

Development of Heterogeneous Single-Site Metal Catalysts Using Metal-Organic Frameworks (MOFs) for Upcycling of Methane & Polyolefins

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by

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Submitted

*In fulfilment of the requirements of the degree of
Doctor of Philosophy*

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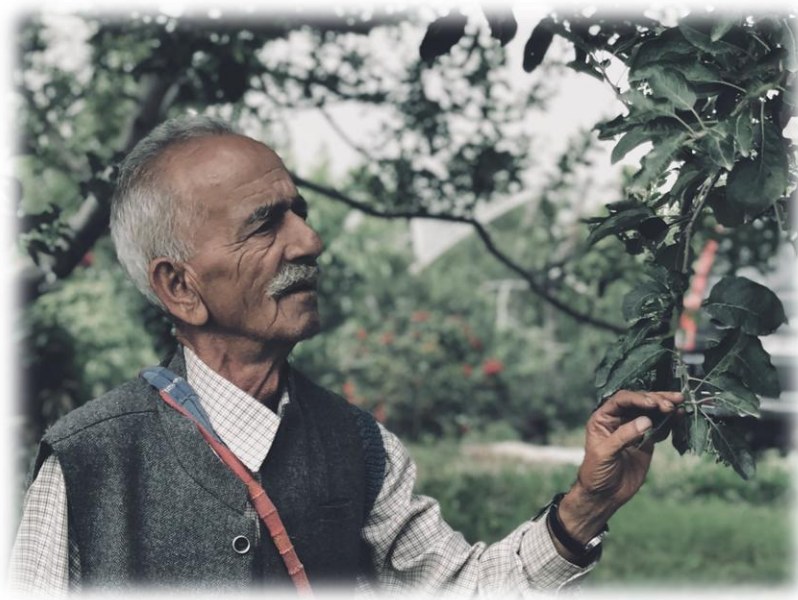


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In Loving Memory *of* My Grandfather



*To my grandfather, **Mr. Bhagat Chand Chauhan** (11 Nov. 1946—23 Aug. 2024),
a teacher who planted seeds of curiosity in every heart he touched.*

*You taught me that learning is not confined to classrooms,
that curiosity is a compass, and that the greatest lessons are woven with love.*

Certificate

This is to certify that the thesis entitled “*Development of Heterogeneous Single-Site Metal Catalysts Using Metal-Organic Frameworks (MOFs) for Upcycling of Methane & Polyolefins*” being submitted by Manav Chauhan (Entry No.: 2020CYZ8051) 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 him. Manav Chauhan has worked under my supervision and has fulfilled all the requirements for the submission of his PhD thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of PhD degree. The work embodied in this thesis has not been submitted, in part or full, to other University or Institute for the award of any degree or diploma.

Date: 18-07-2025

Prof. Kuntal Manna

Place: New Delhi

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Manav Chauhan

Abstract

The catalytic transformation of methane and polyolefins into value-added chemicals represents a frontier in modern chemistry, offering a sustainable pathway to valorize abundant yet recalcitrant feedstocks while mitigating their environmental impacts. Methane (CH₄), the simplest hydrocarbon and a primary constituent of natural gas, possesses exceptionally strong C-H bonds (dissociation energy $\sim 439 \text{ kJ mol}^{-1}$), rendering it chemically inert under ambient conditions. As a potent greenhouse gas with a global warming potential 25 times that of CO₂ over a 100-year horizon, methane is frequently flared or vented during oil and gas extraction due to logistical challenges, squandering its potential as a chemical resource. Concurrently, polyolefins—such as polyethylene (PE) and polypropylene (PP)—dominate plastic waste streams, contributing over 50% of the 300 million tons of plastics produced annually. These polymers feature robust C-C bonds (dissociation energy $\sim 348 \text{ kJ mol}^{-1}$) and lack functional handles, making their selective depolymerization into discrete molecular products a formidable challenge. The selective conversion of these feedstocks into high-value products, including methanol, acetic acid, and liquid hydrocarbons, holds immense promise for reducing greenhouse gas emissions, curbing plastic pollution, and establishing a circular carbon economy.

Achieving such transformations demands catalysts capable of activating inert bonds with precision, operating under mild conditions, and maintaining stability over prolonged cycles. Traditional heterogeneous catalysts, often reliant on noble metals (e.g., Pt, Pd) or harsh conditions ($T > 400 \text{ }^{\circ}\text{C}$, $P > 50 \text{ bar}$), suffer from low selectivity, overoxidation, and rapid deactivation due to sintering or coking. Homogeneous catalysts, while offering molecular-level control, are plagued by separation difficulties and poor recyclability. This thesis addresses these limitations through the development of heterogeneous single-site catalysts supported by Metal-Organic Frameworks (MOFs), a class of crystalline porous materials composed of metal nodes interconnected by organic linkers. MOFs exhibit exceptional properties that revolutionize catalysis: surface areas exceeding $7000 \text{ m}^2 \text{ g}^{-1}$, tunable pore architectures (microporous $< 2 \text{ nm}$ to mesoporous $> 2 \text{ nm}$), and the capacity to anchor isolated metal centers at secondary building units (SBUs). These features generate electrophilic, molecularly dispersed active sites that mimic the precision of enzymatic systems, enabling selective bond activation and steering reaction intermediates toward desired products.

The electronic and steric environments of these active sites can be systematically tailored by varying metal identity, oxidation state, and linker functionality, while pore confinement modulates substrate accessibility and product diffusion, suppressing side reactions. This work leverages these attributes to design MOF-based catalysts that utilize earth-abundant metals (e.g., Co, Cu, Ni, Fe, Ru) and mild oxidants (e.g., H₂O₂, O₂) or hydrogen (H₂) to achieve unprecedented activity, selectivity, and recyclability in methane oxidation and polyolefin hydrogenolysis, respectively. The thesis spans multiple chapters, each dedicated to a specific MOF catalyst engineered for either methane oxidation or polyolefin hydrogenolysis. Through advanced synthetic strategies—such as post-synthetic metalation and reticular chemistry—coupled with rigorous characterization (e.g., XAS, XPS, EPR, NMR) and computational modelling (DFT), this research elucidates the structure-activity relationships and reaction mechanisms underpinning these transformations. The following sections introduce each chapter, highlighting the catalyst design, catalytic performance, and scientific insights:

Chapter 1: Introduction to Metal-Organic Frameworks & Single-Site Catalysts

This chapter introduces the fundamentals of reticular chemistry, which systematically links molecular building blocks via strong, directional bonds to form crystalline, porous metal–organic frameworks (MOFs). It contrasts the predictable mechanisms of organic reactions with the variable nature of metal–ligand coordination, emphasizing the roles of organic linkers and secondary building units (SBUs) in dictating pore size, structural stability, and overall functionality. Key concepts such as modular design and isoreticularity—where variations in linker length allow for precise tuning of pore dimensions while maintaining the original framework topology—are illustrated with examples like MOF-5, HKUST-1, and UiO-66. The chapter also introduces the concept of single-site catalysis, wherein isolated metal atoms are anchored within the robust environment of MOFs. This approach combines the high selectivity and atom efficiency of homogeneous catalysts with the durability and recyclability of heterogeneous systems. Strategies such as intrinsic linker stabilization, post-synthetic modification, and metal node anchoring are briefly discussed as methods to immobilize and stabilize these active sites. Overall, the chapter establishes a comprehensive framework that not only explains the synthesis and structural diversity of MOFs but also sets the stage for their application in advanced catalytic processes. By highlighting both the architectural and

functional versatility of MOFs, it lays the groundwork for exploring next-generation, energy-efficient technologies in gas storage, separation, and sustainable chemical transformations.

