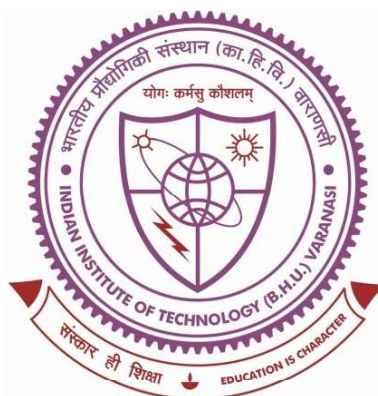


Metal-Organic Framework-Derived Catalysts for Organic Reactions



Thesis submitted in partial fulfillment for the
Award of Degree
Doctor of Philosophy

By
Ved Vyas

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI- 221005
INDIA

Roll No. 18051011


Year 2023

CERTIFICATE

It is certified that the work contained in the thesis titled “**Metal-Organic Framework-Derived Catalysts for Organic Reactions**” by **Ved Vyas** has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy, and SOTA for the award of Ph.D. Degree.

Date: 09/11/2023
Place: Varanasi


Dr. Arindam Indra
Assistant Professor
Department of Chemistry
IIT (BHU), Varanasi
Varanasi-221005
(Supervisor)


Department of Chemistry,
Indian Institute of Technology
(Banaras Hindu University),
Varanasi-221005

DECLARATION BY THE CANDIDATE

I, "Ved Vyas", certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of "Dr. Arindam Indra" from "July-2018" to "October-2023," at the Department of Chemistry, Indian Institute of Technology, (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, theses, etc., or available at websites and have not included them in this thesis and have not cited as my own work.


Date: 09/11/2023

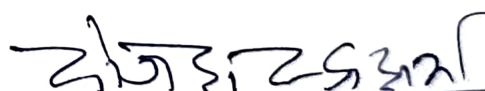
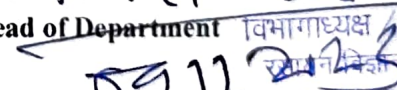
Place: Varanasi


(Ved Vyas)

CERTIFICATE BY THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my/our knowledge.

Supervisor 
Dr. Arindam Indra
Assistant Professor
Department of Chemistry
IIT (BHU), Varanasi
Varanasi-221005
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)
Varanasi- 221005


Head of Department 
Prof. Y. C. Sharma
विभागाध्यक्ष / HEAD
रसायन विभाग
Department of Chemistry
भारतीय प्रौद्योगिकी संस्थान (का.हि.वि.वि.)
Department of Chemistry, Indian Institute of Technology (B.H.U.)
Varanasi-221005 / Varanasi-221005
Department of Chemistry
(Banaras Hindu University),
Varanasi- 221005

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: **Metal-Organic Framework-Derived Catalysts for Organic Reactions.**


Name of the Student: **Ved Vyas**

COPYRIGHT TRANSFER

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the "**Doctor of Philosophy**" degree.

Date: 09/11/2023

Place: Varanasi.


(Ved Vyas)

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for author's personal use provided that the source and the Institute's copyright notice are indicated.

**DEDICATED TO MY LOVING
PARENTS...**

Acknowledgement

It is indeed my proud privilege to express my deep sense of gratitude and indebtedness to my supervisor, Dr. Arindam Indra, Department of Chemistry, Indian Institute of Technology (BHU), Varanasi, for his enormous help, cooperation, and valuable supervision that he has extended to me for the successful completion of this investigation. I am indebted to him for his consistent encouragement, sustained interest, and parental care throughout the research period.

I am obliged very much to express my sincere thanks to HOD, Prof. Y. C. Sharma, and Ex-HOD, Prof. D. Tiwary, Department of Chemistry, IIT (BHU) for providing necessary facilities and constant motivation throughout my research work.

It is my pleasure to express my cheers to all RPEC members Dr. J. Kandaswamy, Dr. P. Makam, Department of Chemistry, IIT (BHU), and Dr. S. K. Jain Department of Pharmaceutical Engineering and Technology IIT (BHU). for their valuable suggestions, constant guidance, and kind encouragement during my research work. They always came forward to assist me whenever I needed.

