

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

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by

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Submitted

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Dedicated to
My Family

Certificate

This is to certify that the thesis entitled “*Metal-Organic Frameworks Confined Single-Site Heterogeneous Catalysts for Sustainable Chemical Transformations*” being submitted by Rahul Kalita (Entry No.: 2021CYZ8379) 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. Rahul Kalita 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.

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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 isorecticular 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 gcat⁻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.

सारांश

यह शोध-प्रबंध “सतत रासायनिक रूपांतरणों के लिए धातु-कार्बनिक फ्रेमवर्क-सीमाबद्ध सिंगल-साइट विषम उत्प्रेरक” शीर्षक से प्रस्तुत किया गया है, जिसमें विभिन्न रासायनिक रूपांतरणों के लिए सक्रिय उत्प्रेरक स्थलों के रूप में ट्रांज़िशन धातुओं को सम्मिलित करने वाले MOF-आधारित उत्प्रेरकों की अभिकल्पना का अध्ययन किया गया है। इस शोध में जिन उत्प्रेरक अभिक्रियाओं की जाँच की गई है, उनमें एल्कीनों का कीमो-चयनात्मक ऑक्सीकरण, एरीन का क्षेत्र-चयनात्मक ऑक्सीडेटिव ब्रोमिनेशन, मीथेन का बोरीलेशन तथा CO₂ का हाइड्रोजनीकरण शामिल हैं। निम्नलिखित अनुभागों में प्रत्येक अध्याय का परिचय प्रस्तुत किया गया है, जिसमें उत्प्रेरक की अभिकल्पना, उत्प्रेरक प्रदर्शन तथा प्राप्त वैज्ञानिक अंतर्दृष्टियों को प्रमुखता से रेखांकित किया गया है:

अध्याय 1. धातु-कार्बनिक फ्रेमवर्क का परिचय

यह अध्याय विषम उत्प्रेरण के एक परिचयात्मक अवलोकन से प्रारंभ होता है, जिसमें सिंगल-साइट और मल्टी-साइट ठोस समर्थनों के बीच मूलभूत अंतरों को रेखांकित किया गया है, तथा इसके बाद रंध्रयुक्त पदार्थों का संक्षिप्त परिचय प्रस्तुत किया गया है। सिंगल-साइट ठोस समर्थनों और रंध्रयुक्त पदार्थों की संक्षिप्त परिभाषाओं के पश्चात, चर्चा को धातु-कार्बनिक फ्रेमवर्क (MOFs) के विस्तृत विवेचन की ओर आगे बढ़ाया गया है, जिसमें उनके ऐतिहासिक विकास और इस क्षेत्र की प्रमुख उपलब्धियों को सम्मिलित किया गया है। अध्याय में आगे MOF-आधारित पदार्थों के भौतिक-रासायनिक गुणों को अनुकूलित करने हेतु अपनाई जाने वाली विभिन्न पोस्ट-सिंथेटिक संशोधन रणनीतियों तथा तर्कसंगत फ्रेमवर्क अभिकल्पना दृष्टिकोणों पर चर्चा की गई है। साथ ही, MOF संश्लेषण के लिए प्रयुक्त विविध संश्लेषणात्मक विधियों का भी एक अवलोकन प्रस्तुत किया गया है। इसके पश्चात, उत्प्रेरण के लिए MOF संरचना और अभिकल्पना के सिद्धांतों पर प्रकाश डाला गया है, जिसमें विषम उत्प्रेरण में MOF-आधारित पदार्थों के विशिष्ट लाभों पर बल दिया गया है। औषधि वितरण, रासायनिक संवेदन, गैस भंडारण तथा उत्प्रेरण जैसे क्षेत्रों में इनके व्यापक अनुप्रयोगों का भी संक्षेप में उल्लेख किया गया है। अध्याय का उत्तरार्द्ध UiO-प्रकार के MOFs पर केंद्रित है, जिसमें उनकी आइसोरेटिकुलर प्रकृति, संरचनात्मक सुदृढ़ता तथा प्रमुख विशेषताओं का विस्तृत विवरण दिया गया है। अध्याय का समापन शोध-प्रबंध की रूपरेखा (थीसिस आउटलाइन) के साथ किया गया है। समग्र रूप से, यह अध्याय MOFs के संश्लेषण, संरचनात्मक विविधता तथा कार्यात्मक बहुमुखी प्रतिभा को स्पष्ट करने वाला एक आधारभूत ढाँचा प्रस्तुत करता है, जो उन्नत उत्प्रेरक प्रणालियों तथा गैस भंडारण, पृथक्करण और रासायनिक रूपांतरणों के लिए सतत एवं ऊर्जा-दक्ष प्रौद्योगिकियों में उनके अनुप्रयोग की पृष्ठभूमि तैयार करता है।

