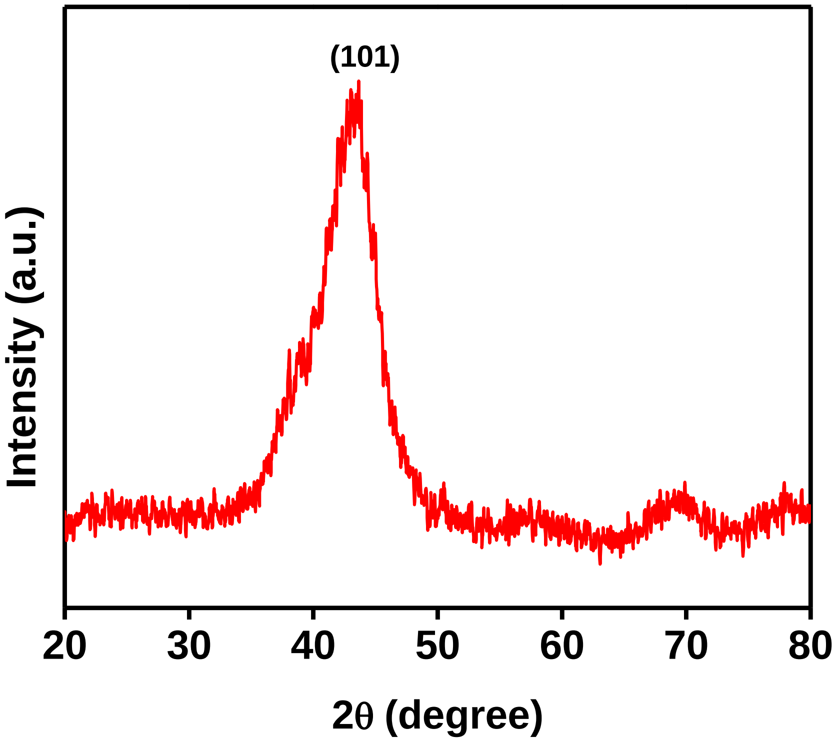


Figure 2. PXRD spectrum of Ru catalyst

To know about the morphology of catalyst FE-SEM analysis was carried out. SEM image and corresponding EDS spectra confirmed the presence of Ru (Figure 3).

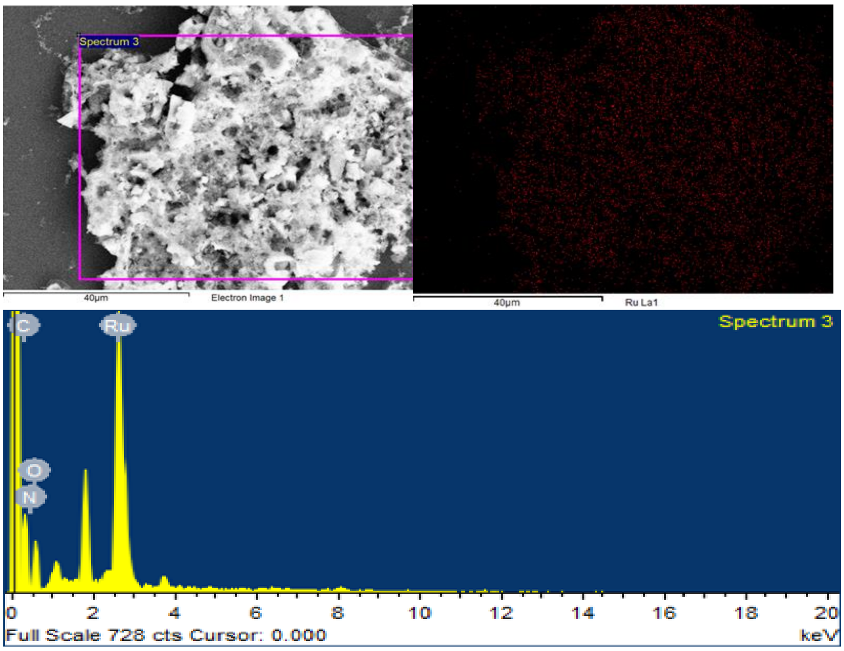


Figure 3. SEM image and corresponding elemental mapping for Ru and EDS spectra of Ru catalyst

We also tested the stability of the Ru catalyst using thermo-gravimetric analysis.

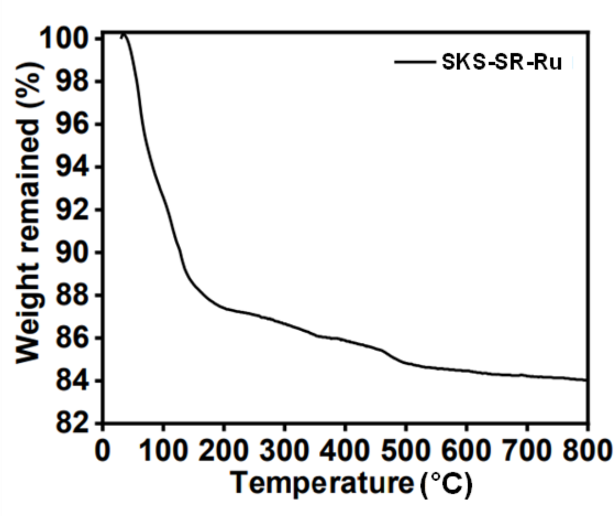
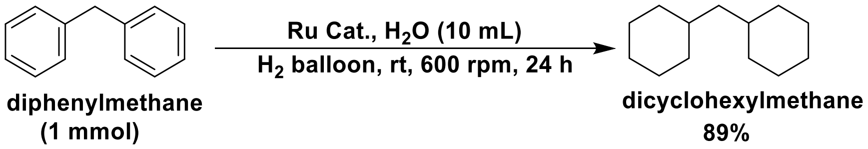


Figure 4. Thermo-gravimetric Analysis (TGA) of Ru catalyst

The results, shown in Figure 4, indicate that the initial 18 % weight loss was because of moisture on the catalyst's surface. After that, there wasn't any significant weight loss observed, suggesting that the catalyst remains stable even at higher temperatures.