Chapter 2: Materials & Methods

This chapter delineates the comprehensive experimental framework and methodologies employed in the synthesis, characterization, and analysis of metal–organic framework (MOF) catalysts. Starting materials, reagents, and solvents were sourced from reputable commercial suppliers, with critical isotope-labeled compounds and specialized ligands procured to ensure precision. Rigorous glassware cleaning, involving sequential solvent rinses, alkaline base baths, and acid neutralization, ensured contamination-free environments. High-pressure reactions, conducted in specialized reactors, incorporated stringent safety measures to mitigate risks associated with explosive gas mixtures, while air- and moisture-sensitive procedures were executed in a nitrogen-purged glovebox. Advanced characterization techniques, including powder X-ray diffraction (PXRD), Brunauer-Emmett-Teller (BET) analysis, Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS), were employed to probe structural, textural, and thermal properties. Elemental composition and surface morphology were assessed via inductively coupled plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), and synchrotron-based X-ray absorption spectroscopy (XAS). Reaction outcomes were analyzed using nuclear magnetic resonance (NMR), gas chromatography (GC), and high-performance liquid chromatography (HPLC), supported by isotope labelling and internal standards. Theoretical insights into catalytic mechanisms were derived from density functional theory (DFT) calculations, incorporating solvent effects and spin-state energetics. Collectively, these protocols ensured robust, reproducible experimental workflows, underpinning the reliability of subsequent catalytic studies.

Chapter 3: Metal-Organic Framework-Encaged Monomeric Cobalt(III)-Hydroperoxides Enable Chemoselective Methane Oxidation to Methanol

The advancement of catalysts capable of mediating the chemoselective oxidation of methane to methanol under mild operational conditions remains a critical challenge in heterogeneous catalysis. Herein, we present the rational design and synthesis of a single-site cobalt-hydroxide

catalyst, Ce-UiO-Co(OH), immobilized on the nodal structures of a cerium-containing metal-organic framework (Ce-UiO-66). This heterogeneous catalyst demonstrates exceptional efficacy in the partial oxidation of methane using hydrogen peroxide at 80°C, achieving a methanol production rate of 2166 mmol g_{cat}⁻¹ with 99% selectivity and a turnover number (TON) of 3250. Comparative analysis reveals that the Ce-UiO-Co system substantially outperforms its isostructural zirconium analogue, Zr-UiO-Co, in both catalytic activity and product selectivity. Integrated experimental and theoretical investigations elucidate the formation of a key Co^{III}(η^2 -hydroperoxide) intermediate, stabilized through coordination with a μ_4 -O⁻ ligand and two carboxylate oxygen atoms derived from the Ce⁴⁺ oxo nodes embedded within the Ce-UiO-66 matrix. The catalytic cycle is governed by a turnover-limiting step involving σ -bond metathesis between the activated cobalt-hydroperoxide species and the C–H bond of methane. Enhanced catalytic efficiency in Ce-UiO-Co is ascribed to the pronounced electron-deficient state of the cobalt center within the Co(η^2 -O₂H) complex, a consequence of electronic modulation by the Ce-UiO support. This electronic configuration significantly reduces the activation energy required for methane C–H bond cleavage, enabling efficient catalytic turnover. The strategic integration of single-metal sites within MOF architectures provides a robust platform for engineering electrophilic catalysts using abundant metals, highlighting their potential for the selective functionalization of inert alkanes and advancing sustainable hydrocarbon conversion technologies.

Chapter 4: Synergetic Ni-Ce Active Sites in Mixed Cerium/Zirconium Metal-Organic Framework Nodes for Selective Methane Oxidation into Ethanol

The catalytic oxidation of methane to ethanol under mild conditions represents a pivotal challenge in sustainable chemistry. This study introduces a heterobimetallic Ce/Zr-UiO metal-organic framework (MOF) functionalized with isolated Ni(II)-hydroxyl species [Ce_x/Zr_y-UiO-Ni(OH)] as a high-performance catalyst for this transformation. The UiO architecture, renowned for its stability, incorporates zirconium to enhance structural integrity and cerium to enable redox flexibility. The Ni²⁺ active sites are uniquely coordinated within the mixed-metal nodes, bonded to a μ_4 -O⁻, a hydroxyl ligand, and two carboxylate oxygen atoms linked to adjacent Ce⁴⁺ ions. Advanced characterization techniques (e.g., X-ray absorption spectroscopy) and density functional theory (DFT) calculations reveal that the synergy between spatially proximate Ni and Ce centers, combined with the confinement of mononuclear Ni species within

the MOF pores, facilitates low-temperature (80°C) methane activation. The catalytic process involves homolytic C–H bond cleavage, generating methyl radicals ($\bullet\text{CH}_3$) that undergo selective C–C coupling within the porous framework to yield ethanol. Remarkably, the catalyst achieves an exceptional productivity of 6521 $\text{mmol}_{\text{ethanol}} \text{g}_{\text{Ni}}^{-1}$ with >93% selectivity. Mechanistic studies highlight a dual catalytic cycle driven by dynamic Ce–O_{carboxylate} bond dissociation and Ni-(μ_2 -OH)-Ce bond formation, enabled by Ce⁴⁺ doping. This reversible structural rearrangement at the node is critical for efficient radical generation and catalytic turnover. The work underscores the potential of mixed-metal MOFs in engineering cooperative active sites for alkane valorization. By leveraging the complementary properties of Ce (redox activity) and Zr (stability), this design strategy offers a pathway to efficient methane conversion at near-ambient temperatures, contrasting energy-intensive industrial processes.

Chapter 5: Selective Methane Oxidation to Acetic Acid using Molecular Oxygen over a Mono-Copper Hydroxyl Catalyst

Acetic acid is an industrially important chemical, produced mainly via carbonylation of methanol using precious metal-based homogeneous catalysts. As a low-cost feedstock, methane is commercially transformed to acetic acid via a multi-step process involving energy-intensive methane steam reforming, methanol synthesis, and subsequently, methanol carbonylation. Here we report a direct single-step conversion of methane to acetic acid using molecular oxygen (O₂) as the oxidant under mild conditions over a mono-copper hydroxyl site confined in a porous cerium metal-organic framework (MOF), Ce-UiO-Cu(OH). The Ce-UiO MOF-supported single-site copper hydroxyl catalyst gave exceptionally high acetic acid productivity of 335 $\text{mmol g}_{\text{cat}}^{-1}$ in 96% selectivity with a Cu TON up to 400 at 115 °C in water. Our spectroscopic and theoretical studies and controlled experiments reveal that the conversion of methane to acetic acid occurs via oxidative carbonylation, where methane is first activated at the copper-hydroxyl site via σ -bond metathesis to give Cu-methyl species followed by carbonylation with in-situ generated carbon monoxide and subsequent hydrolysis by water. This work may guide the rational design of heterogeneous abundant-metal catalysts for the activation and conversion of methane to acetic acid and other valuable chemicals under mild and environment-friendly reaction conditions.

