DEVELOPMENT OF CATALYSTS FOR HYDROGENATION OF CARBON-BASED SUBSTRATES

M.Sc. THESIS

By

SHUBH JHAWAR 2103131025



DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE May, 2023

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A THESIS

Submitted in partial fulfilment 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, 2023



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 Hydrogenation of Carbon-based substrates" 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 2022 to May 2023 under the supervision of Dr. Sanjay K. Singh, Professor, 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.

Shubh Jhawar

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

Signature of the Supervisor of M.Sc. thesis

(Prof. Sanjay K. Singh)

Shubh Jhawar has successfully given her M.Sc. oral examination on 16th May 2023.

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Signature of supervisor of M.Sc. Thesis Prof. Sanjay K. Singh Date: (6.05702)

Venkattsh c

Signature of PSPC member Dr. Chelvam Venkatesh Date: 19.5.2023

Signature of DPGC Convener

Dr. Umesh A. Kshirsagar Date: 15,05.2423

Signature of PSPC member Dr. Selvakumar Sermadurai Date: 19.05.2023

ACKNOWLEDGEMENTS

Firstly, I would like extend my gratitude to my M.Sc. project supervisor, Prof. Sanjay Kumar Singh. He has been a source of constant support and guidance for me throughout these months. He has always supported my ideas and encouraged me to do independent thinking while exploring the field of catalysis and hydrogenation. He allowed me to apply my ideas in my research to try and explore new pathways and guided me through the obstacles and confusion that came in the way. This one-year project had been full of new learnings and experience due to his mentorship and teachings. His consistent and disciplined approach towards work taught me to be more organized and dedicated towards my jobs.

I would also like to thank my PSPC members Dr. Chelvam Venkatesh and Dr. Selvakumar Sermadurai for their suggestion during my project work. I would like to extend my heartfelt thanks to SIC, IIT Indore for providing all the needed instrumentation facilities. I would also like to thank DST-FIST 500 MHz NMR facility of the Department of Chemistry, for the NMR facility to characterize my work.

I would like to present a huge thank you to my dearest lab members, Ms. Bhanu Priya whose fine experimental skills have always fascinated and taught me to do lab work with responsibility, Mr. Ankit Kumar whose rigorous hard-working nature inspired me to do the same, Mr. Sanjeev Kushwaha who has always lovingly guided me with chemistry and future-related advice like a younger sibling, Ms. Vaishnavi Kulkarni whose knowledge of instruments and lab techniques made me spell-bound, Mr. Tushar Ashok Kharde whose playful and joyous nature made me forget about the biggest of my worries, Ms. Jayashree P. whose gentle ways of explaining made me learn so much, Mr. Khanindra Kalita whose puns and laughter always gave me an energy booster , Ms. Poojarani Sahu whose kind nature was extremely admirable and Mr. Pranjal Gupta for being my partner in all my lab and M.Sc. related worries. They have been a source of constant support and encouragement to me. They have always helped me with learning new methodologies and laboratory techniques and solved my laboratory related queries with utmost kindness and patience. I will always be grateful to them for treating me with so much affinity and kindness.

I am deeply indebted to my dearest IIT Indore friends Saryu, Srijita, Ritik, Ankita and Sodoor for being my moral support. They were instrumental in making me forget about my worries and enjoy my time here. I made some of my best life memories with them, who taught me so much about Chemistry and beyond. A huge thank you to all my M.Sc. 2023 batchmates for making this Masters journey full of enjoyment and laughter.

Lastly, this endeavour would not have been possible without my family members especially Mumma who often did not understand the nature of my worries but tried to provide comfort anyways. I would like to give a huge thank you to my dear late Dadaji who always showed his enormous faith in me and encouraged me to step out of the comforts of home and become independent in life. If it would not have been his support, I would never be able to come this far. Thank you, Papa, Radhe, Gopal and Maa for encouraging me always to do my best and give up on my worries. This journey was only possible due to their support and love for me.

> Shubh Jhawar Department of Chemistry

ABSTRACT

Aromatic nitro compounds belong to the class of harmful and toxic chemicals. They are identified as environmental pollutants which persist for a long time and contaminate our resources and health. Hydrogenation of such compounds to their respective amines is favourable to remove these compounds from our environment and convert them to other useful but less harmful chemical compounds. This thesis is focused on aqueous phase hydrogenation of range of aromatic nitro substrates in the presence of bimetallic Ni@Pd nanoparticles. Along with good conversion, the studied nanoparticle catalyst showed good recyclability up to five cycles. The course of my thesis is as follows: The 1st chapter consists of general introduction to nitroarenes and their reduced products. The 2nd chapter involves description of the experimental procedures that were adopted for catalyst synthesis and performing the different catalytic reactions. The 3rd chapter has detailed discussion about the results of various hydrogenation experiments performed. The last chapter includes the conclusion of my thesis with major findings. Main goal of this thesis is to develop an active and efficient heterogeneous catalyst which is active under environment benign conditions. This thesis is majorly focused on development of catalyst to provide a facile pathway for hydrogenation of nitroarenes.