3.2. Catalytic hydrogenation reactions

For analysing the catalytic performance of synthesised catalyst, diphenylmethane was selected as the model substrate which is analogous to 4,4’-methylenedianiline, monomer precursor of rigid refrigerator polyurethane foam. As we wanted to carry out the hydrogenation reaction at milder condition possible, so initially we started with water at room temperature using H_2 balloon. The reaction was performed over Ru catalyst and stirring at 600 rpm with 1 mmol (168 µL) of diphenylmethane (Scheme 3) for 24 hours.



Scheme 3. Schematic representation of hydrogenation of diphenylmethane over Ru catalyst.

And, we have our desired product that is dicyclohexylmethane with 89% of yield.

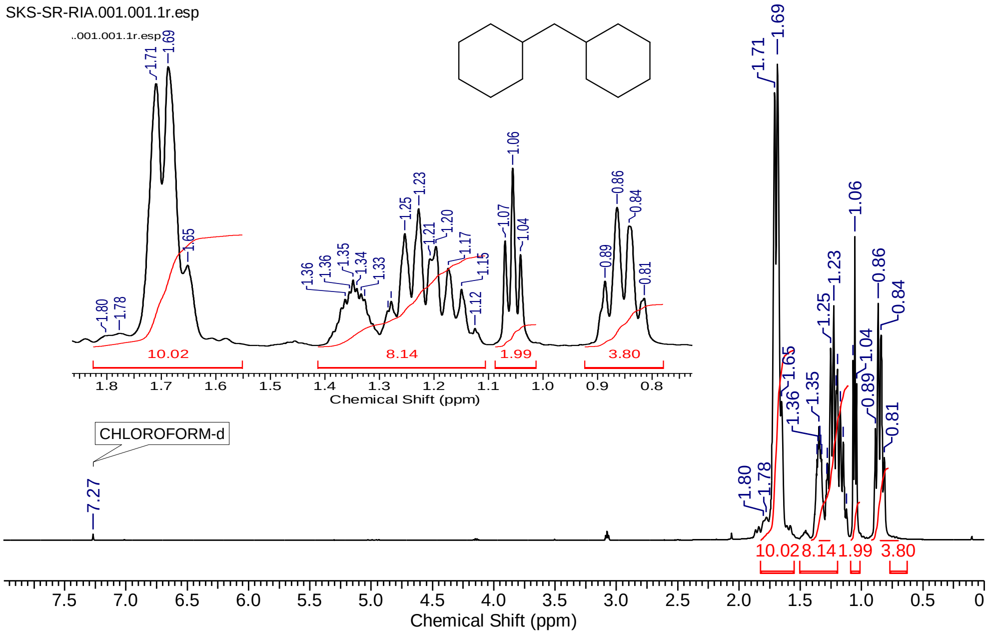


Figure 5. ^{1}H NMR spectra of dicyclohexylmethane in $CDCl_3$

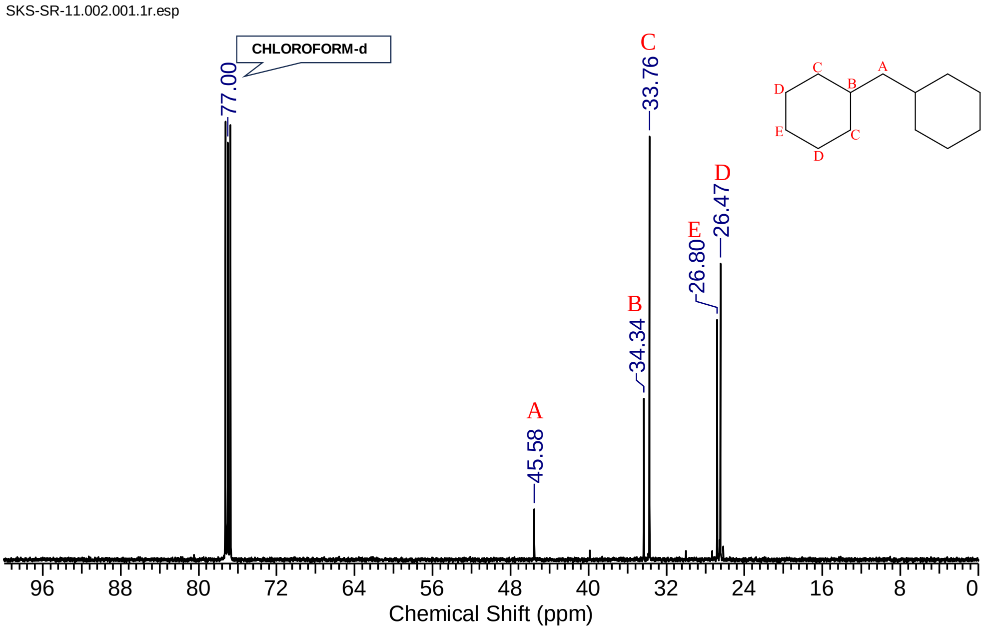
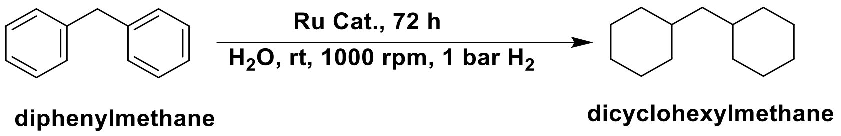