अध्याय 2. सामग्रियाँ एवं विधियाँ

यह अध्याय धातु-कार्बनिक फ्रेमवर्क (MOF)-आधारित उत्प्रेरकों के संश्लेषण, चरित्रण तथा उत्प्रेरक मूल्यांकन के लिए अपनाई गई प्रायोगिक रूपरेखा और कार्यविधियों का विस्तृत विवरण प्रस्तुत करता है। सभी प्रारंभिक पदार्थ, अभिकर्मक और विलायक विश्वसनीय वाणिज्यिक आपूर्तिकर्ताओं से प्राप्त किए गए और जब तक अन्यथा उल्लेख न हो, उन्हें यथावत् उपयोग किया गया। संदूषण-मुक्त परिस्थितियाँ सुनिश्चित करने के लिए काँच के उपकरणों की कठोर सफाई की गई, जिसमें क्रमिक विलायक धुलाई, क्षारीय बेस बाथ तथा अम्लीय न्यूट्रलाइज़ेशन प्रक्रियाएँ शामिल थीं। उच्च-दाब उत्प्रेरक अभिक्रियाएँ विशेष

रिएक्टरों में संचालित की गई, जो ज्वलनशील या विस्फोटक गैस मिश्रणों से जुड़े जोखिमों को कम करने हेतु उपयुक्त सुरक्षा सुविधाओं से सुसज्जित थे, जबकि वायु- एवं आर्द्रता-संवेदी क्रियाएँ नाइट्रोजन के निष्क्रिय वातावरण में ग्लवबॉक्स के भीतर संपन्न की गई।

संश्लेषित पदार्थों का समग्र चरित्रण उन्नत तकनीकों के एक व्यापक समूह द्वारा किया गया, जिसमें संरचनात्मक विश्लेषण के लिए पाउडर एवं सिंगल-क्रिस्टल एक्स-रे विवर्तन (PXRD और ScXRD), सतह क्षेत्रफल एवं रंधता के मूल्यांकन हेतु ब्रुनाउअर-एमेट-टेलर (BET) मापन, कार्यात्मक समूहों की पहचान के लिए फूरियर-ट्रांसफॉर्म इन्फ्रारेड (FT-IR) स्पेक्ट्रोस्कोपी, तापीय स्थिरता के आकलन हेतु थर्मोग्रैविमेट्रिक विश्लेषण (TGA), तथा सतही रासायनिक अवस्थाओं के अध्ययन के लिए एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी (XPS) शामिल हैं। तत्वीय संघटन और आकारिक विशेषताओं की जाँच इंडक्टिवली कपल्ड प्लाज़्मा ऑप्टिकल एमिशन स्पेक्ट्रोस्कोपी (ICP-OES), स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी-एनर्जी-डिस्पर्सिव एक्स-रे स्पेक्ट्रोस्कोपी (SEM-EDS), तथा सिंक्रोट्रॉन-आधारित एक्स-रे अवशोषण स्पेक्ट्रोस्कोपी (XAS) द्वारा की गई। उत्प्रेरक अभिक्रिया उत्पादों की पहचान और मात्रात्मक विश्लेषण न्यूक्लियर मैग्नेटिक रेज़ोनेंस (NMR) स्पेक्ट्रोस्कोपी तथा गैस क्रोमैटोग्राफी (GC) के माध्यम से किया गया, जो मास स्पेक्ट्रोमेट्री (MS), फ्लेम आयोनाइज़ेशन डिटेक्टर (FID) और थर्मल कंडक्टिविटी डिटेक्टर (TCD) से सुसज्जित थी, तथा उपयुक्त आंतरिक मानकों का उपयोग किया गया। इसके अतिरिक्त, उत्प्रेरक प्रक्रियाओं की यांत्रिक समझ प्राप्त करने हेतु डेंसिटी फ़ंक्शनल थ्योरी (DFT) गणनाएँ की गईं, जिनमें विलायक प्रभावों और स्पिन-अवस्था ऊर्जाओं को स्पष्ट रूप से सम्मिलित किया गया। समग्र रूप से, ये प्रायोगिक और संगणकीय प्रोटोकॉल एक सुदृढ़ तथा पुनरुत्पाद्य ढाँचा स्थापित करते हैं, जो आगामी अध्यायों में प्रस्तुत उत्प्रेरक अध्ययनों की विश्वसनीयता और व्याख्येयता का आधार प्रदान करता है।

