METAL-ORGANIC FRAMEWORKS SUPPORTED SINGLE-SITE BASE-METAL CATALYSTS FOR ORGANIC TRANSFORMATIONS

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by

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Dedicated to my beloved Parents &
Grandparents

CERTIFICATE

This is to certify that the thesis entitled, **"Metal-Organic Frameworks Supported Single-Site Base-Metal Catalysts for Organic Transformations"**, being submitted by **Ms. Rajashree Newar** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry is a record of bonafide research work carried out by her. Ms. Rajashree Newar worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

The thesis entitled, “Metal-Organic Frameworks Supported Single-site Base-metal Catalysts for Organic Transformations” deals with the development and characterization of robust single-site solid catalysts based on metal-organic frameworks for carrying out various kind of organic transformation reactions to produce chemically important feedstock for industrially important compounds. Numerous possibilities of designing MOFs based catalyst including metalation with broad range of metals, large pore size and high surface area, and easy synthetic route make MOF advantageous for liquid phase reactions, characteristic of fine chemistry. Targeting the development of real industrial processes based on MOFs, usage of it as a heterogeneous catalyst is still under intense investigation. Considering the added value of fine chemicals and the typical reaction conditions for their production, MOFs appear to be very promising catalysts in this sector. Therefore, my thesis work focuses on synthesis and characterization of single-site solid catalyst based on MOFs and its application towards organic transformation reactions like C-H borylation, asymmetric reactions, CO_2 utilization etc.

The thesis is divided into six chapters.

Chapter I- Introduction

This chapter deals with a brief overview of single-site solid catalyst based on Metal-Organic Frameworks. It also includes survey of literature highlighting recent studies on Metal-Organic Frameworks based catalysis with a brief mention of the historical background.

Chapter II- General Experimental Techniques

This chapter describes the source of various chemicals used for this thesis. The experimental procedures for the drying of solvents, purification of reagents and products, handling of air and moisture sensitive compounds are stated. The detailed description regarding the instruments used for the characterization of the catalysts and compounds are furnished. Further, the details about the software used for theoretical studies are mentioned.

Chapter III- Amino Acid-Functionalized Metal-Organic Frameworks for Asymmetric Base-Metal Catalysis.

This chapter deals with designing a chiral metal catalyst based on MOF for sustainable production of chiral active pharmaceutical ingredients by replacing precious and toxic metals and expensive chiral ligands with earth abundant base metals and naturally occurring amino

acids as a chiral source for asymmetric catalysis. The grafting of amino acids within the pores of a metal-organic framework (MOF), followed by post-synthetic metalation with iron precursor afforded highly active and enantioselective catalysts. The catalytic efficiency of the synthesized catalyst was explored in asymmetric hydrosilylation and hydroboration of carbonyl compounds. Moreover, based on certain spectroscopic and computational studies, a catalytic cycle for asymmetric hydrosilylation of unsymmetric ketone was proposed.

Chapter IV- Mono-Phosphine Metal-Organic Framework-Supported Cobalt Catalyst for Efficient Borylation Reactions.

The synthesis and characterization of a metal-organic frameworks (MOFs) supported monoligated phosphine-cobalt complex has been reported, which is an active heterogeneous catalyst for aromatic C-H borylation and alkene hydroboration reactions us discussed in this chapter. The synthetic procedure for producing mono(phosphine)-Co catalyst (MOF-P-Co), which is the active catalyst for the catalysis reactions was stated, which was done via post synthetic metalation of the porous triarylphosphine-functionalized MOF (MOF-P) with $CoCl_2$ followed by treatment with $NaEt_3BH$. The catalytic properties and the reaction mechanism of MOF-P in C-H borylation reaction was studied and a catalytic cycle was proposed using spectroscopic and computational studies.

Chapter V- Single-site Cobalt-Catalyst Ligated with Pyridylimine-Functionalized Metal-Organic Framework (MOF) for Arene and Benzylic Borylation.