Figure 6. ^{13}C NMR spectra of dicyclohexylmethane in $CDCl_3$

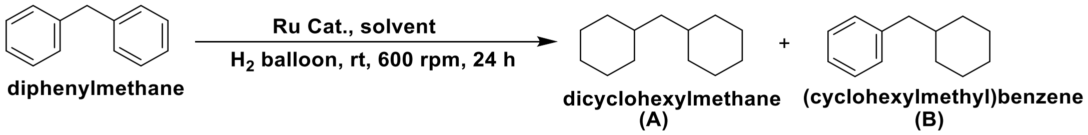
Bulk Scale experiment: The catalytic activity and efficacy of the Ru catalyst was tested by conducting the catalytic hydrogenation reaction with bulk-scale of diphenylmethane 1 mL (6 mmol) at room temperature, 15 mL H_2O with 1 bar H_2 gas and stirring at 1000 rpm for 72 h in a high-pressure (scheme 4) reactor, where we achieved full conversion of diphenylmethane to dicyclohexylmethane with yield of 87%.



Scheme 4. Bulk scale experiment for hydrogenation of diphenylmethane

Recyclability experiment: To check the recyclability of catalyst. The catalyst was recovered by centrifugation and recovered catalyst was used for cycle-2 and we have got full conversion of diphenylmethane to dicyclohexylmethane with yield of 85% for cycle-2, but there was problem in the recovery of catalyst for next catalytic run.

Effect of solvent: Further, for the better recovery of catalyst we performed experiments for the catalytic activity of Ru catalyst in different solvents for hydrogenation of diphenylmethane at room temperature for 24 h by using H_2 balloon as hydrogen source (Scheme 5).



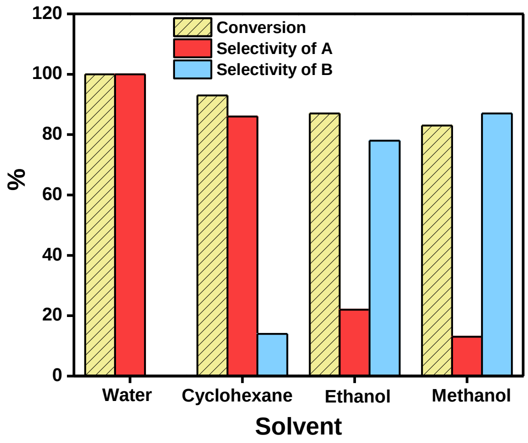
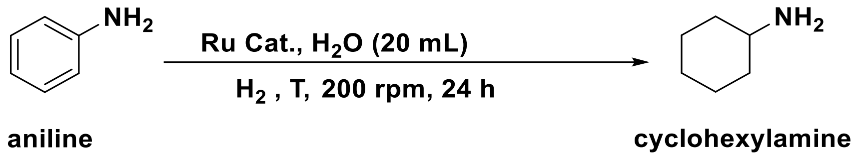


Figure 7. Hydrogenation of diphenyl methane in different solvents. Reaction condition: diphenylmethane (1 mmol), Ru catalyst (0.04 mmol), solvent (10 mL), H_2 balloon, rt, 24 h.

On conducting experiments using various solvents to check their impact on the hydrogenation of diphenylmethane, we observed varying conversion rates: 100%, 83%, 87%, and 93% for water, methanol, ethanol, and cyclohexane, respectively. However, the selectivity for the desired complete hydrogenated product, dicyclohexylmethane, exhibited a decrease as the solvent changed from water to methanol, with selectivity percentages dropping from 100% to 13% (Figure 7). This decrement can be explained by considering the competitive adsorption of both the substrate and the solvents onto the Ru catalyst surface. This competition arises due to the interaction between the metal and the lone pairs of electrons present in the oxygen or other heteroatoms of the solvent molecules, leading to a reduction in the hydrogenation activity of aromatic compounds.[21]

Optimization of the catalytic hydrogenation reaction condition for aniline: We have chosen aniline as a model substrate to optimize the reaction conditions for aniline, which is analogous to diamino toluene, monomer precursor of rigid refrigerator polyurethane foam. Firstly, we performed the reaction using Ru nanoparticles as a catalyst for the hydrogenation of aniline in water using hydrogen balloon for 24 h and observed that there was no conversion of aniline. Then we pressurized the reaction with 5 bar H_2 at room temperature and we got 9% conversion of aniline to cyclohexylamine. In order to achieve the complete conversion, we performed the reactions at 50 °C, 70 °C and 100 °C and achieved 67%, 99% and >99% conversion respectively (Table 2).

Table 2. Hydrogenation of aniline over Ru catalyst



Entry	**Temp. (°C)**	**P_{H_2} (bar)**	**Conv. (%)**	**Yield (%)**
1	rt	H_2 balloon	No conversion	-
2	rt	5	9	6
3	50	5	69	55
4	70	5	>99	69
5	100	5	>99	84

Reaction condition: aniline (1 mmol), Ru catalyst (0.04 mmol), H_2O (20.0 mL), H_2 balloon or 5 bar H_2, rt-100 °C, 24 h, 200 rpm.

