

**DEVELOPMENT OF HETEROGENEOUS EARTH-ABUNDANT
METAL CATALYSTS FOR CHEMOSELECTIVE
FUNCTIONALIZATION OF METHANE AND OTHER
HYDROCARBONS**

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Development of Heterogeneous Earth-Abundant Metal Catalysts for Chemoselective Functionalization of Methane and Other Hydrocarbons

by

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Submitted

In fulfillment of the requirements of the degree of

Doctor of Philosophy

to the



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***Dedicated to my Parents and
Family***

Certificate

This is to certify that the thesis entitled “**Development of Heterogeneous Earth-Abundant Metal Catalysts for Chemoselective Functionalization of Methane and Other Hydrocarbons** ” being submitted by Wahida Begum (Entry No.: 2019CYZ8149) to Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy, is a record of bonafide research work carried out by her. Wahida Begum has worked under my supervision and has fulfilled all the requirements for the submission of her PhD thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of PhD degree. The results embodied in this thesis has 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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Place: New Delhi

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Abstract

This thesis entitled “Development of Heterogeneous Earth-Abundant Metal Catalysts for Chemoselective Functionalization of Methane and Other Hydrocarbons” presents the use of MOFs by fabricating them into suitable catalysts for the chemoselective functionalization of various hydrocarbons such as methane, benzene and others using earth-abundant metal catalysts. The transformations involve methane oxidation into ethanol, arene and alkene borylations, nitrile reductions, etc. The thesis comprises of six chapters.

Chapter I: Introduction.

This chapter offers a summary of metal-organic frameworks (MOFs), their characteristics and various applications including their functioning as single-site catalysts. It primarily delves into the literature works concerning the utilization of MOFs as catalytic platforms and underscores their development as heterogeneous catalysts for producing fine chemicals.

Chapter II: General Experimental Techniques.

This chapter presents an overview of the chemicals utilized in the research. The section includes the experimental processes applied to purify reagents and products, as well as the protocols for solvent drying and handling air- and moisture-sensitive compounds. Detailed information is provided on the instrumental techniques employed for characterizing catalysts and compounds, including specifics on sample preparation. Additionally, the chapter also consists of the details of the software employed in theoretical studies.

Chapter III: Mixed Ce/Zr-MOF Node Supported Single-site Ni Catalyst for Selective Methane Oxidation into Ethanol.

Ethanol is a versatile substance that plays a significant role in various industries as both a commodity and a raw material. As a raw material, ethanol is used in the production of a wide range of chemicals, including pharmaceuticals, polishes, paints, cosmetics, and as a liquid fuel. The primary source of ethanol production is through the fermentation of crops such as sugarcane, corn, wheat, etc. However, as the demand for ethanol is growing day by day, the use of crops for ethanol production has raised concerns about food security due to the potential competition between food and fuel production for land and resources. As an alternative, methane can be a very good feedstock for ethanol synthesis because of its abundance and low cost. Moreover, methane is the second most abundant greenhouse gas in the atmosphere. One-step methane oxidation into ethanol may serve as a promising way of dealing with the problem of food security

as well as environmental issues. Many researchers have developed homogenous as well as heterogeneous catalysts for direct methane to ethanol oxidation but these catalysts have suffered from poor productivity and selectivity. Further research is needed to improve the production of ethanol from methane oxidation through refinement of catalyst design.

In this chapter, we report the synthesis and characterization of a mononuclear nickel (II)-hydroxyl species supported by Ce-doped Zr-MOF nodes ($\text{Ce}_x/\text{Zr}_y\text{-UiO-Ni(OH)}$) which enables the direct conversion of methane to ethanol using H_2O_2 as the oxidant. This chapter also highlights the optimization of the reaction conditions.

Chapter IV: Mechanistic Investigation for Methane Oxidation to Ethanol by Mixed Ce/Zr-MOF Supported Ni Catalyst.

This work emphasizes the critical role of node composition, Ni-Ce synergy, and active-site isolation within porous MOFs for efficient and selective methane-to-ethanol transformation. Spectroscopic and control experiments have unveiled that the synergetic Ni-Ce sites facilitate the easy activation of methane's C–H bonds at 80 °C thereby, triggering the generation of $\bullet\text{CH}_3$ radicals, which then undergo a highly efficient transformation into ethanol, with an excellent yield of $6521 \text{ mmol g}_{\text{Ni}}^{-1}$ with over 93% selectivity. Mechanistic investigations indicate that the incorporation of Ce^{+4} ions into the MOF's nodes, along with the proximity between Ce^{+4} and Ni^{+2} ions, facilitates reversible dissociation of the $\text{Ce-O}_{\text{carboxylate}}$ bond and formation of the Ni- $(\mu_2\text{-OH})\text{-Ce}$ bond. This step is crucial in initiating the catalytic cycle for producing $\bullet\text{CH}_3$, which has been characterized by performing electron paramagnetic resonance (EPR) experiments with 5,5'-dimethyl-1-pyrroline-N-oxide (DMPO) as a radical trapping agent. Computational studies have also been conducted to investigate the catalytic cycle and the turnover limiting step (TLS).