This chapter includes the synthesis and characterization of highly active single-site heterogeneous cobalt-catalyst, based on a porous and robust redox non-innocent ligated pyridylimine functionalized metal−organic frameworks (pyrim-MOF). The synthetic route of pyrim-MOF was discussed. Moreover, the catalytic activity of the pyrim-MOF was studied in chemoselective dehydrogenative borylation of C–H bonds of various activated as well as unactivated arenes and heterocyclic compounds using B_2pin_2 or HBpin (pin = pinacolate) as the borylating agent. Based on theoretical and spectroscopic evidence, a catalytic cycle for C-H borylation reaction was proposed.

Chapter VI- Metal-Organic Framework Supported Single-Site Cobalt Catalyzed *N*-Formylation of Amines utilizing CO_2 as a C1 source.

In this chapter, the development of single site, robust and chemoselective earth-abundant cobalt(II) hydride metal catalyst based on porous Aluminum Metal–Organic Frameworks (MOFs) (DUT-5) is studied for *N*-formylation of amines in different reaction conditions. The preparation of active cobalt catalyst (DUT-5-CoH) by post-synthetic metalation of the secondary building units (SBUs) of DUT-5 with $CoCl_2$ followed by the reaction with $NaEt_3BH$ is mentioned. The catalytic efficiency of MOFs in the formation of *N*-formaldehyde products from various alkyl amines and substituted benzylamines in mild condition, using CO_2 as a C1 source was investigated. Furthermore, the catalytic cycle for *N*-formylation of amines were proposed based on computational studies.

सारांश

थीसिस शीर्षक, "धातु-कार्बनिक ढांचे के आधार पर मजबूत एकल-साइट ठोस उत्प्रेरक का विकास" औद्योगिक रूप से महत्वपूर्ण यौगिकों के लिए रासायनिक रूप से महत्वपूर्ण कच्चे माल के उत्पादन के लिए विभिन्न प्रकार के कार्बनिक परिवर्तन प्रतिक्रियाओं को पूरा करने के लिए धातु-कार्बनिक ढांचे के आधार पर मजबूत एकल-साइट ठोस उत्प्रेरक के विकास और लक्षण वर्णन से संबंधित है। धातुओं की विस्तृत श्रृंखला, बड़े छिद्र आकार और उच्च सतह क्षेत्र, और आसान सिंथेटिक मार्ग के साथ एमओएफ आधारित उत्प्रेरक को डिजाइन करने की कई संभावनाएं एमओएफ को तरल चरण प्रतिक्रियाओं, ठीक रसायन की विशेषता के लिए फायदेमंद बनाती हैं। एमओएफ के आधार पर वास्तविक औद्योगिक प्रक्रियाओं के विकास को लक्षित करना, एक विषम उत्प्रेरक के रूप में इसका उपयोग अभी भी गहन जांच के अधीन है। महीन रसायनों के अतिरिक्त मूल्य और उनके उत्पादन के लिए विशिष्ट प्रतिक्रिया स्थितियों को ध्यान में रखते हुए, एमओएफ इस क्षेत्र में बहुत आशाजनक उत्प्रेरक प्रतीत होते हैं। इसलिए, मेरी थीसिस एमओएफ पर आधारित एकल-साइट ठोस उत्प्रेरक के संश्लेषण और लक्षण वर्णन पर केंद्रित है और C-H बोरिलेशन, असममित प्रतिक्रियाओं, CO_2 उपयोग आदि जैसे कार्बनिक परिवर्तन प्रतिक्रियाओं के लिए इसका अनुप्रयोग है।

अध्याय I- परिचय

यह अध्याय धातु-कार्बनिक ढांचे पर आधारित एकल-साइट ठोस उत्प्रेरक के संक्षिप्त अवलोकन से संबंधित है। इसमें ऐतिहासिक पृष्ठभूमि के संक्षिप्त उल्लेख के साथ धातु-कार्बनिक ढांचे आधारित उत्प्रेरण पर हाल के अध्ययनों पर प्रकाश डालने वाले साहित्य का सर्वेक्षण भी शामिल है।