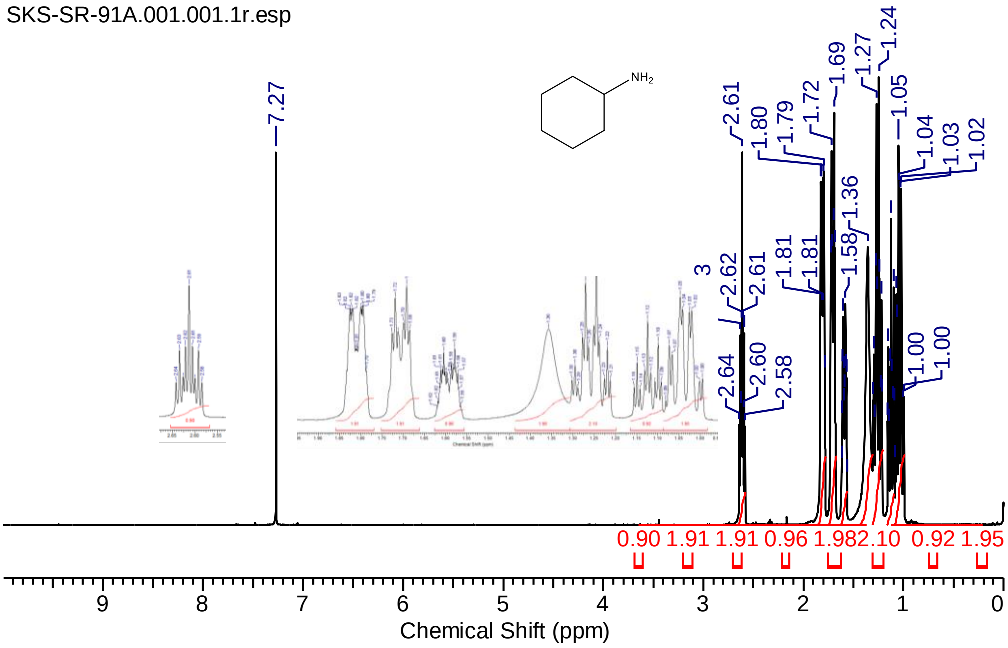


Figure 8. ^{1}H NMR spectra of cyclohexylamine in $CDCl_3$

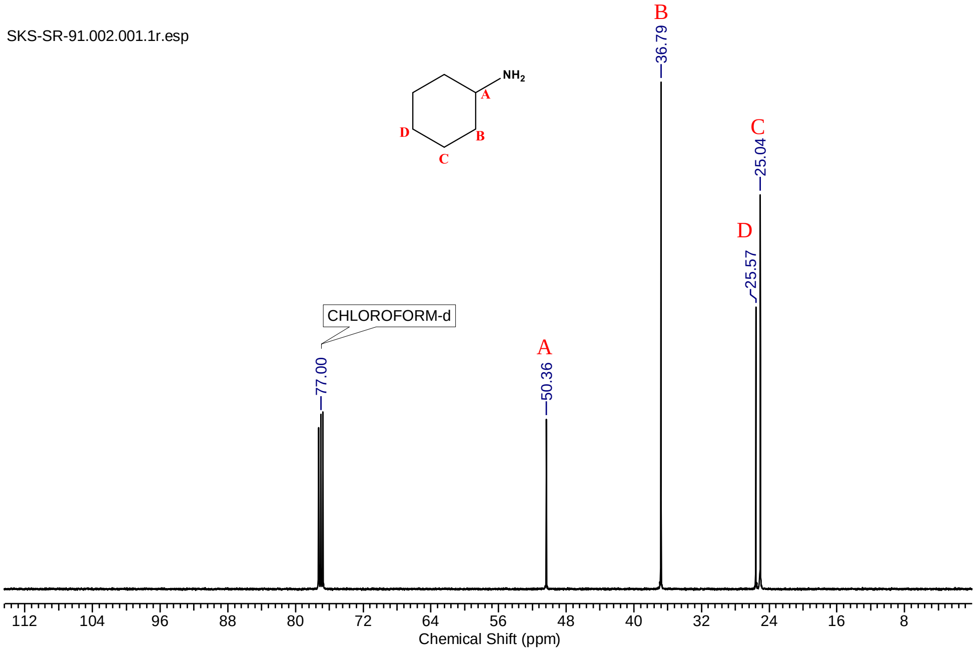


Figure 9. ^{13}C NMR spectra of cyclohexylamine in $CDCl_3$

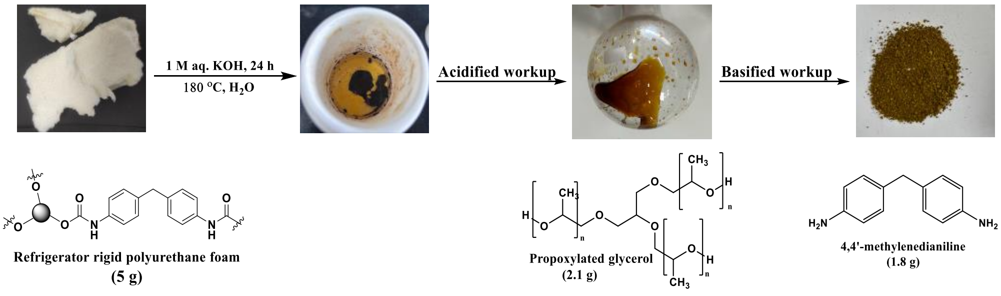
3.3 Depolymerization of polyurethane foam

We have performed hydrolysis of polyurethane foams using blue flexible foam and rigid refrigerator foam to obtain its constituent products: polyols and diisocynates at 180 °C with 10 mL of 1M aqueous KOH for 24 h.

Depolymerization of rigid refrigerator door foam

We have performed hydrolysis of rigid refrigerator foam (100 mg) and we have got extracted products consists of 4,4'-methylenedianiline (34 mg) and polyol (44 mg) fraction with 78 wt% recovery.

Gram scale reaction for depolymerization of rigid refrigerator polyurethane foam: We have performed hydrolysis of rigid refrigerator foam (5 g) and we have got extracted products consists of 4,4'-methylenedianiline (1.8 g) and polyol (2.1 g) fraction with 76 wt% recovery (scheme 5).



