

Title: Metal-Organic Frameworks Confined Single-Site Heterogeneous Catalysts for Sustainable Chemical Transformations

Abstract:

This thesis, entitled “Metal–Organic Framework-Confined Single-Site Heterogeneous Catalysts for Sustainable Chemical Transformations,” explores the design of MOF-based catalysts incorporating transition-metals as active catalytic sites for diverse chemical transformations. The catalytic reactions investigated include chemoselective alkene oxidation, regioselective oxidative bromination of arenes, methane borylation, and CO₂ hydrogenation. The following sections introduce each chapter, highlighting the catalyst design, catalytic performance, and scientific insights:

Chapter 1. Introduction to Metal-Organic Frameworks

This chapter begins with an introductory overview of heterogeneous catalysis, highlighting the fundamental distinctions between single-site and multi-site solid supports, followed by a brief overview of porous materials. After concise definitions of single-site solid supports and porous materials, the discussion advances to a comprehensive examination of metal-organic frameworks (MOFs), including their historical development and key milestones in the field. The chapter further addresses various post-synthetic modification strategies and rational framework design approaches employed to tailor the physicochemical properties of MOF-based materials. An overview of the diverse synthetic methodologies for MOF preparation is also presented. Subsequently, the principles of MOF architecture and design for catalysis are discussed, emphasizing the unique advantages of MOF-based materials in heterogeneous catalysis. Their broader applications in drug delivery, chemical sensing, gas storage, and catalysis are also outlined. The introduction also emphasizes UiO-type MOFs, highlighting their isoreticular architecture and versatile functionalization strategies, including post-synthetic modification. The chapter concludes with an outline of the thesis. Overall, this chapter provides a foundational framework that elucidates the synthesis, structural diversity, and functional versatility of MOFs, thereby setting the stage for their application in advanced catalytic systems and sustainable, energy-efficient technologies for gas storage, separation, and chemical transformations.

Chapter 2. Materials & Methods

This chapter presents a detailed account of the experimental design and methodologies employed for the synthesis, characterization, and catalytic evaluation of metal-organic framework (MOF)-based catalysts. All starting materials, reagents, and solvents were procured from reputable commercial suppliers and used as received unless otherwise specified. To ensure contamination-free conditions, glassware was rigorously cleaned through sequential solvent rinses, alkaline base baths, and acid neutralization procedures. High-pressure catalytic reactions were performed in dedicated reactors equipped with appropriate safety features to mitigate risks associated with flammable or explosive gas mixtures, while air- and moisture-sensitive manipulations were conducted under an inert nitrogen atmosphere in a glovebox.

Comprehensive characterization of the synthesized materials was achieved using a suite of advanced techniques, including powder and single-crystal X-ray diffraction (PXRD and ScXRD) for structural analysis, Brunauer-Emmett-Teller (BET) measurements for surface area and porosity evaluation, Fourier-transform infrared (FT-IR) spectroscopy for functional group identification, thermogravimetric analysis (TGA) for thermal stability assessment, and X-ray photoelectron spectroscopy (XPS) for surface chemical state analysis. Elemental composition and morphological features were examined using inductively coupled plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS), and synchrotron-based X-ray absorption spectroscopy (XAS). Catalytic reaction products were quantified and identified by nuclear magnetic resonance (NMR) spectroscopy and gas chromatography (GC) equipped with mass spectrometric (MS), flame ionization (FID), and thermal conductivity (TCD) detectors, employing appropriate internal standards. In addition, density functional theory (DFT) calculations were performed to gain mechanistic insight into the catalytic processes, explicitly accounting for solvent effects and spin-state energetics. Collectively, these experimental and computational protocols establish a robust and reproducible framework that underpins the reliability and interpretability of the catalytic studies discussed in subsequent chapters.

Chapter 3. Chemoselective Oxidation of Alkenes by Metal-Organic Framework-Supported Copper Catalyst

Oxidation of alkenes to carbonyls or diols compounds is important in synthesizing fine chemicals and pharmaceutical intermediates. We report the synthesis and characterization of an aluminum metal–organic framework node-supported copper(II) chloride (DUT-5-CuCl), which is an efficient heterogeneous catalyst for the oxidation of alkenes using H₂O₂ as an oxidizing agent. Styrene and various substituted styrenes were transformed into the corresponding carbonyl compounds in excellent selectivity and yields. DUT-5-CuCl is tolerant with various functional groups and could be recycled and reused at least 5 times in the oxidation of α -methylstyrene. Unlike the oxidation of styrene derivatives, DUT-5-Cu catalyzed oxidation of aliphatic and cyclic alkenes produced 1,2-diols compounds selectively. The mechanism of the DUT-5-CuCl catalyzed oxidation of styrene to benzaldehyde was investigated in detail by various experiments such as the determination of reaction intermediates and characterization of the catalyst after catalysis, and computational studies. This work highlights the importance of MOF-supported earth-abundant metal catalysts for oxidation reactions to produce fine chemicals.