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ACRONYMS

D_2O	Deuterium Oxide
FE-SEM	Field Emission Scanning Electron Microscope
IS	Internal Standard
MOF	Metal Organic Framework
NMR	Nuclear Magnetic Resonance
PVP	Polyvinlypyrrolidone
PXRD	Powder X-Ray Diffraction
NaBH ₄	Sodium Borohydride
UV-Vis	Ultraviolet-Visible

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
Temp.	Temperature
t	Time

CHAPTER 1

Introduction

1.1 General Introduction

Aromatic nitro compounds are important category of organic compounds with their usefulness as substrates for synthesis of dyes, polymers, perfumes, pharmaceuticals and other important chemicals.¹ However, nitroarenes compounds are also toxic and carcinogenic in nature. The electron withdrawing nature of nitro group attached to stable aromatic ring makes these resistant to oxidative degradation. As a result, they persist in environment for long duration catering to their extensive use and they contaminate the soil and groundwater. These are also registered in U.S. Environmental Protection Agency's pollutants list as the hazardous to health and environment.² The derivatives of nitrophenol are by-products of dyes and pesticides and are known to cause harm to liver, nervous system, kidney and blood. Halonitroarenes are organic pollutants which are known to cause severe damage to tissues in human body.³ Therefore, the reduction of such compounds is desirable for the removal of such harmful compounds from the ecosystem, even from the perspective of green chemistry.

Moreover, the synthesis of amines from the reduction of the nitro compounds is an important organic transformation. The corresponding amines are comparatively safer and are important industrial precursors for manufacturing polymers, dyes, drugs, pigments, agro and fine chemicals etc.⁴ The hydrogenation of aromatic nitro compounds is also a crucial step in synthesis of many industrially important amino compounds and pharmaceutical drugs. Many bioactive molecules such as alkaloids, drugs, natural products have amino moieties which are introduced by reduction of nitro groups, making this hydrogenation process as a matter of increasing interest.



Scheme 1. Reduction of nitroarenes to corresponding industrially relevant amino compounds.

The reduction of 4-nitrophenol to 4-aminophenol is an intermediate step for the Paracetamol (Acetaminophen) synthesis which comes in the class of antipyretic and analgesic drugs.⁵ *m*-Aminobenzenesulphonic acid, also known as metanilic acid is used to synthesize azo-dyes and sulfa-drugs. The industrial process of synthesis of metanilic acid involves sulphonating nitrobenzene using oleum with oleum to get *m*-nitrobenzenesulphonic acid whose further hydrogenation gives *m*-aminobenzenesulphonic acid.⁶ Pauldrine and Primaquine belongs to a class of antimalarial drugs which has *p*-chloroaniline and 8aminoquinoline as an important ingredient in their synthesis respectively, obtained by reducing *p*-chloronitrobenzene and 8-nitroquinoline selectively.⁷⁻⁸ Similarly, this transformation plays an important role in many other such class of drugs and medicines. The direct and selective hydrogenation of such compounds is required at industrial scale. For this to be possible, an economical, sustainable and selective catalyst is required to be able to perform this transformation.

Heterogeneous catalytic hydrogenations, owing to their advantages of being economic, selective and environment friendly, are widely popular in the industrial scenarios. They show properties like high activity, atom efficiency, easy product and catalyst separation and good recyclability which makes them area of great research interest.⁹⁻¹⁰ Industrially, since the catalysts used can be recovered and regenerated retaining the valuable property of the metal, these can be really of huge advantage, especially in case of precious metal catalysts.⁹ These reactions occur via a surface mechanism involving stepwise sequence of reversible and non-reversible processes, starting with adsorption of the unsaturated substrate on to the surface of the catalyst. This is followed by hydrogen adsorption and dissociation on the catalyst surface. Then, the first hydrogen is bonded to the substrate, described as the reversible step, followed by the second hydrogen atom addition which is effectively irreversible. The product formed is finally desorbed from the catalyst surface.¹¹

Among heterogeneous hydrogenation reactions, metal nanoparticles are extremely popular catalysts because of the size, morphology and enhanced surface area / volume ratio they provide for the reaction to occur. This makes them catalytically more efficient than their bulk counterparts, eventually reducing the production cost.¹² For such catalysts, noble metal nanoparticles such as Pt, Pd, Ru, Rh, Au etc., and non-noble metal nanoparticles such as Ni, Co, Fe etc. have been widely explored.¹³ Among the metal nanoparticles, bimetallic nanoparticles comprising of two different elements, are found to show better activity, more selectivity with enhanced stability for hydrogenation reactions. The properties of such catalysts are improved than that of the monometallic nanoparticles, attributed to electronic exchange and synergistic effect between the two elements.¹⁴⁻¹⁸ Different bimetallic catalysts explored for hydrogenation reactions include PdAu¹⁵, CuFe¹⁶, NiFe¹⁷, NiPd¹⁸ etc. There are various ways by which bimetallic nanoparticles its structural,

morphological and physicochemical properties. Bimetallics can be *mixed* such as alloys and intermetallic nanoparticle system (usually single step preparation) or *segregated* such as core-shell, multi-core shell etc. (involving multiple steps in preparation).¹²