My passionate thanks go to all the faculty members, Department of Chemistry IIT (BHU) for their support and encouragement.

I constraint special thanks for all non-teaching staff (Mr. Rambish, Neeraj, Abhishek, and Amit) of the Department of Chemistry, IIT (BHU) as this work would have never been completed without their technical support.

I also gratefully acknowledge to the Council of Scientific and Industrial Research (CSIR), Anushandhan Bhavan, New Delhi, for the financial support in the form of JRF and SRF.

I gratefully acknowledge the facilities provided by CIFC, IIT (BHU), Varanasi for doing various characterization of samples.

I am blessed to have very supportive and caring labmates Ms. Priyanka Maurya, Mr. Deepak kumar, Mr. Vishesh Kumar, Mr. Toufik Ansari, Mr. Abhimanyu Kumar, and Mr. Ajit Kumar Singh for their valuable support and encouragement towards the successful completion of my research work.

I am deeply gratified to express my sincere thanks to my supporter, friend, and senior “Dr. Subhash Chandra” for their encouragement and valuable suggestions during my research work.

I would like to thank my friends and seniors “Ms. Neetu Verma, Mr. Vivek Kumar, Mr. Deepak Kumar, Mr. Sarvatej Kumar, Mr. Satendra Kumar, Ms. Amisha Sony, Dr. Kanaujiya Vimlesh Kumar, Dr. Murli Dhar Mitra, Dr. Bharat Kumar, Dr. Daraksha bano, Dr. Shiv Sunder Yadav, Dr. Devendra Kumar, Dr. Viaksh Kumar, Dr. Vinod Kumar, Dr. Abhay Narayan Singh,” for their help and support.

I would like to my deepest affection to my loving mother “Shanti Devi”, caring father “Late Shiv Pratap Singh,” and sister “Sheela Devi, Rekha Devi, Anjali Singh,” brother “Ved Prakash” and all my family members for their love, concern, continuous moral support and encouragement which enabled me to perform my liabilities.

I am also grateful to my brother-in-law “Uday Bhan Singh, Mahendra Kumar, and Arvind Kumar” for their motivation, support and encouragement.

My special thanks to my younger brother “Mr. Gyan Singh” for their support and encouragement in the entire research period.

At the last but not the least, I thank to all my well-wishers and critics whose names I may have failed to mention here unintentionally. Thanks to all of you for being there for me when times were the toughest.

Date: 09/11/2023

Place: Varanasi

(Ved Vyas)

List of Figures

Figure No.	Title	Page No.
Figure 1.1	Potential energy diagram of a catalyzed and un-catalyzed reaction	2
Figure 1.2	Different types of solid-supported materials	6
Figure 1.3	The graphical chart of different types of catalysts	7
Figure 1.4	Structural modulation of M–N–C@NC catalyst	9
Figure 1.5	M–N–C@NC type catalyst with different N-containing ligands	10
Figure 1.6	Synthetic strategy for the preparation of different types of MOF-derived M–N–C@NC catalysts	12
Figure 1.7	Different types of organic reactions are carried out using M–N–C@NC catalysts	13
Figure 1.8	Examples of the different types of drugs with amine and amide moieties	17
Figure 1.9	Diagram showing the chapter-wise specific objectives of the thesis	18
Figure 2.1	(a) The PXRD graph of ZIF-67@C and Vulcan carbon. (b) & (c) shows the PXRD and Raman spectra of the graph of the Co-N-C@NC. (d) The C 1s spectrum of Co-N-C@NC was deconvoluted into five peaks for C=C, C–C, C=N, C–N, and COOH species. (e) The N 1s spectrum was fitted into four peaks- corresponding to pyridinic, Co–N, pyrrolic, and graphitic nitrogen. (f) Co 2p XPS was fitted into peaks for Co(0), Co–N, Co(III), and Co(II) species. The * marked peaks are originated as the satellite peaks of Co(II). (d) O 1s spectrum of Co–N–C@NC	31
Figure 2.2	(a) FE-SEM image of Co–N–C@NC showing the rhombic dodecahedron morphology of the particles. (b-e) elemental mapping of Co–N–C@NC, (f) TEM images of Co–N–C@NC with spherical morphology. (g) HR-TEM image showing the inter-planar spacing between the graphene layers and inset SAED pattern of the Co–N–C@NC. (h-i) The size of the particles was calculated to be 4-12 nm.	32