Chapter 6: Tailored Pore-Confined Single-Site Iron(III) Catalyst for Selective CH₄ Oxidation to CH₃OH or CH₃CO₂H Using O₂

Direct oxidation of methane to valuable oxygenates like alcohols and acetic acid under mild conditions poses a significant challenge due to high C–H bond dissociation energy, facile overoxidation to CO and CO₂ and the intricacy of C–H activation/C–C coupling. In this work, we develop a multifunctional iron(III) dihydroxyl catalytic species immobilized within a metal-organic framework (MOF) for selective methane oxidation into methanol or acetic acid at different reaction conditions using O₂. The active-site isolation of monomeric Fe^{III}(OH)₂ species at the MOF nodes, their confinement within the porous framework, and their electron-deficient nature facilitate chemoselective C–H oxidation, yielding methanol or acetic acid with high productivities of 38,592 μmol_{CH₃OH} g_{Fe}⁻¹ h⁻¹ and 81,043 μmol_{CH₃CO₂H} g_{Fe}⁻¹ h⁻¹, respectively. Experiments and theoretical calculations suggest that methanol formation occurs via a Fe^{III}-Fe^I-Fe^{III} catalytic cycle, whereas CH₃CO₂H is produced via hydrocarboxylation of in-situ generated CH₃OH with CO₂ and H₂, and direct CH₄ carboxylation with CO₂.

Chapter 7: Architecting Molecularly Dispersed Cu(I)-Active Sites at UiO-MOF Nodes for Thermocatalytic Oxidation of Methane to Ethanol Using O₂

The direct conversion of methane, a cost-effective C1 feedstock, to ethanol presents a sustainable alternative to crop-based production, but faces challenges due to C–H activation, C–C bond formation, and overoxidation. We report a Cu(I)-catalyst supported by zirconium-based UiO-66 metal-organic frameworks (MOFs) that catalyses methane oxidation to ethanol at 100 °C in water, with 5196 μmol g_{Cu}⁻¹ h⁻¹ productivity and up to 71% selectivity. The Cu(I) species, stabilized by Zr₆-oxo nodes in the MOF, activates O₂ and methane under mild conditions, generating •CH₃ and •OH radicals, which couple to form ethanol via a Cu^I-Cu^{II}-Cu^I cycle. Experimental and computational investigations demonstrate that pore confinement, internal mass-transfer limitations, and radical dynamics regulation are pivotal in maximizing ethanol yield, with pore confinement promoting radical recombination, and restricted mass transfer facilitating diffusion of methane over ethanol to the active sites, thereby mitigating overoxidation. A higher Cu-to-Zr ratio enhances •CH₃ formation, promoting C–C coupling and minimizing byproducts by suppressing overoxidation.

Chapter 8: Isorecticular Metal-Organic Frameworks Confined Mononuclear Ru-Hydrides Enable Highly Efficient Shape-Selective Hydrogenolysis of Polyolefins

Upcycling non-biodegradable plastics such as polyolefins is paramount due to their ever-increasing demand and landfills after usage. Catalytic hydrogenolysis is highly appealing to convert polyolefins into targeted value-added products under mild reaction conditions compared to other methods, such as high-temperature incineration and pyrolysis. We have developed three isorecticular zirconium UiO-Metal-Organic Frameworks (UiO-MOFs) node-supported ruthenium dihydrides (UiO-RuH₂), which are efficient heterogeneous catalysts for hydrogenolysis of polyethylene at 200 °C, affording liquid hydrocarbons with a narrow distribution and excellent selectivity via shape-selective catalysis. UiO-66-RuH₂ catalyzed hydrogenolysis of single-use low-density polyethylene (LDPE) produced a C12 centered narrow bell-shaped distribution of C8-C16 alkanes in >80% yield and 90% selectivity in the liquid phase. By tuning the pore sizes of the isorecticular UiO-RuH₂ MOF catalysts, the distribution of the products could be systematically altered, affording different fuel-grade liquid hydrocarbons from LDPE in high yields. Our spectroscopic and theoretical studies and control experiments reveal that UiO-RuH₂ catalysts enable highly efficient upcycling of plastic wastes under mild conditions owing to their unique combination of coordinatively unsaturated single-site Ru-active sites, uniform and tunable pores, well-defined porous structure, and superior stability. The kinetics and theoretical calculation also identify the C–C bond scission involving β -alkyl transfer as the turnover-limiting step.

Chapter 9: Conclusion & Future Outlook

This concluding chapter summarizes the key outcomes of the thesis, which focused on the development of MOF-supported single-site catalysts for the selective transformation of inert hydrocarbons under mild conditions. The research demonstrated that rationally designed metal-organic frameworks, incorporating molecularly dispersed active sites, can facilitate challenging C–H and C–C bond activations with high efficiency and selectivity. The chapter also outlines future directions, including the scalable synthesis of catalytic MOFs, in situ mechanistic investigations, and expansion to photo- and electrocatalytic platforms. Finally, the chapter reflects on the intellectual and experimental evolution throughout the doctoral journey, highlighting the value of perseverance, collaboration, and scientific curiosity.