The core@shell nanoparticles are gradually becoming more frontier due to their highly functional nature and different electronic and catalytic properties. The properties of such nanosystems can be altered by changing the constituting core and shell element or their ratio. Since heterogeneous catalytic reactions majorly takes place on the catalyst surface, large percentage of the noble metal atoms in an alloy kind of nanoparticles are inaccessible to the substrate and remain catalytically inactive. Therefore, this kind of core@shell structure, where core of the nanoparticles can be replaced with non-noble metal can make those inaccessible noble metal atoms active in the reaction and can ensure maximum utilization of the active catalytic sites as well as better control over catalyst activity and selectivity.¹⁹⁻²⁰

1.2 Literature Review and Problem Formulation

Traditionally, nitro group reductions are done in industries using Sn, Mn and Zn catalysts in stoichiometric amounts or Beuchamp's reduction which involves use of iron and sulphuric acid as reductant. But these methods generate a large amount of oxide waste along with toxic side-products, making them non-economical and environmentally unsustainable.⁸ The catalytic reduction was then explored using metal complexes and sulphides which did not involve using additives. However, using homogeneous systems restricted their reusability and selectivity which imposed another limitation.²¹ Therefore, catalytic hydrogenations using heterogeneous system, which are easily recyclable and reusable, making them economically and environmentally efficient needs to be adopted.



Figure 1: Limitations of the traditional nitro reducing methods

Among heterogeneous catalysts, Au and Pt based nanoparticle catalysts have been explored largely. Lang et al. reported the use of Ni-Au alloy nanoparticles for high performance reduction of nitroarenes, particularly halonitroarenes at 120 °C at 20 bar H₂ pressure.²² Reduction of nitrophenol was reported by Lin et al. using Pt nanoparticles supported over reduced Graphine Oxide (rGO) encapsulated over SiO₂ at 25 °C.²³ Corma et al. used Pt nanoparticles over TiO₂ for selective hydrogenation of substituted nitroaromatics at 40 °C using 4 bar H₂ pressure.²⁴ Shi and co-workers employed Au/TiO₂ to demonstrate the reduction of nitrobenzaldehyde at 140 °C and 9 bar H₂ pressure.²⁵ Dong et al. has demonstrated the synthesis of Ni@Pd core shell nanoparticles using consecutive reduction of Ni^{2+} and Pd^{2+} in a single pot followed by immobilizing them over silica support. They showed excellent activity for reduction of 4-nitrophenol with NaBH₄ with recyclability of six times.¹⁹ With halo-nitroarenes, one major problem is the selectivity of the hydrogenation. The reduction of these substrates is accompanied by competitive reductive dehalogenation as the carbon-halogen bond breaking is facilitated by the formed amino substituent on the ring.²⁶ Kosak and co-workers reported using Pt and Pd catalyst along with hypophosphorous acid as an inhibitor to supress the hydrogenolysis during hydrogenation of halonitrobenzene.²⁶ They also reported that the dehalogenation extent is dependent on the substituent position relative to nitro group (ortho, meta or para) and the susceptibility order towards hydrogenolysis of carbon halogen bond was also observed to be I>Br>Cl>F.²⁶ Zhang et. al. reported using Pt/y-Fe₂O₃ nanocomposite for ochloronitrobenzene hydrogenation with complete elimination of dehalogenation with hydrogen pressure varying from 0.1-4.0 MPa.²⁷ Cog et al. studied effect of particle size by using supports and alloying of Ru and Pt based catalyst for selective hydrogenation of *p*-chloronitrobenzene.²⁸ Therefore, selective hydrogenation of halo-nitroarenes is also desirable.

Table 1: Reported heterogeneous hydrogenation catalysts and conditions for

 reduction of different aromatic nitro substrates.