- Figure 2.3** (a) Progress of the *N*-alkylation reaction of aniline and benzyl alcohol with time. (b) Reaction mechanism for the *N*-alkylation reactions. (c) A sequence of the reaction involved as detected by ^1H NMR **39**
- Figure 2.4** Recycling test of Co–N–C@NC for the synthesis of *N*-benzylaniline. Reaction conditions: 1 mmol benzyl alcohol, 0.5 mmol aniline, 10 mg catalyst, 0.5 mmol *tert*-BuOK, 2 mL toluene, 140 °C, 24 h. Conversions and yields are based on aniline and determined by GC **40**
- Figure 2.5** ^1H NMR and ^{13}C NMR spectra of the compound 2a in CDCl_3 **46**
- Figure 2.6** ^1H NMR and ^{13}C NMR spectra of the compound 2d in CDCl_3 **47**
- Figure 3.1** (a) The PXRD pattern of ZIF-67. (b) The SEM image shows the dodecahedron morphology of ZIF-67 and (c-f) images show the elemental mapping, (g) EDX spectra of ZIF-67. (h) PXRD of Co–N–C@NC, (i) Raman spectrum of Co–N–C@NC catalyst **54**
- Figure 3.2** (a) The C 1s spectrum of Co–N–C@NC was deconvoluted into four peaks for C=C, C–C, C=N, and C–N species. (b) The N 1s spectrum was fitted into four peaks- corresponding to pyridinic, Co–N, pyrrolic, and graphitic nitrogen. (c) Co 2p XPS was fitted into peaks for Co(0), Co–N, and Co(II) species. The * marked peaks originated as the satellite peaks of Co(II). (d) The SEM image of the Co–N–C@NC shows the dodecahedron-type morphology. (e) The TEM images of the Co–N–C@NC catalyst shows the nanoparticle nature with different type of support such as CNT and NC in image (f) and (g). (h) HR-TEM image of the Co–N–C@NC with d-spacing 0.207 and 0.340 nm of the cubic plane (111) and graphene (002). (i) The image shows the nanoparticle size between 2-10 nm **56**
- Figure 3.3** ^1H NMR and ^{13}C NMR spectra of the compound 3a in CDCl_3 **64**
- Figure 4.1** (a) PXRD pattern of Ni-ZIF-8, (b) FE-SEM image with rhombic dodecahedron morphology. (c-f) Elemental mapping of Ni-ZIF-8 (with elements: Ni, Zn, N, and C) **72**
- Figure 4.2** (a) The C 1s spectrum of Ni–N–C@NC was deconvoluted into four peaks for C=C, C–C, C=N, and C–N. (b) The N 1s spectrum was fitted **74**

into four peaks- corresponding to pyridinic-N, Ni-N, pyrrolic-N, and graphitic nitrogen. (c) Ni 2p XPS was fitted into peaks for Ni(0) and Ni(II) species. The * marked peaks originated as the satellite peaks of Ni²⁺. (d) O 1s spectrum of Ni-N-C@NC deconvulated into three peaks for Ni-O, C-O, and C-OH