सारांश

मेथेन और पॉलीओलीफिन्स के मूल्यवर्धित रसायनों में उत्प्रेरक परिवर्तन आधुनिक रसायन विज्ञान में एक अग्रणी क्षेत्र के रूप में उभर रहा है, जो प्रचुर मात्रा में उपलब्ध परन्तु कठोर फीडस्टॉक्स को मूल्यवान उत्पादों में परिवर्तित करने का एक स्थायी मार्ग प्रदान करता है, साथ ही उनके पर्यावरणीय प्रभावों को भी कम करता है। मेथेन (CH_4), सबसे सरल हाइड्रोकार्बन और प्राकृतिक गैस का एक प्रमुख घटक, अत्यधिक मजबूत C-H बांड (विघटन ऊर्जा लगभग 439 kJ/mol) रखता है, जिससे यह सामान्य परिस्थितियों में रासायनिक रूप से निष्क्रिय रहता है। एक प्रभावशाली ग्रीनहाउस गैस के रूप में, जिसकी वैश्विक ताप वृद्धि क्षमता CO_2 की तुलना में 100 वर्षों में 25 गुना है, मेथेन को तेल और गैस निष्कर्षण के दौरान अक्सर जलाया या निकाला जाता है, जिससे इसके रासायनिक संसाधन के रूप में उपयोग की संभावनाओं का अपव्यय होता है। साथ ही, पॉलीओलीफिन्स—जैसे कि पॉलीथीन (PE) और पॉलीप्रोपाइलीन (PP)—प्लास्टिक अपशिष्ट धाराओं में प्रमुखता से विद्यमान हैं, जो वार्षिक रूप से उत्पादित 300 मिलियन टन प्लास्टिक में से 50% से अधिक योगदान करते हैं। इन फीडस्टॉक्स का चयनात्मक रूपांतरण, जिसमें मेथानोल, एसिटिक एसिड ($\text{CH}_3\text{CO}_2\text{H}$) और तरल हाइड्रोकार्बन शामिल हैं, ग्रीनहाउस गैस उत्सर्जन को कम करने, प्लास्टिक प्रदूषण को नियंत्रित करने और एक परिक्रामी कार्बन अर्थव्यवस्था की स्थापना में अत्यधिक संभावनाएँ प्रदान करता है। ऐसे परिवर्तन को प्राप्त करने के लिए ऐसे उत्प्रेरकों की आवश्यकता होती है जो निष्क्रिय बांड्स को सटीकता से सक्रिय कर सकें, सौम्य परिस्थितियों में कार्य करें, और लंबे चक्रों के दौरान स्थिरता बनाए रखें। पारंपरिक विषम उत्प्रेरक, जो अक्सर नोबेल धातुओं (जैसे कि Pt, Pd) या कठोर परिस्थितियों ($T > 400^\circ\text{C}$, $P > 50$ बार) पर निर्भर करते हैं, कम चयनशीलता, अत्यधिक ऑक्सीकरण और सिन्टरिंग या कोकिंग के कारण त्वरित निष्क्रियता की समस्या से जूझते हैं। वहीं, समरूप उत्प्रेरक, जो आणविक स्तर पर नियंत्रण प्रदान करते हैं, उन्हें पृथक्करण की कठिनाइयों और कमजोर पुनर्चक्रणता का सामना करना पड़ता है। यह शोध मेटल-ऑर्गेनिक फ्रेमवर्क्स (MOFs) द्वारा समर्थित विषम एकल-स्थल उत्प्रेरकों के विकास के माध्यम से इन सीमाओं को संबोधित करता है। MOFs धातु नोड्स द्वारा आपस में जुड़े जैविक लिंकरों से निर्मित क्रिस्टलीय छिद्रयुक्त पदार्थों की एक श्रेणी हैं, जिनमें ऐसे असाधारण गुण होते हैं जो उत्प्रेरण में क्रांति लाते हैं: $7000\text{ m}^2/\text{g}$ से अधिक की सतह क्षेत्रफल, समायोज्य छिद्र संरचनाएँ (माइक्रोपोरस $< 2\text{ nm}$ से मेसोपोरस $> 2\text{ nm}$ तक), और द्वितीयक निर्माण इकाइयों (SBUs) में पृथक धातु केंद्रों को लंगर देने की क्षमता। ये विशेषताएँ इलेक्ट्रोफिलिक, आणविक रूप से विसरित सक्रिय स्थल उत्पन्न करती हैं, जो एंजाइमेटिक प्रणालियों की सटीकता की नकल करते हैं, चयनात्मक बांड सक्रियण और प्रतिक्रिया मध्यवर्ती को वांछित उत्पादों की ओर निर्देशित करने में सहायक होती हैं।

इन सक्रिय स्थलों के विद्युत और स्थैरिक वातावरण को धातु की पहचान, ऑक्सीकरण अवस्था, और लिंकर कार्यक्षमता में परिवर्तन करके व्यवस्थित रूप से अनुकूलित किया जा सकता है, जबकि छिद्र प्रतिबंध सबस्ट्रेट की पहुँच और उत्पाद प्रसार को नियंत्रित कर साइड प्रतिक्रियाओं को दबाता है। इस शोध में इन गुणों का लाभ उठाते हुए MOF-आधारित उत्प्रेरकों का डिज़ाइन किया गया है, जो पृथ्वी में प्रचुर मात्रा में उपलब्ध धातुओं (जैसे कि Co, Cu, Ni, Fe, Ru) और सौम्य ऑक्सीडेंट्स (जैसे कि H_2O_2 , O_2) या हाइड्रोजन (H_2) का उपयोग करके मेथेन ऑक्सीकरण और पॉलीओलीफिन हाइड्रोजेनोलाइसिस में अभूतपूर्व गतिविधि, चयनशीलता तथा पुनर्चक्रणता प्राप्त करते हैं। यह शोध कई अध्यायों में विभाजित है, जिनमें से प्रत्येक को विशिष्ट MOF उत्प्रेरक के लिए समर्पित किया गया है, जिन्हें या तो मेथेन ऑक्सीकरण या पॉलीओलीफिन हाइड्रोजेनोलाइसिस के लिए अभियांत्रित किया गया है। उन्नत संश्लेषण

रणनीतियों—जैसे कि पोस्ट-सिंथेटिक मेटलेशन और रेटिकुलर रसायन—के साथ-साथ कठोर चरित्रण (जैसे कि XAS, XPS, EPR, NMR) और कंप्यूटेशनल मॉडलिंग (DFT) का उपयोग करते हुए, यह शोध इन परिवर्तन प्रक्रियाओं के अंतर्निहित संरचना-क्रियाशीलता संबंधों और प्रतिक्रिया तंत्रों को स्पष्ट करता है। अगले अनुभागों में प्रत्येक अध्याय का परिचय दिया गया है, जिसमें उत्प्रेरक डिज़ाइन, उत्प्रेरक प्रदर्शन और वैज्ञानिक अंतर्दृष्टियों को उजागर किया गया है।

अध्याय १. मेटल-ऑर्गेनिक फ्रेमवर्क्स और एकल-स्थल उत्प्रेरकों का परिचय

यह अध्याय रेटिक्युलर रसायन के मूल सिद्धांतों का परिचय कराता है, जो मजबूत, दिशा-निर्देशित बांड्स के माध्यम से आणविक निर्माण खंडों को व्यवस्थित रूप से जोड़कर क्रिस्टलीय, छिद्रयुक्त मेटल-ऑर्गेनिक फ्रेमवर्क्स (MOFs) का निर्माण करता है। यह जैविक प्रतिक्रियाओं के पूर्वानुमानित तंत्रों की तुलना धातु-लिगेंड समन्वयन की परिवर्तनीय प्रकृति से करता है, और छिद्र आकार, संरचनात्मक स्थिरता तथा समग्र कार्यक्षमता को निर्धारित करने में जैविक लिंकर और द्वितीयक निर्माण इकाइयों (SBUs) की भूमिकाओं पर बल देता है। मॉड्यूलर डिज़ाइन और आइसोरेटिक्युलैरिटी जैसे प्रमुख सिद्धांत—जहाँ लिंकर की लंबाई में विभिन्नता से मूल फ्रेमवर्क टोपोलॉजी को बनाए रखते हुए छिद्र आयामों का सटीक समायोजन संभव होता है—को MOF-5, HKUST-1, और UiO-66 जैसे उदाहरणों के माध्यम से स्पष्ट किया गया है। अध्याय में एकल-स्थल उत्प्रेरण की अवधारणा को भी प्रस्तुत किया गया है, जिसमें पृथक धातु परमाणुओं को MOFs के मजबूत वातावरण में लंगरित किया जाता है। यह दृष्टिकोण समरूप उत्प्रेरकों की उच्च चयनशीलता और परमाणु दक्षता को विषम प्रणालियों की स्थिरता और पुनर्चक्रणता के साथ जोड़ता है। आंतरिक लिंकर स्थिरीकरण, पोस्ट-सिंथेटिक संशोधन और धातु नोड लंगरन जैसी रणनीतियों पर संक्षेप में चर्चा की जाती है, जिन्हें इन सक्रिय स्थलों को स्थिर और अचल बनाने के तरीके के रूप में अपनाया जाता है। कुल मिलाकर, यह अध्याय MOFs के संश्लेषण और संरचनात्मक विविधता को समझने के साथ-साथ उन्नत उत्प्रेरक प्रक्रियाओं में इनके अनुप्रयोग के लिए एक व्यापक ढांचा प्रस्तुत करता है। MOFs की स्थापत्य और कार्यात्मक बहुमुखी प्रतिभा को उजागर करके, यह गैस भंडारण, पृथक्करण, और स्थायी रासायनिक परिवर्तन में अगली पीढ़ी की, ऊर्जा-कुशल तकनीकों की खोज के लिए आधार तैयार करता है।