Substrate	Catalyst	Solvent	Temp.	pH ₂	t	Conv.	Sel.	Ref.
			(°C)	(bar)	(h)	(%)	(%)	
4-Chloronitrobenzene	Ni-Au/C	EtOH	120	20	3	100	100	22
4-Nitrophenol	Pt- rGO@SiO ₂	H ₂ O	25	1	1	100	100	23
Nitrobenzene	Ru	<i>i</i> -PrOH	180	10	30	100	95	29
4-Chloronitrobenzene	Pd@TiNT	EtOH	25	20	10	100	78	30
Chloronitobenzene	Pt/TiO ₂	THF	40	4	1	98	99	24
Nitro-benzonitrile	Pd/MgO	THF	RT	1	1-3	95	77	31
Nitro-benzaldehyde	Au/TiO ₂	Toluene	140	9	5-6	90	85	25
Halo-nitrobenzene	Pd/CNF	AcOEt	RT	4	10	100	65	32
Nitro-benzaldehyde/ Nitro-benzonitrile	Au/Fe ₂ O ₃	Toluene	140	10	9.5	90	75	25

For reported heterogeneous systems, most nanoparticle catalysts consist of rare noble metals which makes the overall process expensive and industrially unfeasible. Moreover, most of such reductions have been reported at high temperature and pressure which makes them further difficult to implement in industry.

1.3 Objectives of the Project

For hydrogenation of aromatic nitro groups, development of a heterogeneous catalyst to carry out this reduction in environmental benign conditions with minimum waste is desirable. According to literature reports, Pd metal is a widely explored catalyst for performing hydrogenation reactions at room temperature conditions.³³⁻³⁴ Incorporating a bimetallic core@shell systems can ensure the maximum accessibility to the noble metal active sites. Using the synergistic effect between the metal in core and in shell, the activity and selectivity of the catalyst can be controlled and cost-effective catalyst with reduced Pd amount can be synthesized.

This project aims at preparation of a stable heterogeneous catalyst using bimetallic core@shell approach with nickel and palladium to perform hydrogenation of nitro substituted aromatic compound in milder reaction conditions. Also, efforts will be made to make the catalyst more economical and recyclable making it feasible for large scale industrial application. Along with this, various nanoparticle synthesis and characterization techniques will be explored. The reduced products will be characterized and further analysed. The catalyst will be tested for recyclability and heterogeneity through experiments.

CHAPTER 2

Experimental Section

2.1 Materials and Instrumentation

All high-purity chemicals and metal salts were purchased from Sigma Aldrich, Rankem and TCI and used as received. ¹H NMR were recorded in deuterated solvent (D₂O) using Bruker Advance 400 MHz and Bruker Ascend 500 MHz Powder X-ray diffraction (P-XRD) measurements were performed using Rigaku Smart Lab, Automated Multipurpose X-ray diffractometer at 40 KV and 30 mA (Cu α λ = 1.5418 A). UV-Visible spectra were recorded in the wavelength range of 200-800 nm by Agilent UV Cary-60 Spectrophotometer. ESI-Mass spectra were recorded on a micrOTF-Q II mass spectrometer. SEM was performed using JSM-7610FPlus.

2.2 Synthesis of Catalyst

a) General procedure for synthesis of bimetallic Ni_{1-x}Pd_x alloy nanoparticles

Bimetallic Ni_{1-x}Pd_x alloy nanoparticles were prepared using the co-reduction method, which involves simultaneous reduction of Ni²⁺ and Pd²⁺ salts using NaBH₄ as the reducing agent, in the presence of polyvinylpyrrolidone (PVP), as a stabilizer, in water at room temperature as previously reported.³⁴ For the synthesis of bimetallic Ni₉Pd₁, 0.050 g PVP was added to a 5 mL aqueous solution of potassium tetrachloropalladate (II) (0.0016 g, 0.005 mmol) and nickel (II) chloride hexahydrate (0.0107 g, 0.045 mmol). This was followed by dropwise addition of aqueous solution of NaBH₄ (0.025 g in 5 mL of water) to the above solution at room temperature. The resultant mixture was then sonicated for 10 min to obtain a black suspension of bimetallic NiPd nanoparticles. The nanoparticles formed were collected by centrifugation and then washed with distilled water for several times and used for catalytic reactions. The other bimetallic NiPd alloy nanoparticles, with varying Ni and Pd molar ratios and Ni monometallic nanoparticles were also prepared in a similar way using the respective metal salts in specific molar ratios.

b) General procedure for synthesis of bimetallic $Ni_{1-x}@Pd_x$ nanoparticles

For synthesising core-shell bimetallic $Ni_{1-x}Pd_x$ nanoparticles, the method adopted was similar to reduction-trans metalation. For the synthesis of bimetallic Ni_9Pd_1 core-shell nanoparticles, 0.050 g PVP was added to a 5 mL aqueous solution of nickel (II) chloride hexahydrate (0.0107 g, 0.045 mmol). This was followed by dropwise addition of aqueous solution of NaBH₄ (0.025 g in 5 mL of water) to the above solution at room temperature. The resultant mixture was sonicated for 10 minutes. Then, to the above black suspension, potassium tetrachloropalladate (II) (0.0016 g, 0.005 mmol) was added and again sonicated for 10 minutes. The nanoparticles formed were collected by centrifugation and then washing them with distilled water for several times. Similar method was adopted for synthesising other Ni@Pd core-shell nanoparticles with varying amount of Ni²⁺ and Pd²⁺ salts.