Scheme 5. Hydrolysis of rigid refrigerator foam

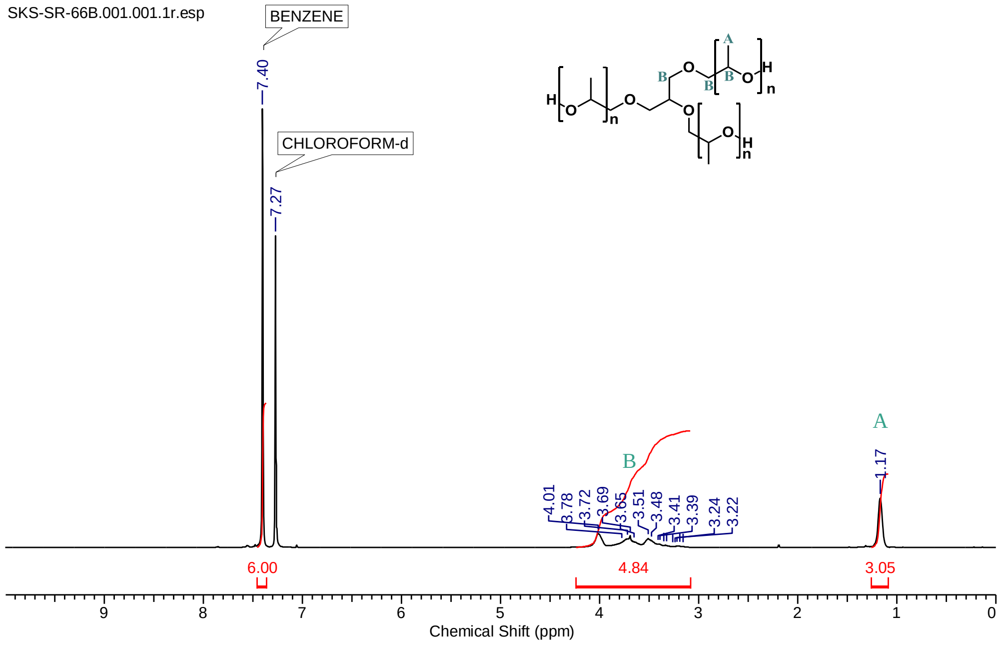


Figure 10. ^{1}H NMR of polyol fraction obtained from depolymerization of refrigerator foam with benzene as internal standard in $CDCl_3$.

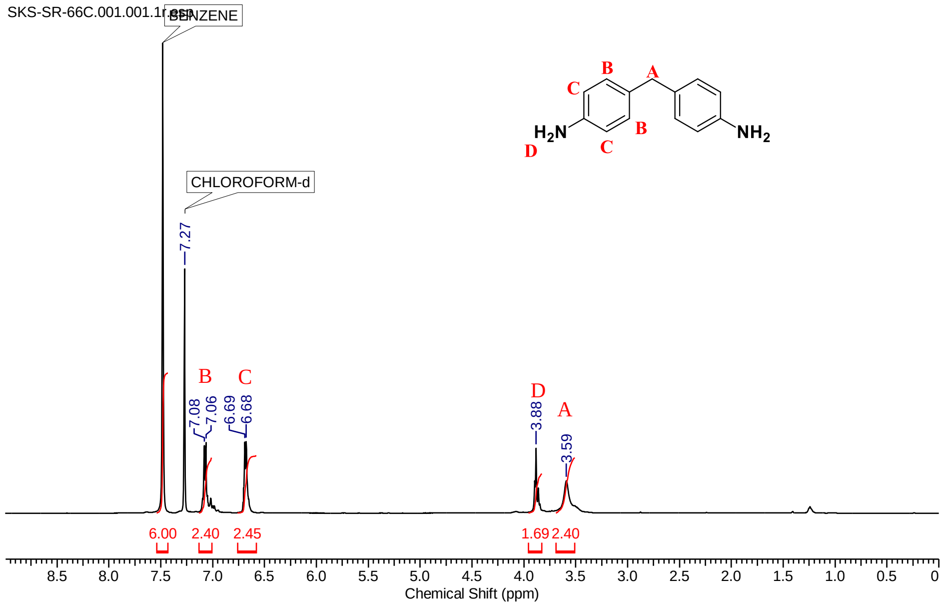
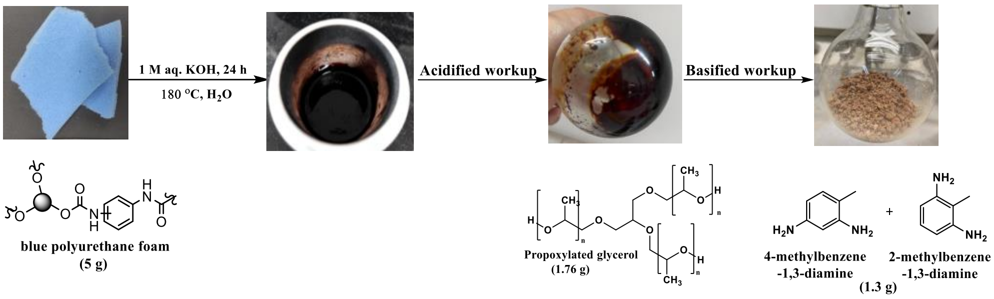


Figure 11. ^{1}H NMR of aniline fraction obtained from depolymerization of refrigerator foam with benzene as internal standard in $CDCl_3$.

Depolymerization of blue flexible foam

We have performed hydrolysis of blue flexible foam (100 mg) and we have got extracted products consists of (26 mg) and polyol (34 mg) fraction with 60 wt% recovery.

Gram scale reaction for depolymerization of blue flexible polyurethane foam: We have performed hydrolysis of blue flexible polyurethane foam (5 g) and we have got extracted products consists of 4-methylbenzene-1,3-diamine,2-methylbenzene-1,3-diamine (1.34 g) and polyol (1.76 g) with 62 wt% recovery (scheme 6).