- Figure 4.3** (a) FE-SEM image of Ni-N-C@NC showing the rhombic dodecahedron morphology of the particles. (b) TEM images of Ni-N-C@NC with nanoparticles and the size of the particles was very fine. (c) HR-TEM image showing the inter-planar spacing between the graphene layers is 0.36 nm with (002) plane and inset SAED pattern of the Ni-N-C@NC **74**
- Figure 4.4** (a) Reaction mechanism of the amide reaction with the Ni-N-C@NC. (b) Recyclability graph of the Ni-N-C@NC nanocatalysts for the amide bond formation reactions **81**
- Figure 4.5** ¹H NMR ¹³C NMR spectra of compound 4a in CDCl₃ **87**
- Figure 4.6** ¹H NMR ¹³C NMR spectra of compound 4b in CDCl₃ **88**
- Figure 5.1** (a) and (b) images show the PXRD and FTIR spectra of the Ni-Ni-CP. (d) and (e) images show the TEM and HR-TEM of the Ni-Ni-CP and (f) shows the EDX of the PBA with the Ni, C, N, and O elements **96**
- Figure 5.2** (a) & (b) image shows PXRD and Raman spectra of NiO@Ni and (c) shows the BET of NiO@Ni. (d) FE-SEM images of NiO@Ni showing spherical nanoparticles. (e) TEM image showing the thickness of the amorphous shell (4–6 nm) and NiO core (14-20 nm) and inset: selected area diffraction pattern showing polycrystalline nature of NiO, (f) HR-TEM image of NiO@Ni showing the amorphous Ni shell on the surface of the crystalline NiO nano-particles (g) magnified image of the shell, (h) corresponding FFT pattern indicating amorphous nature of the shell, (i) magnified image of the crystalline core showing the lattice spacing of 0.24 nm corresponding to (111) plane of cubic NiO and (j) corresponding FFT pattern. (k-n) Elemental mapping of NiO@Ni shows that element Ni, O, and C was homogeneously distributed. (o) **98**

This image shows the XPS spectra of Ni 2p and it was fitted into Ni²⁺ and Ni⁰ and * peaks confirmed the satellite peaks. (p) The O 1s XPS spectra deconvulated into four peaks with corresponding Ni–O (O1), Ni–O–C (O2), and water peaks (O3 & O4). (q) The C 1s XPS spectra with corresponding C=C (C1), C–O (C2) and C=O (C3)

- Figure 5.3** (a) Reaction mechanism for the amide bond formation reactions with the NiO@Ni catalyst and (b) recyclability graph of the NiO@Ni catalyst for the amidation reaction **105**
- Figure 5.4** ¹H NMR ¹³C NMR spectra of compound 5a in CDCl₃ **109**
- Figure 5.5** ¹H NMR ¹³C NMR spectra of compound 5e in CDCl₃ **110**

List of Table

Table No.	Title	Page No.
Table 2.1	Optimization table for the <i>N</i> -alkylation reaction condition	34
Table 2.2	Characterization of the products by ¹ H NMR and ¹³ C NMR	41
Table 3.1	Optimization of the reaction condition	58
Table 3.2	Characterization of the products by ¹ H NMR and ¹³ C NMR	62
Table 4.1	Optimization table for amidation reaction with aldehyde and amine	76
Table 4.2	Characterization of the various products of the ¹ H NMR and ¹³ C NMR	82
Table 5.1	Optimization table of the amidation reactions	100
Table 5.2	¹ H NMR and ¹³ C NMR and spectra of the products	106

List of Symbols/Abbreviations

θ	Angle (degree)
a.u.	Atomic unit
BE	Binding energy
CP	Coordination polymer
¹³C NMR	Carbon nuclear magnetic resonance
eV	Electron volt
EDX	Energy-dispersive X-ray spectroscopy
GC-MS	Gas chromatography and mass spectroscopy
HRSEM	High Resolution Scanning Electron Microscope
¹H NMR	Hydrogen nuclear magnetic resonance
MOF	Metal Organic Framework
mM	Milli-molar
NC	Nitrogen-doped carbon
SiO₂	Silica
SAED	Selected area electron diffraction pattern
s	Second
TEM	Transmission Electron Microscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction
λ	Wavelength
ZIF	Ziolitic Imidazolate Framework