अध्याय २. सामग्रियाँ एवं विधियाँ

यह अध्याय मेटल-ऑर्गेनिक फ्रेमवर्क (MOF) उत्प्रेरकों के संश्लेषण, चरित्रण, और विश्लेषण में प्रयुक्त व्यापक प्रायोगिक ढांचे और कार्यप्रणालियों का विवरण प्रस्तुत करता है। प्रारंभिक पदार्थ, अभिकर्मक और विलायक प्रतिष्ठित वाणिज्यिक आपूर्तिकर्ताओं से प्राप्त किए गए, जबकि महत्वपूर्ण आइसोटोप-लेबल यौगिक और विशेषीकृत लिगेंड सटीकता सुनिश्चित करने हेतु मंगाए गए। सख्त ग्लासवेयर सफाई—जिसमें क्रमिक विलायक धोने, क्षारीय बेस स्नान और अम्ल न्यूटलाइजेशन शामिल थे—ने प्रदूषण-मुक्त वातावरण सुनिश्चित किया। विशेषीकृत रिएक्टरों में संचालित उच्च-दाब प्रतिक्रियाओं में विस्फोटक गैस मिश्रणों से जुड़े जोखिमों को कम करने हेतु कड़े सुरक्षा उपाय अपनाए गए, जबकि हवा और नमी-संवेदनशील प्रक्रियाएँ नाइट्रोजन-निर्मुक्त ग्लोवबॉक्स में निष्पादित की गईं। उन्नत चरित्रण तकनीकों, जैसे कि पाउडर एक्स-रे विवर्तन (PXRD), ब्रुनॉयर-एमेट-टेलर (BET) विश्लेषण, फूरियर ट्रांसफॉर्म इन्फ्रारेड (FT-IR) स्पेक्ट्रोस्कोपी, थर्मोग्रैविमेट्रिक विश्लेषण (TGA) और एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी (XPS) का उपयोग संरचनात्मक, बनावटीय और तापीय गुणों की जांच हेतु किया गया। तत्वीय संघटन और सतह

संरचना का आकलन इंडक्टिवली कपल्ड प्लाज्मा ऑप्टिकल एमिशन स्पेक्ट्रोस्कोपी (ICP-OES), स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी-एनर्जी डिस्पर्सिव एक्स-रे स्पेक्ट्रोस्कोपी (SEM-EDS) और सिंक्रोट्रॉन-आधारित एक्स-रे अब्जॉर्प्शन स्पेक्ट्रोस्कोपी (XAS) द्वारा किया गया। प्रतिक्रिया परिणामों का विश्लेषण न्यूक्लियर मैग्नेटिक रेजोनेंस (NMR), गैस क्रोमैटोग्राफी (GC) और उच्च प्रदर्शन तरल क्रोमैटोग्राफी (HPLC) के माध्यम से किया गया, जिसे आइसोटोप लेबलिंग और आंतरिक मानकों द्वारा समर्थन प्राप्त था। उत्प्रेरक तंत्रों में सैद्धांतिक अंतर्दृष्टियाँ घनत्व फलन सिद्धांत (DFT) गणनाओं से प्राप्त की गईं, जिनमें विलायक प्रभाव और स्पिन-स्थिति ऊर्जा सम्मिलित हैं। इन प्रोटोकॉल्स ने सामूहिक रूप से मजबूत एवं पुनरुत्पादक प्रायोगिक कार्य प्रवाह सुनिश्चित किए, जो आगे चलकर उत्प्रेरक अध्ययनों की विश्वसनीयता का आधार बने।

अध्याय ३. मेटल-ऑर्गेनिक फ्रेमवर्क में संलग्न मोनोमेरिक कॉकल(III)-हाइड्रोपेरोक्साइड्स द्वारा केमोसलेक्टिव मेथेन ऑक्सीकरण से मेथानोल का उत्पादन

सौम्य परिचालन परिस्थितियों में मेथेन के केमोसलेक्टिव ऑक्सीकरण द्वारा मेथानोल का उत्पादन करने में सक्षम उत्प्रेरकों की उन्नति विषम उत्प्रेरण में एक महत्वपूर्ण चुनौती बनी हुई है। यहाँ हम एकल-स्थल कॉकल-हाइड्रोक्साइड उत्प्रेरक, Ce-UiO-Co(OH), के तर्कसंगत डिज़ाइन और संश्लेषण को प्रस्तुत करते हैं, जिसे सेरियम-युक्त मेटल-ऑर्गेनिक फ्रेमवर्क (Ce-UiO-66) के नोडल संरचनाओं पर अचल किया गया है। यह विषम उत्प्रेरक 80°C पर हाइड्रोजन पेरोक्साइड का उपयोग करते हुए मेथेन के आंशिक ऑक्सीकरण में असाधारण प्रभावशीलता प्रदर्शित करता है, जहाँ 99% चयनशीलता के साथ 2166 mmol g_{cat}⁻¹ की मेथानोल उत्पादन दर और 3250 का टर्नओवर नंबर (TON) प्राप्त होता है। तुलनात्मक विश्लेषण से यह स्पष्ट होता है कि Ce-UiO-Co प्रणाली उत्प्रेरक गतिविधि और उत्पाद चयनशीलता दोनों में अपने समरूप ज़िरकोनियम एनालॉग, Zr-UiO-Co, से काफी श्रेष्ठ प्रदर्शन करती है। समेकित प्रायोगिक एवं सैद्धांतिक अनुसंधान से एक प्रमुख Co(III)(η^2 -हाइड्रोपेरोक्साइड) मध्यवर्ती के निर्माण को स्पष्ट किया गया है, जिसे μ^4 -O⁻ लिगेंड और Ce-UiO-66 मैट्रिक्स में अंतर्निहित Ce⁴⁺ ऑक्सो नोड्स से प्राप्त दो कार्बोक्सिलेट ऑक्सीजन परमाणुओं के समन्वय द्वारा स्थिर किया जाता है। उत्प्रेरक चक्र एक टर्नओवर-सीमित चरण द्वारा नियंत्रित होता है, जिसमें सक्रिय कॉकल-हाइड्रोपेरोक्साइड प्रजाति और मेथेन के C-H बांड के बीच σ -बांड मेटाथेसिस शामिल होता है। Ce-UiO-Co में बड़ी हुई उत्प्रेरक दक्षता को Co(η^2 -O₂H) कॉम्प्लेक्स के भीतर कॉकल केंद्र की उल्लेखनीय इलेक्ट्रॉन-घटकहीन अवस्था के कारण माना जाता है, जो Ce-UiO समर्थन द्वारा विद्युत मॉड्यूलेशन का परिणाम है। यह विद्युत विन्यास मेथेन के C-H बांड विभाजन के लिए आवश्यक सक्रियण ऊर्जा को काफी कम कर देता है, जिससे प्रभावी उत्प्रेरक टर्नओवर संभव हो पाता है। MOF संरचनाओं के भीतर एकल-धातु स्थलों का रणनीतिक एकीकरण प्रचुर मात्रा में उपलब्ध धातुओं का उपयोग करते हुए इलेक्ट्रोफिलिक उत्प्रेरकों के निर्माण के लिए एक मजबूत मंच प्रदान करता है, जिससे जिह्वा अल्केनों के चयनात्मक फंक्शनलाइज़ेशन एवं स्थायी हाइड्रोकार्बन परिवर्तन प्रौद्योगिकियों के विकास की संभावनाएँ उजागर होती हैं।