Chapter V: Cobalt Catalyst Supported by Mono-Phosphine Metal-Organic Frameworks for Highly Effective Borylation Reactions.

Phosphine ligands have always been of utmost importance in the production of many transition metal catalysts due to their distinctive property of enabling convenient adjustment of electronic effect without experiencing significant change in steric effects. In particular, mono-phosphine ligands are easy to use because of their flexible structures and excellent catalytical activity. The synthesis of monoligated phosphine base metal complexes is challenging because of their tendency to undergo ligand exchange reactions. The site-isolation in metal-organic frameworks (MOFs) could be employed to prevent such ligand exchange reactions.

In this chapter, we present a monoligated phosphine-cobalt complex supported by a MOF that is an active heterogeneous catalyst for aromatic C-H borylation and alkene hydroboration. The metalation of a porous triarylphosphine-functionalized MOF (MOF-P) with CoCl_2 was followed by activation with NaEt_3BH to synthesize the mono(phosphine)-Co catalyst (MOF-P-Co). The arene- and alkyl-boronate esters can be produced with good yields and selectivity using the MOF catalyst's broad substrate scope and excellent functional group tolerance. In arene C-H borylation, MOF-P-Co provided a TON of 30,000 and could be recycled and utilised at least 13 times. Importantly, the attempt to prepare the homogeneous control ($\text{Ph}_3\text{P-Co}$) using triphenylphosphine was unsuccessful due to the facile disproportionation reactions or intermolecular ligand exchanges in the solution. In contrast, the site isolation of the active mono(phosphine)-Co species within the MOF affords robust and coordinatively unsaturated metal complexes, allowing us to explore their catalytic properties and the reaction mechanism.

Chapter VI: Metal-Organic Framework Supported Bipyridyl-Ni(II) Hydride Catalyst for Chemoselective hydrogenation of aromatic nitriles.

Primary amines play pivotal roles as intermediates in the production of fine chemicals, pharmaceuticals, agrochemicals, and industrial materials. In recent times, several new catalytic techniques have been developed to produce primary amines. These methods include the hydrogenation of nitriles, amide hydrogenation, aryl halide amination, carbonyl compound reduction amination, and direct alcohol amination. Among these, the hydrogenation of nitriles is particularly noteworthy due to its cost-effectiveness, availability of nitriles, and atom-economic nature. However, the selectivity of the reaction has been strongly decreased due to the formation of by-products. For the transformation of nitriles into primary amines, various reducing agents such as LiAlH_4 , ammonia borane, etc. have been employed in recent years. Nonetheless, employing these reducing agents resulted in poor selectivity and produced a substantial amount of waste, posing challenges for effective treatment. Hydrogen (H_2) is a preferable reducing agent due to its theoretical atom efficiency of 100%.

In this chapter, we represent the development and characterization of a UiO-metal-organic framework (MOF)-supported bipyridyl-Ni(II) hydride catalyst (bpy-UiO-NiH₂), and its application in catalytic hydrogenation of aromatic nitriles into primary amines in the presence of H_2 as the reducing agent under mild conditions. bpy-UiO-NiH₂ has shown excellent recyclability for many runs. Spectroscopic and control experiments were done to study the mechanistic pathway.

सारांश

इस थीसिस का शीर्षक है "मीथेन और अन्य हाइड्रोकार्बन के केमोसिलेक्टिव फंक्शनलाइजेशन के लिए विषम पृथ्वी-प्रचुर धातु उत्प्रेरकों का विकास" पृथ्वी-प्रचुर धातु उत्प्रेरकों का उपयोग करके मीथेन, बेंजीन और अन्य जैसे विभिन्न हाइड्रोकार्बन के केमोसिलेक्टिव फंक्शनलाइजेशन के लिए उपयुक्त उत्प्रेरकों में उन्हें तैयार करके **MOFs** का उपयोग प्रस्तुत करता है। रूपांतरण में इथेनॉल, एरीन और एल्केन बोरिलेशन, नाइट्राइल रिडक्शन आदि में मीथेन ऑक्सीकरण शामिल है। थीसिस में छह अध्याय शामिल हैं।

अध्याय 1: परिचय.