2.3 General procedure for catalytic hydrogenation reactions

For carrying out hydrogenation reactions, 50 mL round-bottom flask was used. Typically, 1.0 mmol of nitro substrate was added to a 5 mL aqueous suspension of the freshly prepared nanoparticles catalyst. The reaction mixture was equipped with a hydrogen balloon and stirred (900 rpm) at room temperature. The progress of the reaction was monitored by Thin Layer Chromatography (TLC). After reaction completion, the reaction mixture was centrifuged at 6000 rpm for 10 minutes to recover the catalyst and separate it from reaction mixture. The obtained supernatant was analysed by ¹H NMR using D₂O as the solvent. The conversion and selectivity were calculated using sodium acetate (20.5 mg, 0.25 mmol) as an internal standard.

2.4 General procedure for recyclability reactions

To perform the recyclability experiments for catalyst, the nanoparticles were separated from the reaction mixture by centrifugation. It was washed with distilled water (4 mL x 2) and then dispersed in 5 mL distilled water for performing the next catalytic run.

CHAPTER 3

Results and Discussion

3.1 Characterization of the Catalyst

As synthesized nanoparticles were characterized by Powder XRD. As Vegard's law suggest, XRD peaks for bimetallic nanoparticles appear between XRD pattern of both the elements.³⁵ The Powder X-ray diffractogram shows broad peaks around 2θ value of 40° which corresponds to (111) lattice plane of Pd nanoparticles (JCPDS 46-1043) and the peak at 45° represents the (111) plane of Ni nanoparticles (JCPDS 65-0380) (Figure 2). The broad peaks of PXRD spectrum indicates amorphous nature and small crystallite size of the formed nanoparticles.



Figure 2. PXRD spectra of a.) Ni₉@Pd₁, b.) Ni₉₅@Pd₅, c.) Ni₉₉@Pd₁, d.) Ni₉@Pd₁ and e.) Ni nanoparticles.

The different nanoparticles were also characterized by UV-Visible Spectroscopy. The transformation from Ni²⁺ ion and Pd²⁺ ion to Ni⁰ and Pd⁰ respectively, is indicated by the absence of major peaks corresponding to Ni and Pd salt solutions. This indicates the formation of nanoparticles (Figure 3). The broadening of peak for nanoparticles is the indicator of its size in nanometre range.³⁶





FE-SEM Imaging of Ni₉@Pd₁ nanoparticles catalyst was done to see the morphology. The images demonstrated flake-like morphology for the synthesized nanoparticles.



Figure 4: FE-SEM images of Ni₉@Pd₁ catalyst.

3.2 Catalytic hydrogenation reaction of 3-nitrobenzenesulphonic acid

The 3model substrate chosen for these catalytic reactions was nitrobenzenesulphonic acid (1). As water is a universal solvent, the reactions were carried out in an aqueous medium. Firstly, the hydrogenation reaction of 1 was performed without any catalyst in the presence of H₂ balloon for extended period of 12 h. There was no conversion observed in this case (Table 2, entry 1) indicating that catalyst is necessary for this hydrogenation reaction. Then, the reaction was performed using Ni nanoparticles catalyst and again there was no conversion observed (Table 2, entry 2). As Pd was reported for performing hydrogenations at mild room temperature conditions,³³⁻³⁴ we incorporated Pd in small amount in the form of Ni₉₉Pd₁ alloy bimetallic system. With Ni₉₉Pd₁, the reaction was found to give 28.6% conversion in 1 h (Table 2, entry 3). This highlighted the importance of Pd for activating the hydrogen for this hydrogenation reaction. Since core@shell systems were reported to be more efficient with less Pd content,¹⁵ we tried Ni₉₉@Pd₁ nanoparticle catalyst to perform this reaction. 33.3% conversion to **1a** was observed in this case (Table 2, entry 4). After that, varying Ni/Pd ratios were analysed to obtain the optimum reaction condition for hydrogenation of aromatic nitro substrates. The hydrogenation of 1 was tried with 90:10, 95:5, 50:1 and 30:1 Ni@Pd ratio and full conversion to 1a was observed in 2-4 h (Table 2, entry 5-9). The reaction was also found to be good to excellent in terms of yield. Based on the activity of the catalyst and conversion in lesser time, Ni₉@Pd₁ catalyst was chosen for further catalytic reactions and study.





1	without catalyst	12	n.r.	-	
2	Ni	12	n.r. ^b	-	
3	Ni99Pd1	1	28.6	-	
4	Ni99@Pd1	1	33.3	-	
5	Ni99@Pd1	4	>99	>99/1.00	
6	Ni50@Pd1	2	>99	90/0.90	
7	Ni ₃₀ @Pd ₁	4	>99	95/0.95	
8	Ni95@Pd1	2.5	>99	>99/1.00	
9	Ni9@Pd1	2	>99	>99/1.00	
^a Reaction conditions: 1 (1 mmol), Catalyst (5 mol%), H ₂ balloon, 30 °C, water (5.0					
mL), n.r.: no reaction, ^b Ni catalyst oxidized after the reaction, ^c Determined by ¹ H NMR					
using sodium	acetate as an internal	standard.			