अध्याय ४. मिश्रित सेरियम/ज़िरकोनियम मेटल-ऑर्गेनिक फ्रेमवर्क नोड्स में सहयोगी Ni-Ce सक्रिय स्थलों द्वारा चयनात्मक मेथेन ऑक्सीकरण से एथेनॉल का उत्पादन

सौम्य परिस्थितियों में मेथेन का एथेनॉल में उत्प्रेरक ऑक्सीकरण स्थायी रसायन विज्ञान में एक महत्वपूर्ण चुनौती प्रस्तुत करता है। यह अध्ययन एक विषम-द्वि-धातु Ce/Zr-UiO मेटल-ऑर्गेनिक फ्रेमवर्क (MOF) प्रस्तुत करता है, जिसे पृथक Ni(II)-हाइड्रॉक्सिल प्रजातियों $[Ce_x/Zr_y-UiO-Ni(OH)]$ के साथ कार्यशील बनाया गया है, जो इस परिवर्तन के लिए एक उच्च प्रदर्शन उत्प्रेरक के रूप में कार्य करता है। UiO संरचना, अपनी स्थिरता के लिए प्रसिद्ध, संरचनात्मक अखंडता बढ़ाने हेतु ज़िरकोनियम और रेडॉक्स लचीलेपन के लिए सेरियम को शामिल करती है। Ni^{2+} सक्रिय स्थल मिश्रित-धातु नोड्स के भीतर विशिष्ट रूप से समन्वित होते हैं, जो एक μ_4-O , एक हाइड्रॉक्सिल लिगेंड, तथा दो कार्बोक्सिलेट ऑक्सीजन परमाणुओं से बंधे होते हैं, जो आसन्न Ce^{4+} आयनों से जुड़े होते हैं। उन्नत चरित्रण तकनीकों (जैसे कि एक्स-रे अब्जॉर्प्शन स्पेक्ट्रोस्कोपी) और घनत्व फलन सिद्धांत (DFT) गणनाओं से यह पता चलता है कि स्थानिक रूप से निकट Ni और Ce केंद्रों के बीच सहयोग, MOF छिद्रों के भीतर मोनोन्यूक्लियर Ni प्रजातियों के प्रतिबंध के साथ मिलकर, $80^\circ C$ पर निम्न तापमान पर मेथेन सक्रियण को सरल बनाता है। इस उत्प्रेरक प्रक्रिया में होमोलेटिक C-H बांड विभाजन शामिल होता है, जिसके परिणामस्वरूप मिथाइल रेडिकल ($\bullet CH_3$) उत्पन्न होते हैं, जो छिद्रयुक्त फ्रेमवर्क के भीतर चयनात्मक C-C युग्मन के माध्यम से एथेनॉल का निर्माण करते हैं। विशेष रूप से, यह उत्प्रेरक $>93\%$ चयनशीलता के साथ $6521 \text{ mmol एथेनॉल g}_{Ni}^{-1}$ की असाधारण उत्पादकता हासिल करता है। तांत्रिक अध्ययन यह भी उजागर करते हैं कि गतिशील Ce-O-कार्बोक्सिलेट बांड विघटन एवं Ni-(μ_2-OH)-Ce बांड निर्माण द्वारा संचालित एक द्वैध उत्प्रेरक चक्र कार्यरत है, जिसे Ce^{4+} डोपिंग सक्षम बनाती है। नोड पर यह प्रतिवर्तनीय संरचनात्मक पुनर्व्यवस्था प्रभावी रेडिकल निर्माण और उत्प्रेरक टर्नओवर के लिए अत्यंत महत्वपूर्ण है। यह कार्य मिश्रित-धातु MOFs की क्षमता को रेखांकित करता है, जो अल्केन के मूल्यवर्धन के लिए सहयोगी सक्रिय स्थलों के अभियांत्रिकी में सहायक सिद्ध होते हैं। Ce (रेडॉक्स गतिविधि) और Zr (स्थिरता) के परस्पर पूरक गुणों का लाभ उठाकर, यह डिज़ाइन रणनीति लगभग सामान्य तापमान पर प्रभावी मेथेन परिवर्तन का मार्ग प्रदान करती है, जो ऊर्जा-गहन औद्योगिक प्रक्रियाओं के विपरीत है।

अध्याय ५. मोनो-कॉपर हाइड्रॉक्सिल उत्प्रेरक पर आणविक ऑक्सीजन का उपयोग करते हुए चयनात्मक मेथेन ऑक्सीकरण से एसिटिक एसिड का उत्पादन

एसिटिक एसिड एक औद्योगिक रूप से महत्वपूर्ण रासायनिक है, जिसे मुख्य रूप से कीमती धातु-आधारित समरूप उत्प्रेरकों का उपयोग करते हुए मेथानोल के कार्बोनाइलेशन द्वारा उत्पादित किया जाता है। एक निम्न-लागत फीडस्टॉक के रूप में, मेथेन को व्यावसायिक रूप से एसिटिक एसिड में परिवर्तित करने हेतु एक बहु-चरणीय प्रक्रिया अपनाई जाती है, जिसमें ऊर्जा-गहन मेथेन स्टीम सुधार, मेथानोल संश्लेषण और पश्चात मेथानोल कार्बोनाइलेशन शामिल हैं। यहाँ हम एक मोनो-कॉपर हाइड्रॉक्सिल स्थल पर, जो एक छिद्रयुक्त सेरियम मेटल-ऑर्गेनिक फ्रेमवर्क (MOF), Ce-UiO-Cu(OH) में सीमित है, के ऊपर सौम्य परिस्थितियों में आणविक ऑक्सीजन (O_2) को ऑक्सीडेंट के रूप में उपयोग करते हुए मेथेन से एसिटिक एसिड का प्रत्यक्ष एकल-चरणीय परिवर्तन रिपोर्ट करते हैं। Ce-UiO MOF द्वारा समर्थित एकल-स्थल कॉपर हाइड्रॉक्सिल उत्प्रेरक ने जल में $115^\circ C$ पर 96% चयनशीलता के साथ $335 \text{ mmol g}_{cat}^{-1}$ की असाधारण उच्च एसिटिक एसिड उत्पादकता तथा Cu का टर्नओवर नंबर (TON) 400 तक प्राप्त किया। हमारे स्पेक्ट्रोस्कोपिक, सैद्धांतिक अध्ययनों और नियंत्रित प्रयोगों से स्पष्ट होता है कि मेथेन