Scheme 6: Hydrolysis of blue flexible foam polyurethane

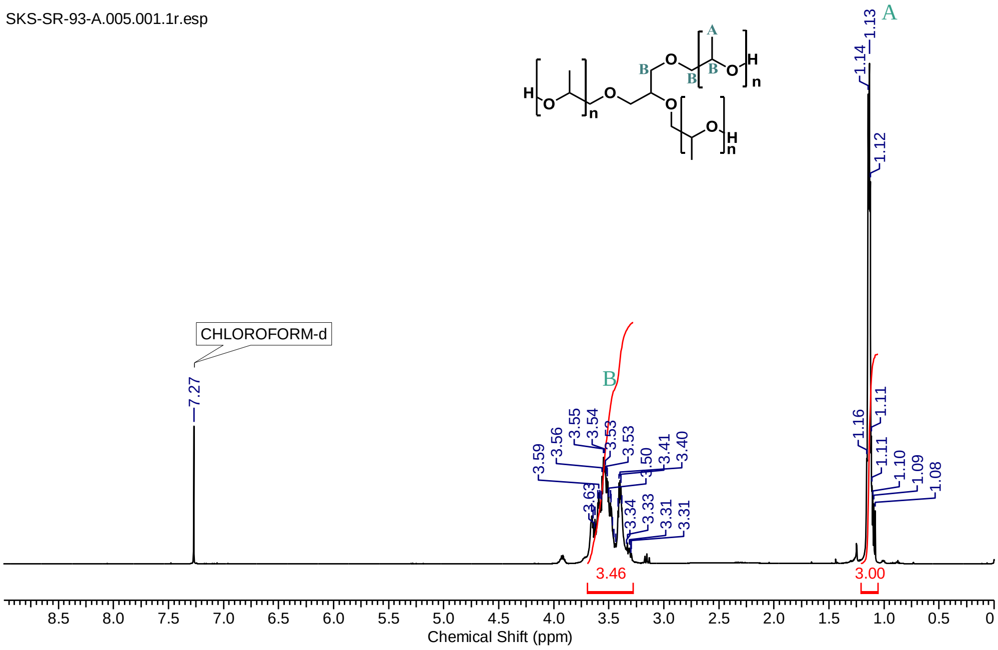


Figure 12. ^{1}H NMR of polyol fraction obtained from depolymerization of blue flexible foam in $CDCl_3$.

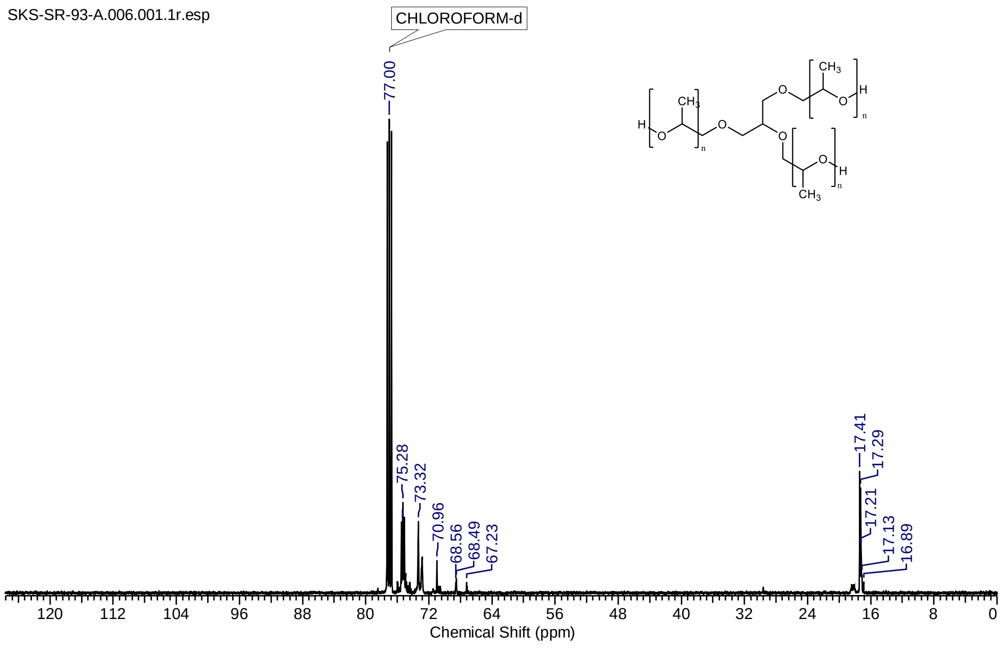


Figure 13. ^{13}C NMR of polyol fraction obtained from depolymerization of blue flexible foam in CDCl$_3$.