List of Schemes

Scheme No.	Title	Page No.
Scheme 2.1	The schematic representation for the synthesis of ZIF-67@C and its pyrolysis to produce Co-N-C@NC	27
Scheme 2.2	<i>N</i> -alkylation of aniline and substituted-anilines with different benzyl alcohols using Co-N-C@NC catalyst. Reaction conditions: 1 mmol substituted benzyl alcohol, 0.5 mmol aniline, 10 mg catalyst, 0.5 mmol <i>tert</i> -BuOK, 2 mL toluene, 140 °C, 24 h. For 3a (18 h), 3e (18 h), and 3f (18 h) optimized at different times	36
Scheme 2.3	Co-N-C@NC catalyzed the <i>N</i> -alkylation reaction of different anilines with benzyl alcohols. Reaction condition: 1 mmol substituted benzyl alcohol, 0.5 mmol aniline, 10 mg catalyst, 0.5 mmol <i>tert</i> -BuOK, 2 mL toluene, 140 °C, 24 h. For 4d (18 h), 4e (20 h), and 4f (20 h) optimized at different times	37
Scheme 3.1	Schematic representation for the synthesis of Co-N-C@NC catalyst	52
Scheme 3.2	The cyclization of benzimidazole reaction with Co-N-C@NC catalyst. Reaction conditions: 1 mmol benzyl alcohol, 0.5 mmol of <i>o</i> -phenylenediamine, 0.5 mmol of <i>tert</i> -BuOK, toluene (2 mL), 140 °C, for 12 h	60
Scheme 3.3	Reaction mechanism of benzimidazole reaction with Co-N-C@NC catalyst	61
Scheme 4.1	Schematic representation of the synthesis of Ni-N-C@NC catalyst	69
Scheme 4.2	Ni-N-C@NC catalyzed amidation reaction of substituted benzaldehydes with piperidine. Reaction conditions: Benzaldehyde (1 mmol), piperidine (1 mmol), catalyst (5 mg), TBHP (0.35 eq), dioxane (2 mL), 60 °C, and 4 h	77
Scheme 4.3	Amidation reaction with various amines and aldehyde with Ni-N-C@NC catalyst. Reaction condition: Aldehyde (1 mmol), amine (1 mmol), catalyst (5 mg), TBHP (0.35 eq), dioxane (2 mL), 60 °C, and 4 h	79
Scheme 5.1	Schematic representation for the synthesis of NiO@Ni core-shell Mott-Schottky catalyst formed by the calcination of Ni-Ni-CP	93
Scheme 5.2	Catalytic performance of NiO@Ni catalyst for amide bond formation. Reaction conditions: under nitrogen atmosphere, aldehyde (1 mmol), amine	102

(1 mmol), TBHP (4 mmol), NiO@Ni (5 mg), 1,4-dioxane (1 mL).

Temperature: 60 °C, time: 8 h

Scheme 5.3 Catalytic performance of NiO@Ni Mott-Schottky catalyst for amide bond formation. Reaction conditions: Aldehyde (1 mmol), amine (1 mmol), TBHP (4 mmol), NiO@Ni (5 mg), 1,4-dioxane (1 mL). Temperature: 60 °C, time: 8 h

103

Contents

Title	Page No.
Title of thesis	i
Dedication	ii
Certificate	iii
Declaration by the candidate and certificate by the supervisor	iv
Copyright transfer certificate	v
Acknowledgment	vi-vii
Contents	viii-xi
List of Figures	xii-xv
List of Schemes	xvi-xvii
List of Tables	xviii
List of Symbols/Abbreviations	xix
Preface	xx-xxiii
Chapter 1: General Introduction	1-25
1. Introduction	1
1.1. History of catalysis	1
1.2. Factor related to catalysis	2
1.2.1. Thermodynamics and kinetics of catalytic reaction	2
1.2.2. Turn over number and turn over frequency	3
1.2.3. Selectivity in product formation	3
1.3. Classification of the catalysis process	3
1.3.1. Homogeneous catalysts	4
1.3.2. Heterogeneous catalysts	4
1.4. Nanocatalysis	5
1.5. Supported nanocatalyst	5
1.6. M–N–C@NC type catalyst	7
1.7. Metal-organic framework (MOF)-derived M–N–C@NC catalyst	11
1.7.1. Metal-organic framework (MOF) as the precursor	11