Chapter 4. Regioselective oxidative bromination of arenes by a metal-organic framework-confined mono-bipyridyl iron(III) catalyst

Oxidative bromination of arenes is an effective and environmentally friendly method for synthesizing bromoarenes. We have developed a highly robust zirconium-metal-organic framework (MOF)-supported mono bipyridyl-iron(III) chloride catalyst (bpy-UiO-FeCl₃) for oxidative bromination of arenes using H₂O₂ as the oxidant and KBr as the bromine source. The bpy-UiO-FeCl₃ catalyst exhibits high conversion rates for various substituted arenes, yielding significant amounts of bromoarenes with excellent regioselectivity, and recyclability under

mild reaction conditions. The MOF-catalyst outperforms its homogeneous counterparts in terms of both activity and regioselectivity due to the stabilization of the mononuclear bipyridyl-iron(III) species within the active sites in the MOF's pores. Furthermore, the confinement of these active sites within the robust, well-defined, and uniform porous framework enhances the regioselectivity of the bromination through shape-selective catalysis. The mechanism of bpy-UiO-FeCl₃ catalyzed oxidative bromination of arenes was thoroughly investigated by a combination of control experiments, spectroscopic analyses, and computational studies. These findings underscore the importance of MOFs in the development of heterogeneous catalysts based on earth-abundant metals for the sustainable synthesis of haloarenes.

Chapter 5: Selective Monoborylation of Methane over Pore Confined Mononuclear Pyridylimine-Iridium(I)-Hydride

Chemoselective C–H borylation of methane has drawn significant attention in recent years due to the abundance of methane as the low-cost carbon feedstock and the application of organoborane products as versatile synthetic intermediates in organic synthesis. However, achieving high-yield, chemoselective monoborylation of methane remains a significant challenge. We have developed a metal-organic framework confined pyridylimine-iridium hydride catalyst (pyrim-UiO-IrH), which is efficient in methane C–H borylation using bis(pinacolato)diboron to afford methyl boronic acid pinacol ester (CH₃Bpin) in 98% GC-yield at 130 °C. As a heterogeneous catalyst, pyrim-UiO-IrH could be recycled and reused at least 5 times with consistent activity without noticeable changes in structure or crystallinity, leading to the total TON up to 980. Importantly, pyrim-UiO-IrH was at least 24 times more active than its homogeneous control ([Ph(pyrim)(PhCO₂Me)₂]Ir, due to the greater stability of the pyrim-IrH species *via* active-site isolation at the linkers that prevent intermolecular decomposition. Mechanistic investigation suggests that oxidative addition of methane to Ir^{III}(Bpin)₂(H) species to form Ir^V(Bpin)₂(CH₃)(H)₂ as the turnover limiting step.

Chapter 6: Selective Monoborylation of Methane by a Mono Bipyridyl-Nickel(II) Hydride Catalyst

We report the development of an earth-abundant metal catalyst for methane C–H borylation. The post-synthetic metalation of bipyridine-functionalized zirconium metal-organic framework (MOF) with NiBr₂, followed by treatment of NaEt₃BH affords MOF-supported monomeric bipyridyl-nickel(II) dihydride species via active site isolation. The heterogeneous and recyclable nickel catalyst selectively borylates methane at 200 °C using pinacolborane (HBpin) to afford CH₃Bpin in 61% yield with a turnover number (TON) up to 1388. The confinement of the active NiH₂-species within the uniformly porous MOF allows selective monoborylation of methane via shape-selective catalysis by preventing the formation of sterically encumbered overborylated products. Unlike MOF-Ni catalyst, its homogeneous control is almost inactive in methane borylation due to its intermolecular decomposition. Our mechanistic investigation, including spectroscopic, kinetic, and control experiments, as well as DFT calculations, revealed that stabilizing mononuclear bipyridyl-nickel dihydride and diboryl species by MOF is crucial for achieving efficient methane borylation via turnover-limiting σ -bond metathesis. This work shows promise in designing MOF-based abundant metal catalysts

for the chemoselective functionalization of methane and other inert molecules into valuable chemicals.

Chapter 7: Leveraging Conformational Dynamics of MOFs to Overcome Conversion-Selectivity Trade-off in CO₂ Hydrogenation to Ethanol

In this study, we harness the intrinsic structural dynamics of the MIL-53(Al) metal-organic framework (MOF) to develop a highly efficient and selective aqueous-phase heterogeneous catalyst, MIL-53-Co(OH), featuring atomically dispersed Co^{II}-OH active species anchored at the MOF nodes for CO₂ homologation to ethanol. Under mild reaction conditions (130 °C, 20 bar, H₂/CO₂ = 3), MIL-53-Co(OH) delivers 92% CO₂ conversion with 93% ethanol selectivity and an ethanol productivity of 10,133 μmol g_{cat}⁻¹ h⁻¹. Comparative studies with the rigid MIL-68(Al) framework and breathing-suppressed MIL-53 analogues demonstrate that lattice flexibility is a decisive factor, enhancing ethanol productivity by at least 3.5-fold while effectively suppressing CH₃OH formation. Combined experimental, structural, and computational investigations reveal that the reversible narrow-pore (np) ⇌ large-pore (lp) breathing behavior periodically modulates the Al₂(μ₃-O-Co(OH)) node geometry, synchronizing *in situ* CH₃OH activation with subsequent CO insertion to promote C-C bond formation. During the np→lp transition, transient lattice expansion relaxes the Al-(μ₃-O-Co(OH))-Al hinge, significantly lowering the activation barrier for σ-bond metathesis between the Co-H bond and the C-O bond of CH₃OH, a key elementary step in the catalytic cycle. Overall, this work demonstrates that exploiting MOF conformational dynamics as an active-site engineering strategy offers a powerful and generalizable approach for designing highly efficient and selective heterogeneous catalysts for challenging chemical transformations.