अध्याय 3. धातु-कार्बनिक फ्रेमवर्क-समर्थित तांबा उत्प्रेरक द्वारा एल्कीनों का कीमो-चयनात्मक ऑक्सीकरण

एल्कीनों का ऑक्सीकरण कर उन्हें कार्बोनिल या डायोल यौगिकों में परिवर्तित करना सूक्ष्म रसायनों तथा औषधीय मध्यवर्तियों के संश्लेषण में अत्यंत महत्वपूर्ण है। इस अध्याय में एल्युमिनियम धातु-कार्बनिक फ्रेमवर्क के नोड पर समर्थित कॉपर(II) क्लोराइड (DUT-5-CuCl) के संश्लेषण और चरित्रण की रिपोर्ट प्रस्तुत की गई है, जो H_2O_2 को ऑक्सीकारक के रूप में उपयोग करते हुए एल्कीनों के ऑक्सीकरण के लिए एक प्रभावी विषम उत्प्रेरक के रूप में कार्य करता है। स्टाइरीन तथा विभिन्न प्रतिस्थापित स्टाइरीन उत्कृष्ट चयनात्मकता और उच्च उपज के साथ संबंधित कार्बोनिल यौगिकों में परिवर्तित किए गए। DUT-5-CuCl विभिन्न कार्यात्मक समूहों के प्रति सहनशील है तथा α -मेथिलस्टाइरीन के ऑक्सीकरण में इसे कम से कम पाँच बार पुनर्चक्रित और पुनः उपयोग किया जा सकता है।

स्टाइरीन व्युत्पन्नों के ऑक्सीकरण के विपरीत, DUT-5-Cu द्वारा उत्प्रेरित ऐलिफैटिक और चक्रीय एल्कीनों के ऑक्सीकरण से चयनात्मक रूप से 1,2-डायोल यौगिक प्राप्त हुए। स्टाइरीन से बेंज़ाल्डिहाइड में DUT-5-CuCl द्वारा उत्प्रेरित ऑक्सीकरण की यांत्रिकी का विस्तार से अध्ययन विभिन्न प्रयोगों—जैसे अभिक्रिया मध्यवर्तियों की पहचान, उत्प्रेरण के पश्चात उत्प्रेरक का चरित्रण—तथा संगणकीय अध्ययनों के माध्यम से किया गया। यह कार्य सूक्ष्म रसायनों के उत्पादन हेतु ऑक्सीकरण अभिक्रियाओं में MOF-समर्थित, पृथ्वी पर प्रचुर मात्रा में उपलब्ध धातु उत्प्रेरकों के महत्व को रेखांकित करता है।

अध्याय 4. धातु-कार्बनिक फ्रेमवर्क में सीमाबद्ध मोनो-बाइपाइरिडिल आयरन(III) उत्प्रेरक द्वारा एरीन का क्षेत्र-चयनात्मक ऑक्सीडेटिव ब्रोमिनेशन