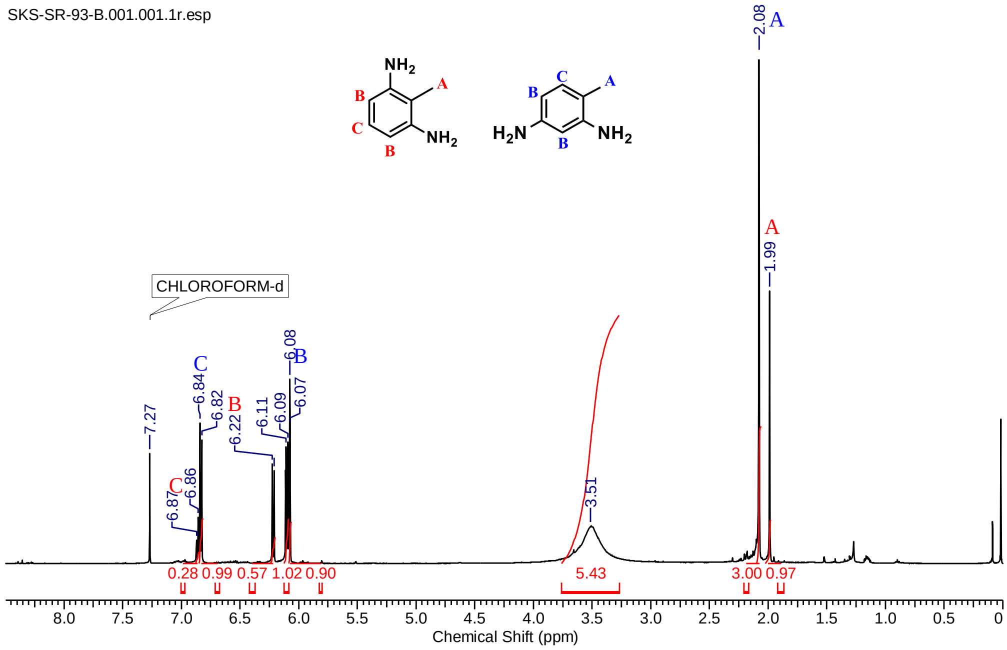


Figure 14. ^{1}H NMR of aniline fraction obtained from depolymerization of blue flexible foam in CDCl$_3$

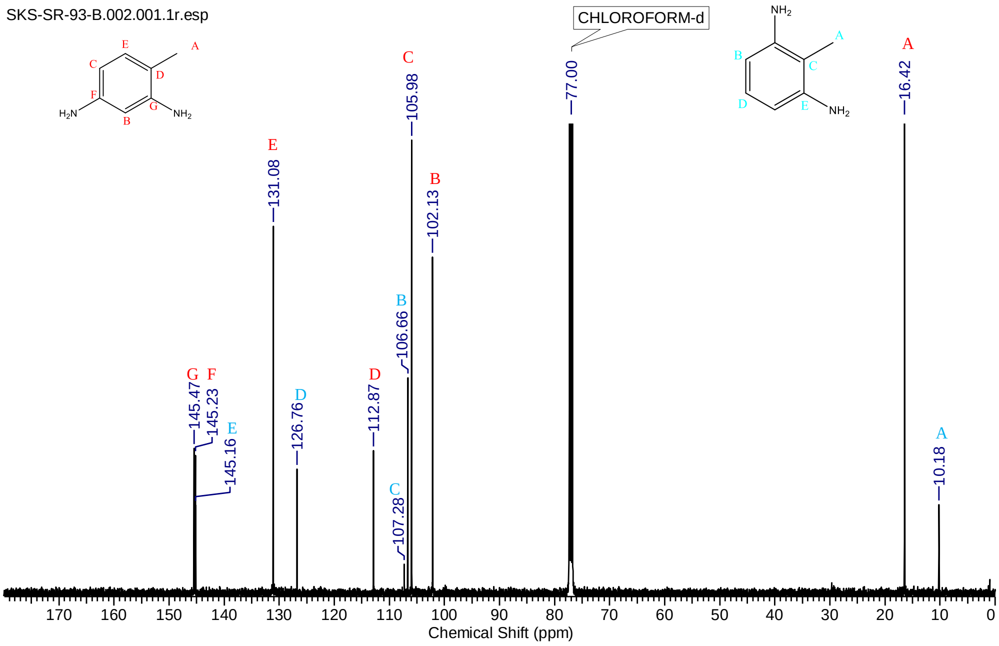
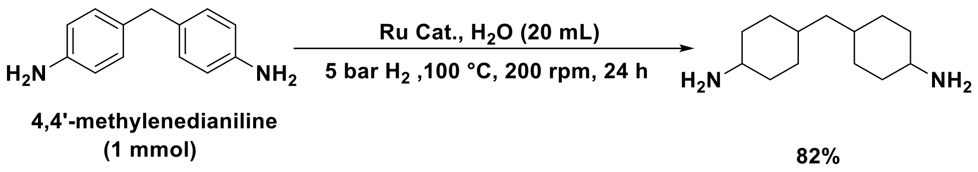


Figure 15. ^{13}C NMR of aniline fraction obtained from depolymerization of blue flexible foam in $CDCl_3$

3.4 Catalytic hydrogenation reactions of aniline fractions obtained from depolymerization of polyurethane foams

We performed hydrogenation reactions of aniline fractions obtained from the depolymerization of polyurethane foams, specifically targeting 4-methylbenzene-1,3-diamine,2-methylbenzene-1,3-diamine and 4,4'-methylenedianiline. These reactions were carried out at 5 bar of hydrogen pressure and 100 °C temperature for a duration of 24 hours (scheme 7). The resulting hydrogenated product was identified as 4,4'-methylenebis(cyclohexan-1-amine.