यह अध्याय धातु-कार्बनिक ढाँचों (**MOFs**), उनकी विशेषताओं और एकल-साइट उत्प्रेरक के रूप में उनके कामकाज सहित विभिन्न अनुप्रयोगों का सारांश प्रस्तुत करता है। यह मुख्य रूप से उत्प्रेरक प्लेटफॉर्म के रूप में **MOFs** के उपयोग से संबंधित साहित्य कार्यों में गहराई से उतरता है और बढ़िया रसायनों के उत्पादन के लिए विषम उत्प्रेरक के रूप में उनके विकास को रेखांकित करता है।

अध्याय II: सामान्य प्रयोगात्मक तकनीकें।

यह अध्याय शोध में उपयोग किए गए रसायनों का अवलोकन प्रस्तुत करता है। इस खंड में अभिकर्मकों और उत्पादों को शुद्ध करने के लिए लागू की गई प्रायोगिक प्रक्रियाएँ, साथ ही विलायक सुखाने और वायु- और नमी-संवेदनशील यौगिकों को संभालने के प्रोटोकॉल शामिल हैं। उत्प्रेरकों और यौगिकों की विशेषता के लिए उपयोग की जाने वाली वाद्य तकनीकों पर विस्तृत जानकारी प्रदान की गई है, जिसमें नमूना तैयार करने के बारे में विवरण शामिल हैं। इसके अतिरिक्त, इस अध्याय में सैद्धांतिक अध्ययनों में उपयोग किए जाने वाले सॉफ्टवेयर का विवरण भी शामिल है।

अध्याय III: इथेनॉल में चयनात्मक मीथेन ऑक्सीकरण के लिए मिश्रित Ce/Zr-MOF नोड समर्थित एकल-साइट Ni उत्प्रेरक।

इथेनॉल एक बहुमुखी पदार्थ है जो विभिन्न उद्योगों में कमोडिटी और कच्चे माल दोनों के रूप में महत्वपूर्ण भूमिका निभाता है। कच्चे माल के रूप में, इथेनॉल का उपयोग फार्मास्यूटिकल्स, पॉलिश, पेंट, सौंदर्य प्रसाधन और तरल ईंधन सहित कई प्रकार के रसायनों के उत्पादन में किया जाता है। इथेनॉल उत्पादन का प्राथमिक स्रोत गन्ना, मक्का, गेहूं आदि जैसी फसलों के किण्वन के माध्यम से होता है। हालाँकि, जैसे-जैसे इथेनॉल की माँग दिन-प्रतिदिन बढ़ रही है, इथेनॉल उत्पादन के लिए फसलों के उपयोग ने भूमि और संसाधनों के लिए खाद्य और ईंधन उत्पादन के बीच संभावित प्रतिस्पर्धा के कारण खाद्य सुरक्षा के बारे में चिंताएँ बढ़ा दी हैं। एक विकल्प के रूप में, मीथेन अपनी प्रचुरता और कम लागत के कारण इथेनॉल संश्लेषण के लिए एक बहुत अच्छा फीडस्टॉक हो सकता है। इसके अलावा, मीथेन वायुमंडल में दूसरी सबसे प्रचुर ग्रीनहाउस गैस है। इथेनॉल में एक-चरण मीथेन ऑक्सीकरण खाद्य सुरक्षा की समस्या के साथ-साथ पर्यावरणीय मुद्दों से निपटने का एक आशाजनक तरीका हो सकता है। कई शोधकर्ताओं ने मीथेन से इथेनॉल ऑक्सीकरण के लिए समरूप और विषम उत्प्रेरक विकसित किए हैं, लेकिन ये उत्प्रेरक खराब उत्पादकता और चयनात्मकता से ग्रस्त हैं। उत्प्रेरक डिजाइन के परिशोधन के माध्यम से मीथेन ऑक्सीकरण से इथेनॉल के उत्पादन में सुधार के लिए आगे के शोध की आवश्यकता है। इस अध्याय में, हम Ce-doped Zr-MOF नोड्स (Ce_x/Zr_{1-x} -UiO-Ni(OH)) द्वारा समर्थित एक मोनोन्यूक्लियर निकल (II)-हाइड्रॉक्सिल प्रजाति के संश्लेषण और लक्षण वर्णन की रिपोर्ट करते हैं जो ऑक्सीडेंट के रूप में H_2O_2 का उपयोग करके मीथेन को इथेनॉल में सीधे रूपांतरण करने में सक्षम बनाता है। यह अध्याय प्रतिक्रिया स्थितियों के अनुकूलन पर भी प्रकाश डालता है।