से एसिटिक एसिड का परिवर्तन ऑक्सीडेटिव कार्बोनाइलेशन के माध्यम से होता है, जहाँ मेथेन को पहले कॉपर-हाइड्रॉक्सिल स्थल पर σ -बांड मेटाथेसिस द्वारा सक्रिय कर Cu-मिथाइल प्रजाति उत्पन्न की जाती है, जिसके पश्चात इन-सिटू उत्पन्न कार्बन मोनोऑक्साइड के साथ कार्बोनाइलेशन और जल द्वारा हाइड्रोलाइसिस होता है। यह कार्य सौम्य एवं पर्यावरण-अनुकूल प्रतिक्रिया परिस्थितियों में मेथेन के सक्रियण और परिवर्तन हेतु विषम प्रचुर-धातु उत्प्रेरकों के तर्कसंगत डिज़ाइन में मार्गदर्शन प्रदान कर सकता है।

अध्याय ६. अनुकूलित छिद्र-प्रतिबंधित एकल-स्थल आयरन(III) उत्प्रेरक द्वारा चयनात्मक CH_4 ऑक्सीकरण से CH_3OH या CH_3CO_2H का उत्पादन (O_2 का उपयोग करते हुए)

सौम्य परिस्थितियों में मेथेन का सीधे ऑक्सीकरण करके अल्कोहल्स और एसिटिक एसिड जैसे मूल्यवान ऑक्सीजनयुक्त यौगिक प्राप्त करना एक महत्वपूर्ण चुनौती है, क्योंकि इसमें उच्च C–H बांड विघटन ऊर्जा, CO एवं CO_2 में आसानी से अत्यधिक ऑक्सीकरण तथा C–H सक्रियण एवं C–C युग्मन की जटिलता शामिल है। इस अध्ययन में, हम एक बहुउद्देशीय आयरन(III) डाइहाइड्रॉक्सिल उत्प्रेरक प्रजाति का विकास करते हैं, जिसे एक मेटल-ऑर्गेनिक फ्रेमवर्क (MOF) के भीतर अचल किया गया है, ताकि विभिन्न प्रतिक्रिया परिस्थितियों में O_2 का उपयोग करते हुए मेथेन का चयनात्मक रूप से मेथानोल या एसिटिक एसिड में ऑक्सीकरण किया जा सके। MOF नोड्स पर मोनोमेरिक $Fe^{III}(OH)_2$ प्रजातियों के सक्रिय स्थल पृथक्करण, छिद्रयुक्त फ्रेमवर्क के भीतर उनका प्रतिबंध तथा उनकी इलेक्ट्रॉन-घटकहीन प्रकृति के मोसलेक्टिव C–H ऑक्सीकरण को सुविधाजनक बनाते हैं, जिसके फलस्वरूप क्रमशः $38,592 \mu mol CH_3OH gFe^{-1} h^{-1}$ और $81,043 \mu mol CH_3CO_2H gFe^{-1} h^{-1}$ की उच्च उत्पादकता प्राप्त होती है। प्रयोग एवं सैद्धांतिक गणनाएँ संकेत देती हैं कि मेथानोल का निर्माण $Fe(III)$ – $Fe(I)$ – $Fe(III)$ उत्प्रेरक चक्र के माध्यम से होता है, जबकि CH_3CO_2H का उत्पादन इन-सिटू उत्पन्न CH_3OH के CO_2 एवं H_2 के साथ हाइड्रोकार्बोक्साइलेशन तथा CO_2 के साथ सीधे CH_4 कार्बोक्साइलेशन से होता है।

अध्याय ७. UiO -MOF नोड्स पर आणविक रूप से विभक्त $Cu(I)$ -सक्रिय स्थलों का निर्माण करके थर्मोकैटेलिटिक ऑक्सीकरण द्वारा O_2 के उपयोग से मेथेन से एथेनॉल का उत्पादन

मेथेन, जो कि एक किफायती C_1 फीडस्टॉक है, का सीधे एथेनॉल में परिवर्तन फसल-आधारित उत्पादन के लिए एक स्थायी विकल्प प्रस्तुत करता है, परन्तु इसमें C–H सक्रियण, C–C बांड निर्माण एवं अत्यधिक ऑक्सीकरण की चुनौतियाँ विद्यमान हैं। हम एक $Cu(I)$ -उत्प्रेरक की रिपोर्ट करते हैं, जिसे ज़िरकोनियम-आधारित UiO -66 मेटल-ऑर्गेनिक फ्रेमवर्क्स (MOFs) द्वारा समर्थित किया गया है, जो जल में $100^\circ C$ पर मेथेन ऑक्सीकरण से एथेनॉल का उत्पादन करता है, $5196 \mu mol gCu^{-1} h^{-1}$ की उत्पादकता तथा 71% तक चयनशीलता प्राप्त करते हुए। MOF में Zr_6 -ऑक्सो नोड्स द्वारा स्थिरित $Cu(I)$ प्रजाति सौम्य परिस्थितियों में O_2 तथा मेथेन को सक्रिय करती है, जिससे $\bullet CH_3$ तथा $\bullet OH$ रेडिकल उत्पन्न होते हैं, जो $Cu(I)$ – $Cu(II)$ – $Cu(I)$ चक्र के माध्यम से युग्मित होकर एथेनॉल का निर्माण करते हैं। प्रायोगिक एवं संगणकीय अनुसंधान से यह सिद्ध होता है कि छिद्र प्रतिबंध, आंतरिक द्रव्यमान-स्थानांतरण सीमाएँ एवं रेडिकल गतिशीलता का नियंत्रण एथेनॉल उपज को अधिकतम करने में निर्णायक भूमिका निभाते हैं, जहाँ छिद्र प्रतिबंध रेडिकल पुनःमिलन को प्रोत्साहित करता है तथा सीमित द्रव्यमान स्थानांतरण सक्रिय स्थलों तक मेथेन के प्रसार को सुविधाजनक बनाता है, जिससे अत्यधिक ऑक्सीकरण को रोका जा सके।

उच्च Cu-से-Zr अनुपात $\cdot\text{CH}_3$ निर्माण को बढ़ाता है, जिससे C-C युग्मन को प्रोत्साहन मिलता है एवं अत्यधिक ऑक्सीकरण को दबाकर उपोत्पादों को न्यूनतम किया जाता है।