अध्याय II- सामान्य प्रायोगिक तकनीक

इस अध्याय में इस थीसिस के लिए प्रयुक्त विभिन्न रसायनों के स्रोत का वर्णन किया गया है। विलायकों के सुखाने, अभिकर्मकों और उत्पादों के शुद्धिकरण, हवा और नमी संवेदनशील यौगिकों के संचालन के लिए प्रयोगात्मक प्रक्रियाओं को बताया गया है। उत्प्रेरकों और यौगिकों की विशेषता के लिए उपयोग किए जाने वाले उपकरणों के बारे में विस्तृत विवरण प्रस्तुत किया गया है। इसके अलावा, सैद्धांतिक अध्ययन के लिए उपयोग किए जाने वाले क्रमानुदेश के बारे में विवरण का उल्लेख किया गया है।

अध्याय III-असममित क्षारीय धातु उत्प्रेरण के लिए अमीनो अम्ल कार्यात्मक धातु-कार्बनिक ढांचे।

यह अध्याय कीमती और जहरीली धातुओं और महंगे काईरल लिगैंड्स के साथ पृथ्वी पर प्रचुर मात्रा में उपलब्ध क्षारीय धातुओं और असममित उत्प्रेरण के लिए काईरल स्रोत के रूप में प्राकृतिक रूप से पाए जाने वाले अमीनो अम्ल को बदलकर कमोडिटी और महीन रसायनों के स्थायी उत्पादन के लिए एमओएफ पर आधारित एक काईरल धातु उत्प्रेरक को डिजाइन करने से संबंधित है। धातु-कार्बनिक ढांचे (एमओएफ) के छिद्रों के भीतर अमीनो अम्ल का ग्राफ्टिंग, इसके बाद लोहे के

अग्रदूत के साथ सिंथेटिक धातुकरण के बाद अत्यधिक सक्रिय और एनैन्सियोसेलेक्टिव उत्प्रेरक का वहन किया जाता है। संश्लेषित उत्प्रेरक की उत्प्रेरक दक्षता असममित हाइड्रोसिलिलेशन और कार्बोनिल यौगिकों के हाइड्रोबोरेशन में खोजी गई थी। इसके अलावा, कुछ स्पेक्ट्रोस्कोपिक और संगणकीय अध्ययनों के आधार पर, असममित कीटोन के असममित हाइड्रोसिलिलेशन के लिए एक उत्प्रेरक चक्र प्रस्तावित किया गया था।

अध्याय IV- कुशल बोरिलेशन प्रतिक्रियाओं के लिए मोनो-फॉस्फीन धातु-कार्बनिक ढांचे-समर्थित कोबाल्ट उत्प्रेरक।

धातु-कार्बनिक ढांचे (एमओएफ) समर्थित मोनोलिगेटेड फॉस्फीन-कोबाल्ट कॉम्प्लेक्स के संश्लेषण और लक्षण वर्णन की सूचना दी गई है, जो सुगंधित **C-H** बोरिलेशन और एल्केन हाइड्रोबोरेशन प्रतिक्रियाओं के लिए एक सक्रिय विषम उत्प्रेरक है कि इस अध्याय में चर्चा की गई है। मोनो (फॉस्फीन)-सह उत्प्रेरक (MOF-P-Co) के उत्पादन के लिए सिंथेटिक प्रक्रिया, जो कि उत्प्रेरण प्रतिक्रियाओं के लिए सक्रिय उत्प्रेरक है, को बताया गया था, जो झरझरा ट्राईरिलफॉस्फीन-कार्यात्मक MOF (MOF-P) के $CoCl_2$ के साथ $NaEt_3BH$ के साथ उपचार के बाद सिंथेटिक धातुकरण किया गया था। C-H बोरिलेशन प्रतिक्रिया में MOF-P के उत्प्रेरक गुणों और प्रतिक्रिया तंत्र का अध्ययन किया गया था और स्पेक्ट्रोस्कोपिक और संगणकीय अध्ययनों का उपयोग करके एक उत्प्रेरक चक्र का प्रस्ताव किया गया था।