अध्याय IV: मिश्रित Ce/Zr-MOF समर्थित Ni उत्प्रेरक द्वारा इथेनॉल में मीथेन ऑक्सीकरण के लिए यांत्रिक जांच।

यह कार्य कुशल और चयनात्मक मीथेन-से-इथेनॉल परिवर्तन के लिए छिद्रपूर्ण MOFs के भीतर नोड संरचना, Ni-Ce तालमेल और सक्रिय-साइट अलगाव की महत्वपूर्ण भूमिका पर जोर देता है।

स्पेक्ट्रोस्कोपिक और नियंत्रण प्रयोगों ने खुलासा किया है कि सहक्रियात्मक Ni-Ce साइटें 80 °C पर मीथेन के C-H बॉन्ड को आसानी से सक्रिय करने में मदद करती हैं, जिससे •CH₃ रेडिकल्स की पीढ़ी शुरू होती है, जो तब 93% से अधिक चयनात्मकता के साथ 6521 mmol/gNi-1 की उत्कृष्ट उपज के साथ इथेनॉल में अत्यधिक कुशल परिवर्तन से गुजरती हैं। यांत्रिक जांच से पता चलता है कि Ce⁺⁴ आयनों को MOF के नोड्स में शामिल करने के साथ-साथ Ce⁺⁴ और Ni⁺² आयनों के बीच निकटता, Ce-Oकार्बोक्सिलेट बॉन्ड के प्रतिवर्ती पृथक्करण और Ni-(μ₂-OH)-Ce बॉन्ड के निर्माण की सुविधा प्रदान करती है। यह चरण •CH₃ के उत्पादन के लिए उत्प्रेरक चक्र को आरंभ करने में महत्वपूर्ण है, जिसे रेडिकल ट्रैपिंग एजेंट के रूप में 5,5'-डाइमिथाइल-1-पाइरोलाइन-एन-ऑक्साइड (DMPO) के साथ इलेक्ट्रॉन पैरामैग्नेटिक रेजोनेंस (EPR) प्रयोगों को निष्पादित करके चिह्नित किया गया है। उत्प्रेरक चक्र और टर्नओवर सीमित चरण (TLS) की जांच करने के लिए कम्प्यूटेशनल अध्ययन भी किए गए हैं।

अध्याय V: अत्यधिक प्रभावी बोरिलीकरण अभिक्रियाओं के लिए मोनो-फॉस्फीन धातु-कार्बनिक ढांचे द्वारा समर्थित कोबाल्ट उत्प्रेरक।

स्थैतिक प्रभावों में महत्वपूर्ण परिवर्तन का अनुभव किए बिना इलेक्ट्रॉनिक प्रभाव के सुविधाजनक समायोजन को सक्षम करने की उनकी विशिष्ट संपत्ति के कारण फॉस्फीन लिगेंड हमेशा कई संक्रमण धातु उत्प्रेरकों के उत्पादन में अत्यंत महत्वपूर्ण रहे हैं। विशेष रूप से, मोनो-फॉस्फीन लिगेंड अपनी लचीली संरचनाओं और उत्कृष्ट उत्प्रेरक गतिविधि के कारण उपयोग में आसान हैं। लिगेंड विनिमय अभिक्रियाओं से गुजरने की उनकी प्रवृत्ति के कारण मोनोलिगेटेड फॉस्फीन बेस मेटल कॉम्प्लेक्स का संश्लेषण चुनौतीपूर्ण है। धातु-कार्बनिक ढांचे (MOF) में साइट-अलगाव को ऐसे लिगेंड विनिमय अभिक्रियाओं को रोकने के लिए नियोजित किया जा सकता है।