3.3 Time dependent UV-Visible Spectroscopy Study

Synthesis of core@shell nanoparticle catalyst was monitored using UV-Visible spectroscopy. Firstly, the spectra of Ni²⁺ salt (NiCl₂.6H₂O) aqueous solution was recorded with characteristic peak intensity of around 400 nm (Figure 4, Curve A). The Ni salt solution was reduced with NaBH₄ to obtain a black coloured solution indicating the formation of Ni⁰ nanoparticles. The spectra of these freshly synthesized nanoparticles were immediately recorded and no peak corresponding to Ni salt was observed indicating complete reduction of Ni²⁺ ions (Figure 4, Curve B). Then spectra of Pd²⁺ salt (K₂PdCl₄) solution was recorded with peak intensity of 424 nm (Figure 4, Curve C). The Pd salt solution was added to the previously obtained black suspension and the spectra was recorded (Figure 4, Curve D). The disappearance of peak corresponding to Pd²⁺ salt indicated the complete reduction of Pd²⁺ to Pd⁰ and formation of Ni⁰@Pd⁰ nanoparticles (Figure 4, Curve E).



Figure 5: Sequential reduction and corresponding UV-Visible Spectra for **Curve A:** Ni^{2+} salt (NiCl₂.6H₂O) in water, **Curve B:** Ni^0 nanoparticles in water, **Curve C:** Pd^{2+} salt (K₂PdCl₄) in water, **Curve D:** after Pd^{2+} addition to Ni^0 nanoparticles in water and **Curve E:** Ni^0 @Pd⁰ nanoparticles in water.

The monitoring of the reaction profile over time was done using UV-Visible Spectroscopy. The conversion of **1** to **1a** using Ni₉@Pd₁ was recorded by change in the characteristic peak at 260 nm of 3-nitrobenzenesulphonic acid to peak at 237 nm of 3-aminobenzenesulphonic acid (Figure 5a). The reduction of 4nitrophenol to 4-aminophenol using Ni₉@Pd₁ was also recorded with gradual decreasing intensity of characteristic peak of 4-nitrophenol at 348 nm and gradual increasing intensity of characteristic peak of its reduced product 4-aminophenol at 300 nm with time (Figure 5b). Similarly, a gradual decrease in the intensity of the characteristic absorbance peak of *p*-nitroaniline at 367 nm was observed, along with the development of new absorbance peaks at 239 and 305 nm corresponding to the formation of p-phenylenediamine by the reduction of p-nitroaniline (Figure 5c). The nitrobenzene to aniline conversion was also recorded by decreasing intensity of the characteristic absorbance peak of nitrobenzene at 267 nm was observed and increasing intensity of the characteristic absorbance peak of aniline at 230 nm (Figure 5d).





Figure 6: Time dependent UV-Visible Spectrum for hydrogenation of a.) 3nitrobenzenesulphonic acid (0.2 M) in water, b.) 4-nitropehnol (0.2 M) in water, c.) 4-nitroaniline in water (0.2 M), and d.) nitrobenzene in water (0.2 M).

3.4 Substrate Scope

The catalytic activity of the Ni₉@Pd₁ catalyst was checked for the reduction of some other nitro substrates using the same optimized reaction condition. The reactions for these substrates were timely monitored with the help of Thin Layer Chromatography (TLC). Firstly, hydrogenation of mono substituted nitrobenzene derivaties such as 4-nitroaniline (2), 4-nitrophenol (3), 4-nitrobenzonitrile (5), 4- chlorobenzene (6) and 3-nitrotoluene (7) was performed. Complete conversion of these substrates was observed in 1-4 h (Table 3, entries 2-6). The reduction of 4- nitrobenzonitrile happened along with the reduction of the nitrile group to amino group indicating that the catalyst offers no selectivity towards other reducible groups. Reduction of disubstituted nitrobenzene, in the form of 2-nitro-m-xylene (8) was also performed (Table 3, entry 7). The catalyst activity was checked for heterocyclic compounds, 8-nitroquinoline (9). Full conversion to 8- aminoquinoline (9a) was obtained in 2 h (Table 3, entry 8).