एरीन का ऑक्सीडेटिव ब्रोमिनेशन ब्रोमोएरीन के संश्लेषण के लिए एक प्रभावी तथा पर्यावरण-अनुकूल विधि है। इस अध्याय में H_2O_2 को ऑक्सीकारक और KBr को ब्रोमीन स्रोत के रूप में उपयोग करते हुए एरीन के ऑक्सीडेटिव ब्रोमिनेशन हेतु एक अत्यंत सुदृढ़ ज़िरकोनियम-धातु-कार्बनिक फ्रेमवर्क (MOF)-समर्थित मोनो-बाइपाइरिडिल आयरन(III) क्लोराइड उत्प्रेरक (bpy-UiO-FeCl₃) के विकास की रिपोर्ट प्रस्तुत की गई है। bpy-UiO-FeCl₃ उत्प्रेरक विभिन्न प्रतिस्थापित एरीन के लिए उच्च रूपांतरण दर्शाता है और मृदु अभिक्रिया परिस्थितियों में उत्कृष्ट क्षेत्र-चयनात्मकता तथा पुनर्चक्रण क्षमता के साथ पर्याप्त मात्रा में ब्रोमोएरीन प्रदान करता है।

MOF उत्प्रेरक अपनी समांगी समकक्ष प्रणालियों की तुलना में गतिविधि और क्षेत्र-चयनात्मकता—दोनों के संदर्भ में बेहतर प्रदर्शन करता है, जिसका कारण MOF के रंध्रों में सक्रिय स्थलों पर मोनोन्यूक्लियर बाइपाइरिडिल-आयरन(III) प्रजातियों का स्थिरीकरण है। इसके अतिरिक्त, सुदृढ़, सुव्यवस्थित और समान रंध्रयुक्त फ्रेमवर्क के भीतर इन सक्रिय स्थलों का सीमाबद्ध होना आकार-चयनात्मक उत्प्रेरण के माध्यम से ब्रोमिनेशन की क्षेत्र-चयनात्मकता को और अधिक बढ़ाता है। bpy-UiO-FeCl₃ द्वारा उत्प्रेरित एरीन के ऑक्सीडेटिव ब्रोमिनेशन की यांत्रिकी का गहन अध्ययन नियंत्रण प्रयोगों, स्पेक्ट्रोस्कोपिक विश्लेषणों तथा संगणकीय अध्ययनों के संयोजन से किया गया। ये निष्कर्ष हेलोएरीन के सतत संश्लेषण के लिए पृथ्वी पर प्रचुर मात्रा में उपलब्ध धातुओं पर आधारित विषम उत्प्रेरकों के विकास में MOFs के महत्व को रेखांकित करते हैं।

अध्याय 5. रंध्र-सीमाबद्ध मोनोन्यूक्लियर पाइरिडिलइमीन-इरिडियम(II)-हाइड्राइड पर मीथेन का चयनात्मक मोनोबोरीलेशन

मीथेन के C-H बंध का कीमो-चयनात्मक बोरीलेशन हाल के वर्षों में विशेष ध्यान आकर्षित कर रहा है, क्योंकि मीथेन एक प्रचुर एवं कम लागत वाला कार्बन कच्चा माल है तथा ऑर्गेनोबोरेन उत्पाद कार्बनिक संश्लेषण में बहुपयोगी मध्यवर्ती के रूप में प्रयुक्त होते हैं। तथापि, मीथेन का उच्च उपज के साथ कीमो-चयनात्मक मोनोबोरीलेशन प्राप्त करना अब भी एक बड़ी चुनौती बना हुआ है। इस अध्याय में एक धातु-कार्बनिक फ्रेमवर्क में सीमाबद्ध पाइरिडिलइमीन-इरिडियम हाइड्राइड उत्प्रेरक (pyrim-UiO-IrH) के विकास की रिपोर्ट प्रस्तुत की गई है, जो बिस(पिनाकोलैटो)डाइबोरोन का उपयोग करते हुए 130 °C पर मीथेन के C-H बोरीलेशन में अत्यंत प्रभावी है और 98% GC-उपज के साथ मिथाइल बोरोनिक अम्ल पिनाकोल एस्टर (CH₃Bpin) प्रदान करता है।