इस अध्याय में, हम एक MOF द्वारा समर्थित एक मोनोलिगेटेड फॉस्फीन-कोबाल्ट कॉम्प्लेक्स प्रस्तुत करते हैं जो सुगंधित C-H बोरिलीकरण और एल्केन हाइड्रोबोरेशन के लिए एक सक्रिय विषम उत्प्रेरक है। एक छिद्रयुक्त ट्राइएरिलफॉस्फीन-कार्यात्मक MOF (MOF-P) का CoCl_2 के साथ धातुकरण करने के बाद NaEt_3BH के साथ सक्रियण करके मोनो(फॉस्फीन)-Co उत्प्रेरक (MOF-P-Co) को संश्लेषित किया गया। MOF उत्प्रेरक के व्यापक सबस्ट्रेट स्कोप और उत्कृष्ट कार्यात्मक समूह सहिष्णुता का उपयोग करके एरेन- और एल्काइल-बोरोनेट एस्टर को अच्छी पैदावार और चयनात्मकता के साथ उत्पादित किया जा सकता है। एरेन C-H बोरिलीकरण में, MOF-P-Co ने 30,000 का TON प्रदान किया और इसे कम से कम 13 बार पुनर्चक्रित और उपयोग किया जा सकता है। महत्वपूर्ण रूप से, ट्राइफेनिलफॉस्फीन का उपयोग करके सजातीय नियंत्रण ($\text{Ph}_3\text{P-Co}$) तैयार करने का प्रयास समाधान में आसान अनुपातहीन प्रतिक्रियाओं या अंतर-आणविक लिगेंड एक्सचेंजों के कारण असफल रहा। इसके विपरीत, MOF के भीतर सक्रिय मोनो (फॉस्फीन)-Co प्रजातियों का साइट अलगाव मजबूत और समन्वयात्मक रूप से असंतृप्त धातु परिसरों को प्रदान करता है, जिससे हमें उनके उत्प्रेरक गुणों और प्रतिक्रिया तंत्र का पता लगाने की अनुमति मिलती है।

अध्याय VI: सुगंधित नाइट्राइल के कीमोसेलेक्टिव हाइड्रोजनीकरण के लिए बाइपिरिडाइल-Ni(II) हाइड्राइड उत्प्रेरक द्वारा समर्थित धातु-कार्बनिक ढांचा।

प्राथमिक अमीनों, महीन रसायनों, फार्मास्यूटिकल्स, एग्रीकेमिकल्स और औद्योगिक सामग्रियों के उत्पादन में मध्यवर्ती के रूप में महत्वपूर्ण भूमिका निभाते हैं। हाल के दिनों में, प्राथमिक अमीनों के उत्पादन के लिए कई नई उत्प्रेरक तकनीकें विकसित की गई हैं। इन विधियों में नाइट्राइल का हाइड्रोजनीकरण, एमाइड हाइड्रोजनीकरण, एरिल हैलाइड एमिनेशन, कार्बोनिल यौगिक कमी एमिनेशन और प्रत्यक्ष अल्कोहल एमिनेशन शामिल हैं। इनमें से, नाइट्राइल का हाइड्रोजनीकरण इसकी लागत-प्रभावशीलता, नाइट्राइल की उपलब्धता और परमाणु-आर्थिक प्रकृति के कारण विशेष रूप से उल्लेखनीय है। हालांकि, उप-उत्पादों के निर्माण के कारण प्रतिक्रिया की

चयनात्मकता में भारी कमी आई है। नाइट्राइल्स को प्राथमिक अमीनों में बदलने के लिए हाल के वर्षों में विभिन्न अपचायक एजेंट जैसे LiAlH_4 , अमोनिया बोरेन, आदि का उपयोग किया गया है। बहरहाल, इन अपचायक एजेंटों के उपयोग से खराब चयनात्मकता हुई और काफी मात्रा में अपशिष्ट उत्पन्न हुआ, जिससे प्रभावी उपचार के लिए चुनौतियां उत्पन्न हुईं। हाइड्रोजन (H_2) अपनी सैद्धांतिक परमाणु दक्षता 100% होने के कारण एक बेहतर अपचायक एजेंट है। इस अध्याय में, हम एक UiO-धातु-कार्बनिक फ्रेमवर्क (MOF) समर्थित बाइपिरिडाइल-Ni(II) हाइड्राइड उत्प्रेरक (bpy-UiO-NiH₂) के विकास और लक्षण वर्णन का प्रतिनिधित्व करते हैं, और हल्की परिस्थितियों में अपचायक एजेंट के रूप में H_2 की उपस्थिति में सुगंधित नाइट्राइल्स के प्राथमिक अमीनों में उत्प्रेरक हाइड्रोजनीकरण में इसके अनुप्रयोग का वर्णन करते हैं। bpy-UiO-NiH₂ ने कई बार उत्कृष्ट पुनर्चक्रण क्षमता दिखाई है। यांत्रिक मार्ग का अध्ययन करने के लिए स्पेक्ट्रोस्कोपिक और नियंत्रण प्रयोग किए गए।

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