Entry	Substrate	Product	t	Conv.	Sel.	Yield
			(h)	(%)	(%)	(%)
1	NO ₂	NH ₂	1	>99	>99	60
2	<u>2</u>		1	> 00	> 00	07
	NH ₂ 3	NH ₂ 3a	1	~77	~77	07
3	NO ₂ OH 4	NH ₂ OH 4a	3	>99	>99	30

Table 3: Catalytic hydrogenation of different nitro substrate over Ni₉@Pd₁^a



The reaction with 4-chloronitrobenzene (6) was found be less selective as dehalogenation was observed along with hydrogenation. The catalytic hydrogenation of 4-chloronitrobenzene (6) was further explored with different catalytic ratios. For these reactions, 0.5 mmol (78.7 mg) of 4-chloronitrobenzene (6) was added to freshly prepared nanoparticles. The reaction was equipped with H_2 gas balloon and was carried out for 1 hour at room temperature to compare the activity of differently synthesised nanoparticle catalyst with varying Ni and Pd ratios.

Initially, the reaction was carried out using only Ni nanoparticles. There was no conversion observed in this case (Table 4, entry 1). Since Pd was found to facilitate the H_2 activation in previous results, the effect of incorporation of Pd was

checked by synthesising bimetallic NiPd nanoparticles. By employing alloy Ni₉Pd₁ nanoparticles, the hydrogenation of 4-chloronitrobenzene (6) was observed with 95% conversion in 1h. 100% selectivity was observed for phenylhydroxylamine (6c) (Table 4, entry 2). With Ni₉@Pd₁, 95% conversion was observed with aniline (6a) as the major product (Table 4, entry 3). The Ni₉@Pd₁ nanoparticles synthesized by reducing the solution after adding Pd²⁺ solution was also used for catalytic hydrogenation. 96% conversion was obtained in 1 h with phenylhydroxylamine (6c) as the major product (Table 4, entry 4). Since Pd is known to facilitate the bond dissociation,²³ we tried to reduce the amount of Pd to obtain halogenated reduced product with major selectivity. Varying Ni/Pd ratios were explored with alloy and core@shell nanoparticle formation techniques. With Ni₉₅Pd₅ and Ni₉₉Pd₁ nanoparticle catalyst, good conversion (~90%) was observed with aniline (6a) as the major product (Table 4, entries 5-6). With Ni₉₅@Pd₅ and Ni₉₉@Pd₁, 4-chloronitroaniline (6b) and 4-chlorophenylhydroxylamine (6d) was formed with maximum selectivity respectively (Table 4, entries 7-8). These results implied that lesser Pd content can help us tune the selectivity of the reaction with minimum dehalogenation.

Table 4: Catalytic hydrogenation of 4-chloronitrobenzene over various synthesised catalyst^a

NO₂

CI 6	Ni _{1-x} Pd _x H₂O, 30 °C H₂ balloon 1h	+ CI 6a 6b	+ + + CI CI 6c 6d	
Entry	Catalyst	Conv.	Sel. (%)	
		(70)	(00.00.00.00)	
1	Ni	-	-	
2	Ni ₉ Pd ₁	95.0	0:0:>99:0	
3	Ni9@Pd1	95.5	78:22:0:0	
4	Ni ₉ @Pd ₁ (later reduction)	96.0	0:0:65:35	

NH_a

NH₂

NHOH

NHOH

5	Ni95Pd5	90.6	77:23:0:0			
6	Ni99Pd1	90.3	80:20:0:0			
7	Ni ₉₅ @Pd ₅	96.1	26:66:0:8			
8	Ni99@Pd1	93.3	0:27:0:73			
^{<i>a</i>} Reaction condition: 4-chloronitrobenzene (0.5 mmol), catalyst (10 mol%), H ₂ balloon, water (5.0 mL), 30 °C, 1 h						



Figure 7: Graphical distribution of reaction products over different NiPd catalysts (corresponding to Table 4).

3.5 Synthesis of industrially important metanilic acid by catalytic hydrogenation of 3-nitrobenzenesulphonic acid

Metanilic acid or 3-aminobenzenesulphonic acid is an important commercial compound that finds its use in synthesis of azo, acid and sulpha dyes. It is an important intermediate compound in synthesis of pesticides and sulphonated polyanilines. It is a stable compound with less toxicity than aniline. Industrially, the synthesis involves hydrogenation of 3-nitrobenzenesulphonic acid, obtained by sulphonating nitrobenzene. Basic aqueous solution of 3-nitrobenzenesulphonic acid is pressured to 0.8 to 2 MPa of hydrogen gas at 60-130 °C using activated carbon Pd catalyst followed by the acidification to give metanilic acid (**Scheme 2a**).

We carried out the synthesis of metanilic acid by using the optimized reaction condition with Ni₉@Pd₁ catalyst (**Scheme 2b**). The aqueous solution of 3-nitrobenzenesulphonic acid (1) (in bulk amounts, Table 5), containing the catalyst was equipped with hydrogen balloon and stirred at room temperature perform the hydrogenation. This was followed by acidification using conc. HCl to precipitate the solid Metanilic acid (**Table 4**). The amorphous while solid obtained was characterized by ¹H NMR and Mass Spectroscopy (**Appendix A**, **Figure 18-19**) which showed the peaks corresponding to the desired product.