1.7.2. Zeolitic imidazolate framework as the precursor of the M–N–C@NC catalyst	11
1.8. Catalytic reaction with M–N–C@NC	12
1.9. Importance of amines and amides	14
1.9.1. Importance of amines	14
1.9.2. Importance of amides	16
1.10. Objectives of the thesis	18
1.11. References	20
Chapter-2 Metal-organic framework-derived Co–N–C nanoparticles on N-doped carbon for selective N-alkylation of anilines	26-50
2.1. Introduction	26
2.2. Chemicals	27
2.3. Instruments	28
2.4. Experimental	29
2.4.1 Synthesis of ZIF-67@C	29
2.4.2 Synthesis of Co–N–C@NC	29
2.4.3 Synthesis of Co@C	29
2.5 Results and discussion	30
2.5.1 Characterizations of the catalyst	30
2.6 Optimization of the reaction condition	33
2.7 Scope of different alcohols	35
2.8 Scope of different anilines	36
2.9 Reaction path and mechanism	38
2.10 Recycling of the catalyst	39
2.11 Conclusions	40
2.12 ¹ H NMR and ¹³ C NMR spectra of product	46
2.13 References	48
Chapter-3 Metal-organic framework-derived Co–N–C@NC catalyzed synthesis of benzimidazoles	51-67
3.1. Introduction	51

3.2. Chemicals	52
3.3. Instruments	52
3.4. Experimental	53
3.4.1. Synthesis of ZIF-67	53
3.4.2. Synthesis of Co-N-C@NC	53
3.4.3. Synthesis of Co@C	53
3.5. Results and discussion	53
3.5.1. Characterizations of the catalyst	53
3.6. Optimization of the reaction condition	57
3.7. Scope of alcohols	59
3.8. Reaction mechanism and recyclability	60
3.9 Conclusion	61
3.10. ¹ H NMR and ¹³ C NMR spectra of the product	64
3.11. References	65
Chapter-4 Metal-organic framework-derived Ni-N-C@NC catalyzed amide formation by the reaction of benzaldehyde and amine	68-91
4.1. Introduction	68
4.2. Chemicals	70
4.3. Instruments	70
4.4. Experimental	70
4.4.1. Synthesis of Ni-ZIF-8	70
4.4.2. Synthesis of ZIF-8	70
4.4.3. Synthesis of Ni-N-C@NC	71
4.4.4. Synthesis of NC	71
4.4.5. Synthesis of Ni@C	71
4.5. Results and discussion	71
4.5.1. Characterizations of the catalyst	71
4.6. Optimization of the reaction condition	75
4.7. Scope of aldehydes	77
4.8. Scope of amine	78
4.9. Reaction mechanism of amide bond formation	80

4.10. Conclusions	81
4.11. ¹ H NMR and ¹³ C NMR spectra of the product	87
4.12. References	89
Chapter-5 Metal-organic framework-derived NiO@Ni Mott-Schottky catalyst for amidation reactions	92-113
5.1. Introduction	92
5.2. Chemicals	94
5.3. Instruments	94
5.4. Experimental	94
5.4.1. Synthesis of Ni–Ni CP	94
5.4.2. Synthesis of NiO@Ni from Ni–Ni CP	94
5.4.3. Synthesis of NiO-Ni from Ni(OAc) ₂ ·4H ₂ O	95
5.4.4. Synthesis of Ni@C from Ni–Ni CP	95
5.4.5. General procedure for amide synthesis	95
5.5. Results and discussion	95
5.5.1. Characterizations of the catalyst	96
5.6. Optimization of the reaction condition	99
5.7. Scope of aldehydes	101
5.8. Scope of amine substitution	103
5.9. Reaction mechanism and recyclability	104
5.10. Conclusions	105
5.11. ¹ H NMR and ¹³ C NMR spectra of the product	109
5.12. References	111
Chapter-6 Summary and Future Prospective	114-116
6.1 Summary and Conclusions	114
6.2 Future scope and perspective	116
List of publications	117