अध्याय V- एरेन और बेंजाइलिक बोरिलेशन के लिए एकल-साइट कोबाल्ट-उत्प्रेरक पाइरिडीलिमाइन-कार्यात्मक धातु-कार्बनिक ढांचे (एमओएफ) के साथ जुड़ा हुआ है।

इस अध्याय में अत्यधिक सक्रिय एकल-साइट विषम कोबाल्ट-उत्प्रेरक का संश्लेषण और लक्षण वर्णन शामिल है, जो एक झरझरा और मजबूत रेडॉक्स नॉन-इनोसेंट लिगेटेड पाइरिडीलिमाइन कार्यात्मक धातु-कार्बनिक ढांचे (पाइरीम-एमओएफ) पर आधारित है। पिरिम-एमओएफ के संश्लेषण मार्ग पर चर्चा की गई। इसके अलावा, पाइरीम-एमओएफ की उत्प्रेरक गतिविधि का अध्ययन बोरीलेटिंग एजेंट के रूप में B_2pin_2 or HBpin (pin = pinacolate) का उपयोग करते हुए विभिन्न सक्रिय के साथ-साथ गैर-सक्रिय डेरेन्स और हेट्रोसायक्लिक यौगिकों के C-H बांडों के इनकेमोसेलेक्टिव डीहाइड्रोजनेटिव बोराइलेशन का अध्ययन किया गया था। सैद्धांतिक और स्पेक्ट्रोस्कोपिक साक्ष्य के आधार पर, C-H बोरिलेशन प्रतिक्रिया के लिए एक उत्प्रेरक चक्र प्रस्तावित किया गया था।

अध्याय VI- C1 स्रोत के रूप में CO_2 का उपयोग कर धातु-कार्बनिक ढांचे समर्थित सिंगल-साइट कोबाल्ट उत्प्रेरित एमाइन का N-फॉर्माइलेशन।

इस अध्याय में, मजबूत और झरझरा एल्यूमीनियम धातु-कार्बनिक ढांचे (एमओएफ) (डीयूटी -5) पर आधारित केमोसेलेक्टिव और विजातीय, पृथ्वी पर प्रचुर मात्रा में उपस्थित एकल-साइट कोबाल्ट **(II)** हाइड्राइड धातु उत्प्रेरक के विकास का अध्ययन किया गया है। विभिन्न प्रतिक्रिया स्थितियों में **$CoCl_2$** के साथ **DUT-5** की सेकेंडरी बिल्डिंग यूनिट्स **(SBUs)** के पोस्ट सिंथेटिक मेटलेशन द्वारा सक्रिय कोबाल्ट उत्प्रेरक (**DUT-5-CoH)** की तैयारी के बाद

$NaEt_3BH$ के साथ प्रतिक्रिया का उल्लेख किया गया है। विभिन्न एल्काइल एमाइनों से एन-फॉर्मेल्डिहाइड उत्पादों के निर्माण में एमओएफ की उत्प्रेरक दक्षता और हल्के स्थिति में प्रतिस्थापित बेंज़िलमाइन को सी 1 स्रोत के रूप में **CO_2** का उपयोग करके जांच की गई थी। इसके अलावा, एमाइन के एन-फॉर्माइलेशन के लिए उत्प्रेरक चक्र संगणकीय के आधार पर प्रस्तावित किया गया था।