Scheme 2: Synthesis of metanilic acid by industrial (Scheme 2a) and our work (Scheme 2b) by catalytic hydrogenation of 3-nitrobenzenesulphonic acid (1).



(NO ₂ SO ₃ H		i.) Ni ₉ @Pd _{1,} H ₂ O, 30 °C H ₂ balloon ii.) excess conc. HCI		NH ₂ SO ₃ H	
Entry	Substrate (mmol/g)	t (h)	Conv. (%)	Yield (%)	Amount of Metanilic Acid (mmol/g)	Yield of Metanilic Acid (%)
1	3/0.61	8	>99	94	1.2/0.22	40
2	6/1.22	18	>99	90	3.9/0.68	65
Reactio	n conditions:	catalyst	(5 mol%), I	H ₂ balloon,	30 °C, water	(5.0 mL)

3.6 Stability experiments for Ni₉@Pd₁ nanoparticle catalyst

Recyclability of catalyst: Recyclability experiments were carried out for 6 consecutive catalytic runs for hydrogenation of 3-nitrobenzenesulphonic acid (1) over the Ni₉@Pd₁ catalyst under the optimized reaction conditions, indicating towards long term stability of the catalyst. For all the 5 cycles, full conversion was observed in optimized reaction time. However, the yield was found to decrease with successive catalytic cycle.



Figure 8: Recyclability of Ni₉@Pd₁ catalyst for catalytic hydrogenation of 3nitrobenzenesulphonic acid (1)

Catalyst heterogeneity test: As shown in Scheme 3, Heterogeneity experiments with 3-nitrobenzenesulphonic acid (1) over the Ni₉@Pd₁ catalyst under the optimized reaction conditions was performed. After 1 h of the reaction, the Ni₉@Pd₁ catalyst was removed and the supernatant was separated into two parts – first part was analyzed by ¹H NMR which showed 55% conversion, while in the second part and the reaction was allowed to run without the catalyst for rest of the reaction time (1 h) using a H₂ balloon. The result inferred that the reaction could not proceed in the absence of the Ni₉@Pd₁ catalyst, hence supporting the heterogeneous nature of the Ni₉@Pd₁ catalyst for the hydrogenation of nitro substrates.



Scheme 3: Catalyst heterogeneity test



Figure 9: (1) Catalytic hydrogenation of 3-nitrobenzenesulphonic acid (1) under the optimized reaction conditions. Leaching experiments: (2) Catalytic hydrogenation of 3-nitrobenzenesulphonic acid (1) over $Ni_9@Pd_1$ at room temperature in 1 h and subsequently (3) after recovering the catalyst by centrifugation, supernatant liquid was again stirred under H₂ atmosphere for another 1 h.

CHAPTER 4

Conclusion

Bimetallic nanoparticles using varying amount of Ni and Pd were synthesized using different methods and characterized. The core@shell approach for nanoparticles was utilized to make maximum utilization of the added Pd content and reduce the cost of catalyst synthesis. The hydrogenation of the different aromatic nitro substrates was performed in mild reaction conditions using water as solvent and hydrogen balloon at room temperature. The heterogeneous nature of the catalyst restricted its tolerance towards other reducible functional groups. For chloronitrobenzene, the selectivity was found to increase with decreasing Pd content. The progress of the reaction and the synthesis of catalyst was monitored using UV-Visible spectroscopy. The recyclability of the catalyst was checked with optimized condition. The catalyst was found to be active up to 6 catalytic cycles with good conversion and yield. The synthesis of Metanilic acid was carried out with bulk scale reactions and the obtained solid was characterized by ¹H NMR and Mass Spectroscopy. The heterogeneity of the catalyst was confirmed by performing the leaching experiment.

APPENDIX-A



Figure 10 :¹H NMR spectrum of compound 1a in D_2O with internal standard (sodium acetate).



Figure 11 :¹H NMR spectrum of compound 2a in D₂O with internal standard (sodium acetate).



Figure 12:¹H NMR spectrum of compound 3a in D₂O with internal standard (sodium acetate).



Figure 13:¹H NMR spectrum of compound 4a in D₂O with internal standard (sodium acetate).



Figure 14:¹H NMR spectrum of compound 5a in D₂O with internal standard (maleic acid)



Figure 15:¹H NMR spectrum of compound 6a in D₂O with internal standard (sodium acetate)



Figure 16:¹H NMR spectrum of compound 7a in D₂O with internal standard (sodium acetate)



Figure 17:¹H NMR spectrum of compound 8a in D₂O with internal standard (maleic acid)



Figure 18:¹H NMR spectrum of compound 9a in D_2O with internal standard (sodium acetate)



Figure 19:¹H NMR spectrum of synthesized metanilic acid in D₂O.



Figure 20: Mass spectrum of synthesized metanilic acid.

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