Scheme 7. Hydrogenation of 4,4'-methylenedianiline

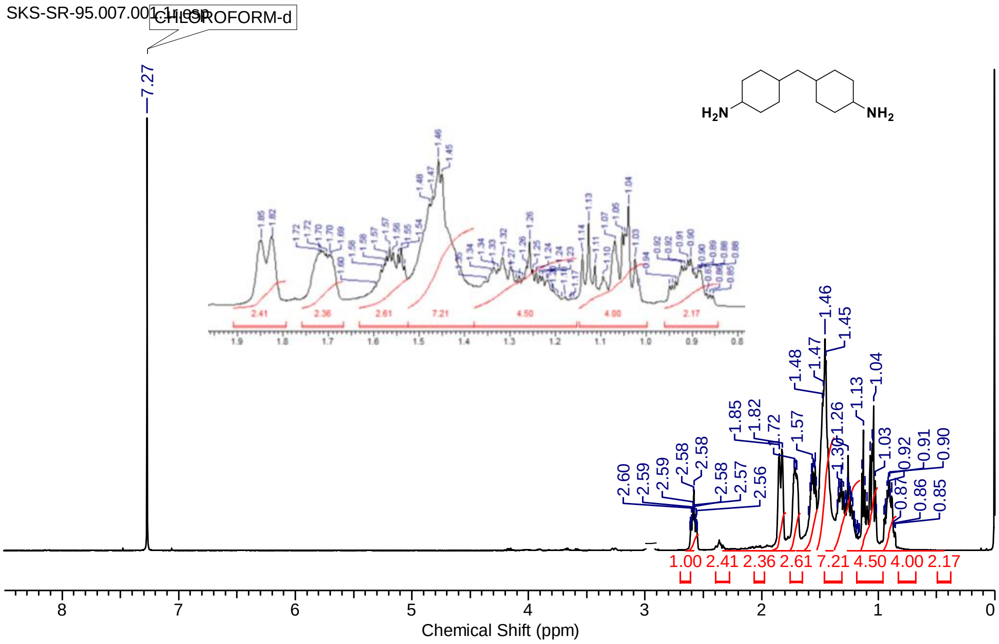


Figure 16. ^{1}H NMR spectra of 4,4'-methylenebis(cyclohexan-1-amine) in $CDCl_3$

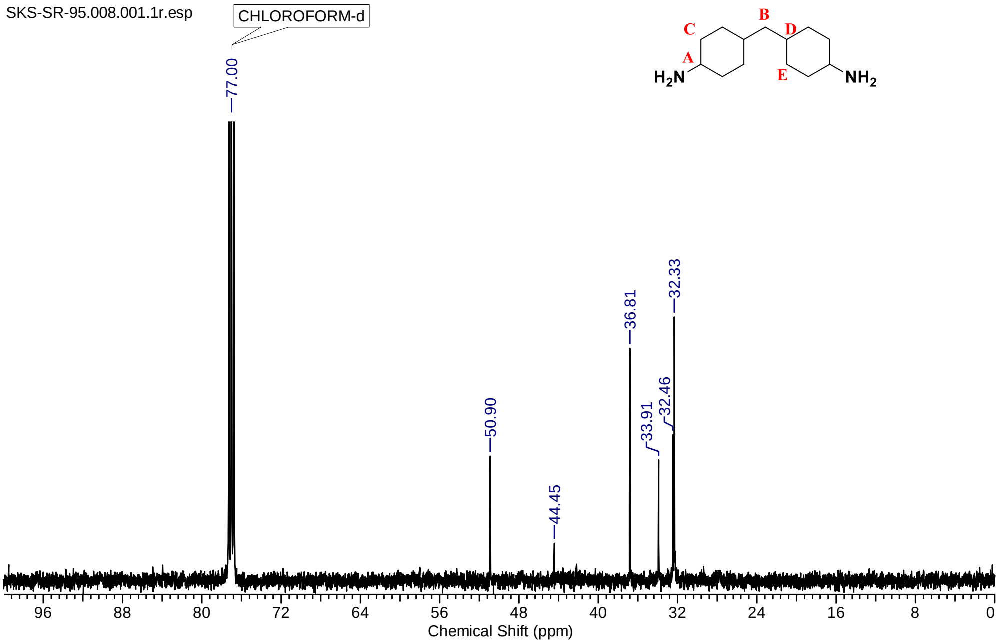


Figure 17. ^{13}C NMR spectra of 4,4'-methylenebis(cyclohexan-1-amine) in $CDCl_3$

CHAPTER 4

Conclusion

We have successfully synthesized Ru nanoparticle catalyst and characterized our catalyst by PXRD, TGA, SEM-EDS and UV-Vis. Furthermore, the process involved the use of heterogeneous catalyst which was easy to separate and reuse. So, we found an efficient way to hydrogenate the model compound diphenylmethane. Into value-added chemicals achieving good conversions using water as a solvent and hydrogen balloon. We have also performed bulk scale recyclability experiment with 1 mL (~6 mmol) of diphenylmethane in high-pressure reactor using 1 bar H_2 wherein we have achieved complete conversion for two cycles with 87 and 85 % yield of dicyclohexylmethane for cycle-1 and cycle-2, respectively.

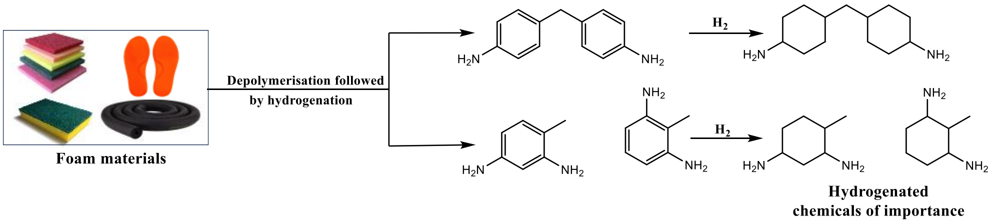


Figure 18. Schematic representation of upcycling of waste polyurethane foams

Further, we have explored depolymerization of waste polyurethane foams, rigid refrigerator foam and flexible blue foam, into its constituent anilines along with polyols at 180 °C which is lower temperature than reported methods (Figure 18). We have also scaled up this process for depolymerization of 5 g of foam to get good recovery (>70 wt%) of anilines and polyols. Initially, we optimized the reaction conditions for the hydrogenation of a model substrate, aniline, achieving complete conversion to cyclohexylamine with an 84% yield at 100 °C under 5 bar H_2. Subsequently, we applied these optimized conditions to hydrogenate aniline fraction obtained from the depolymerization of polyurethane foams i.e., methylene dianiline, to get their hydrogenated products, 4,4'-methylenedicyclohexylamine with the yield of 82%. The developed methodology demonstrates an alternative way to obtain cyclohexyl amine based fine chemicals for industrial applications such as 4,4'-methylenedicyclohexylamine used as epoxy resins.

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