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SBU	secondary building unit	TON	turnover number
TOF	turnover frequency	*tert*	tertiary
MOF	metal-organic framework	1-D	1-dimensional
2-D	2-dimensional	3-D	3-dimensional
4-D	4-dimensional	%	percentage
h	hour	bpy	bipyridine
HT	High-Throughput	˚	degree
ZIF	zeolitic imidazole frameworks	CO_2	carbon dioxide
˚C	degree centigrade	CO	carbon monoxide
BDC	benzene dicarboxylate	H_2	dihydrogen
BPDC	biphenyl dicarboxylate	INT	intermediate
TPDC	terphenyl dicarboxylate	*sec*	secondary
PSM	post-synthetic modification	THF	Tetrahydrofuran
B2pin2	pinacol diborane	HBpin	pinacolborane
DEF	N,N'-diethylformamide	o:m:p	ortho:meta:para
Fmoc	Fluorenylmethyloxycarbonyl	m:p	meta:para
HBTU	N,N,N′,N′-Tetramethyl-O-	*p*-cymene	*para*-cymene
	(1H-benzotriazol-1-yl)uronium	*m*-xylene	*meta*-xylene
	hexafluorophosphate,	*p*-xylene	*para*-xylene
	O-(Benzotriazol-1-yl)-	*o*-xylene	*ortho*-xylene
	N,N,N′,N′-tetramethyluronium	g	gram
	Hexafluorophosphate	M	mole
DMF	N,N′-dimethylformamide	TS	transition state

boc	*tert*-butoxycarbonyl	err.	error
DIEA	diisopropylethylamine	µL	microlitre
HOBt	Hydroxybenzotriazole	EtOAc	ethylacetate
TFA	Trifluoroacetic acid	mL	milli litre
ee	enantiomeric excess	mmol	milli mole
DMSO	dimethyl sulfoxide	Anal.	ananlysis
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl	Calcd	calculated
		$M{\cdot}s^{-1}$	Mole per second
DPEN	1,2-diphenylethylenediamine	eV	electron volt
MIL	Matériaux de l′Institut Lavoisier	μM	micro molar
UiO	Universitetet i Oslo	R_f	Retention factor
DUT	Dresden University of Technology	*p*-methoxy	*para*-methoxy
		Temp	temperature
HRMS	high-resolution mass spectrometry	RB	Round bottom
		eq.	equivalent
GOF	Goodness of fit	Å	angstrom
DSC	Dichroic Spectral Combiner	*J*	coupling constant
XPS	X-ray photoelectron spectroscopy	Inj.	Injection
		Det.	Detector
ICP-OES	Inductively Coupled Plasma Optical Emission spectroscopy	d	doublet
		MHz	megahertz
BET	Brunauer−Emmett−Teller	Hz	hertz
TGA	Thermogravimetric analysis	m	multiplet
FID	flame ionization detector	t	triplet

HPLC	high-performance liquid Chromatography	s	singlet
		q	quartet
m^2/g	meter per Square gram	dd	double doublet
MLCT	metal-to-ligand charge-transfer	IR	infra red
CIF	crystallographic information file	K	Kelvin
XANES	X-ray absorption near edge Structure	Kcal	kilocalorie
		bs	broad singlet
EXAFS	extended X-ray absorption fine structure	dt	double triplet
		sex	sextet
m/z	mass-to-charge ratio	quin	quintet
NMR	nuclear magnetic resonance	Et	ethyl
COD	cyclooctadiene	mg	milligram
Cp	cyclopentadienyl	min.	minute
DCM	dichloromethane	Me	methyl
DFT	density functional theory	λ (lambda)	wave length
PCM	Polarizable Continuum Model	Ph	phenyl
IEFPCM	integral equation formalism Variant	ppm	parts per million
		rt	room temperature
NBO	natural bond orbital	*t*-Bu	tertiary-butyl
GC	Gas chromatography	*n*-Bu	normal-butyl
ESI-MS	electrospray ionisation mass spectrometry	TMS	trimethylsilyl
		UV	ultra violet
PXRD	powder X-ray diffraction	Vis	visible
MS	Mass spectrometry	ΔH	change in enthalpy

ΔG	change in free energy	δ (delta)	chemical shift
ORTEP	Oak Ridge Thermal Ellipsoid Plot	e.g	For example
		aq.	aqueous
Sol.	solution		