अध्याय ८. आइसोरेटिक मेटल-ऑर्गेनिक फ्रेमवर्क्स में प्रतिबंधित मोनोन्यूक्लियर Ru-हाइड्राइड्स द्वारा पॉलीओलीफिन्स के आकार-चयनात्मक हाइड्रोजेनोलाइसिस में उच्च दक्षता

पॉलीओलीफिन्स जैसे गैर-जैविक प्लास्टिक का अपसाइक्लिंग अत्यंत महत्वपूर्ण है, क्योंकि इनकी लगातार बढ़ती मांग तथा उपयोग के पश्चात इनके निपटान की समस्या बनी रहती है। उत्प्रेरक हाइड्रोजेनोलाइसिस पॉलीओलीफिन्स को लक्षित मूल्यवर्धित उत्पादों में परिवर्तित करने के लिए अत्यंत आकर्षक है, विशेष रूप से उच्च तापमान पर दहन एवं पाइरोलाइसिस जैसी विधियों की तुलना में, क्योंकि यह सौम्य प्रतिक्रिया परिस्थितियों में किया जाता है। हमने तीन आइसोरेटिक ज़िरकोनियम UiO-मेटल-ऑर्गेनिक फ्रेमवर्क्स (UiO-MOFs) द्वारा समर्थित रुतेनियम डाइहाइड्राइड्स (UiO-RuH₂) विकसित किए हैं, जो 200 °C पर पॉलीथीन के हाइड्रोजेनोलाइसिस के लिए कुशल विषम उत्प्रेरक सिद्ध होते हैं, और आकार-चयनात्मक उत्प्रेरण के माध्यम से संकीर्ण वितरण तथा उत्कृष्ट चयनशीलता के साथ तरल हाइड्रोकार्बन प्रदान करते हैं। UiO-66-RuH₂ द्वारा उत्प्रेरित एकल-उपयोग लो-डेन्सिटी पॉलीथीन (LDPE) का हाइड्रोजेनोलाइसिस तरल अवस्था में >80% उपज एवं 90% चयनशीलता के साथ C₈-C₁₆ अल्केनों का C₁₂ केंद्रित संकीर्ण घंटी-आकार वितरण प्रदान करता है। आइसोरेटिक UiO-RuH₂ MOF उत्प्रेरकों के छिद्र आकार को समायोजित करके, उत्पादों के वितरण को व्यवस्थित रूप से परिवर्तित किया जा सकता है, जिससे LDPE से उच्च उपज में विभिन्न ईंधन-ग्रेड तरल हाइड्रोकार्बन प्राप्त किए जा सकें। हमारे स्पेक्ट्रोस्कोपिक एवं सैद्धांतिक अध्ययनों तथा नियंत्रित प्रयोगों से यह सिद्ध होता है कि UiO-RuH₂ उत्प्रेरक, समन्वयात्मक रूप से असंतृप्त एकल-स्थल Ru-सक्रिय स्थलों, समान एवं समायोज्य छिद्रों, सुव्यवस्थित छिद्रयुक्त संरचना एवं उत्कृष्ट स्थिरता के अद्वितीय संयोजन के कारण, सौम्य परिस्थितियों में प्लास्टिक अपशिष्टों के अत्यधिक कुशल अपसाइक्लिंग को सक्षम करते हैं। साथ ही, गतिकी एवं सैद्धांतिक गणनाएँ यह भी संकेत देती हैं कि β -एल्काइल ट्रांसफर को शामिल करते हुए C-C बांड का विच्छेदन टर्नओवर-सीमित चरण है।

अध्याय ९: निष्कर्ष और भविष्य की रूपरेखा

यह समापन अध्याय इस शोध प्रबंध के मुख्य निष्कर्षों का सार प्रस्तुत करता है, जिसका केंद्र बिंदु मृदु परिस्थितियों में निष्क्रिय हाइड्रोकार्बनों के चयनात्मक रूपांतरण के लिए MOF-समर्थित एकल-साइट उत्प्रेरकों का विकास था। इस शोध में यह प्रदर्शित किया गया कि युक्तिपूर्वक डिज़ाइन किए गए मेटल-ऑर्गेनिक फ्रेमवर्क्स, जिनमें आणविक रूप से वितरित सक्रिय स्थल शामिल हैं, उच्च दक्षता और चयनात्मकता के साथ कठिन C-H और C-C बंधों की सक्रियता को सक्षम कर सकते हैं। अध्याय में भविष्य की संभावित दिशाओं का भी वर्णन किया गया है, जिनमें उत्प्रेरक MOFs का बड़े पैमाने पर संश्लेषण, यथास्थिति यांत्रिक जांच, तथा फोटो- और विद्युत-उत्प्रेरक प्लेटफ़ॉर्मों की ओर विस्तार शामिल है। अंततः, यह अध्याय पूरे डॉक्टोरल यात्रा के दौरान बौद्धिक और प्रयोगात्मक विकास पर भी विचार करता है, और यह दर्शाता है कि दृढ़ता, सहयोग, और वैज्ञानिक जिज्ञासा का कितना महत्व है।

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List of Acronyms/Abbreviations

Acronym/ Abbreviation	Full-form	Acronym/ Abbreviation	Full-form
MOF	Metal-Organic Framework	SBU	Secondary Building Unit
BDC	Benzene-1,4-dicarboxylic Acid	BPDC	Biphenyl-4,4'-dicarboxylic Acid
DMF	N, N-dimethyl Formamide	THF	Tetrahydrofuran
0D	Zero dimension	1D	One dimension
2D	Two dimensions	3D	Three dimensions
PXRD	Powder X-ray Diffraction	BET	Brunauer-Emmett-Teller
FT-IR	Fourier-transform Infrared Spectroscopy	ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
<i>fcu</i>	Face Centered Cubic	SEM- EDS	Scanning Electron Microscopy Elemental Dispersive X-ray Spectroscopy
TGA	Thermogravimetric Analysis	EPR	Electron Paramagnetic Resonance
XPS	X-ray Photoelectron Spectroscopy	XAS	X-ray Absorption Spectroscopy
XANES	X-ray Absorption Near Edge Structure	EXAFS	Extended X-ray Absorption Fine Structure
DFT	Density Functional Theory	NMR	Nuclear Magnetic Resonance
GC	Gas Chromatography	FID	Flame Ionization Detector
MS	Mass Spectrometry	TCD	Thermal Conductivity Detector
HPLC	High Performance Liquid Chromatography	GPC	Gel Permeation Chromatography
UiO	Universitetet i Oslo	DUT	Dresden University of Technology
<i>n</i> -BuLi	<i>n</i> -butyllithium	TON	Turnover Number
INT	Intermediate	TS	Transition state
HK	Horvath-Kawazoe	TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
DMPO	5,5-dimethyl-1-pyrroline N-oxide	R _f	Retention Factor
M _w	Weight Average Molecular Weight	M _n	Number Average Molecular Weight
LDPE	Low Density Polyethylene	SCRF	Self-Consistent Reaction Field
PCM	Polarizable Continuum Model	IEFPCM	Integral Equation Formalism Polarizable Continuum Model
h	hour	min	minute