एक विषम उत्प्रेरक के रूप में, pyrim-UiO-IrH को कम से कम पाँच बार पुनर्चक्रित और पुनः उपयोग किया जा सकता है, तथा संरचना या स्फटिकीयता में किसी उल्लेखनीय परिवर्तन के बिना इसकी गतिविधि स्थिर बनी रहती है, जिससे कुल टर्नओवर संख्या (TON) 980 तक पहुँचती है। विशेष रूप से, pyrim-UiO-IrH अपने समांगी नियंत्रण उत्प्रेरक ([Ph(pyrim)(PhCO₂Me)₂]IrH) की तुलना में कम से कम 24 गुना अधिक सक्रिय पाया गया, जिसका कारण लिंक्स पर सक्रिय-स्थल पृथक्करण के माध्यम से pyrim-IrH प्रजाति की अधिक स्थिरता है, जो अंतःआणविक अपघटन को रोकती है। यांत्रिक अध्ययन से संकेत मिलता है कि मीथेन का Ir³⁺(Bpin)₂(H) प्रजाति पर ऑक्सीडेटिव एडिशन होकर Ir⁵⁺(Bpin)₂(CH₃)(H)₂ का निर्माण होना टर्नओवर-सीमित चरण है।

अध्याय 6. मोनो-बाइपाइरिडिल-निकेल(II) हाइड्राइड उत्प्रेरक द्वारा मीथेन का चयनात्मक मोनोबोरीलेशन

इस अध्याय में मीथेन के C-H बोरीलेशन हेतु पृथ्वी पर प्रचुर मात्रा में उपलब्ध धातु पर आधारित एक उत्प्रेरक के विकास की रिपोर्ट प्रस्तुत की गई है। बाइपाइरिडीन-कार्यात्मकित ज़िरकोनियम धातु-कार्बनिक फ्रेमवर्क (MOF) का NiBr_2 के साथ पोस्ट-सिंथेटिक मेटलेशन करने के पश्चात NaEt_3BH से उपचार करने पर सक्रिय-स्थल पृथक्करण के माध्यम से MOF-समर्थित मोनोमैरिक बाइपाइरिडिल-निकेल(II) डाइहाइड्राइड प्रजातियाँ प्राप्त होती हैं। यह विषम एवं पुनर्चक्रणीय निकेल उत्प्रेरक 200 °C पर पिनाकोलबोरेन (HBpin) का उपयोग करते हुए मीथेन का चयनात्मक बोरीलेशन करता है और 61% उपज के साथ CH_3Bpin प्रदान करता है, जहाँ टर्नओवर संख्या (TON) 1388 तक पहुँचती है।

समान रंध्रयुक्त MOF के भीतर सक्रिय NiH_2 प्रजातियों का सीमाबद्ध होना आकार-चयनात्मक उत्प्रेरण के माध्यम से मीथेन के चयनात्मक मोनोबोरीलेशन को संभव बनाता है, क्योंकि यह स्थानिक रूप से अवरुद्ध अतिबोरीलेशन उत्पादों के निर्माण को रोकता है। MOF-Ni उत्प्रेरक के विपरीत, इसका समांगी नियंत्रण उत्प्रेरक अंतःआणविक अपघटन के कारण मीथेन बोरीलेशन में लगभग निष्क्रिय पाया गया। स्पेक्ट्रोस्कोपिक, गतिज एवं नियंत्रण प्रयोगों के साथ-साथ DFT गणनाओं को सम्मिलित करते हुए किए गए यांत्रिक अध्ययनों से यह स्पष्ट हुआ कि MOF द्वारा मोनोन्यूक्लियर बाइपाइरिडिल-निकेल डाइहाइड्राइड तथा डाइबोरील प्रजातियों का स्थिरीकरण, टर्नओवर-सीमित σ -बॉन्ड मेटाथेसिस के माध्यम से प्रभावी मीथेन बोरीलेशन प्राप्त करने के लिए अत्यंत महत्वपूर्ण है। यह कार्य मीथेन तथा अन्य निष्क्रिय अणुओं के कीमो-चयनात्मक कार्यात्मकन द्वारा मूल्यवान रसायनों में रूपांतरण हेतु MOF-आधारित, प्रचुर धातु उत्प्रेरकों की अभिकल्पना में उल्लेखनीय संभावनाएँ प्रदर्शित करता है।

अध्याय 7. CO_2 के एथेनॉल में हाइड्रोजनीकरण के दौरान रूपांतरण-चयनात्मकता ट्रेड-ऑफ को दूर करने हेतु MOFs की संरचनात्मक गतिकी का उपयोग

इस अध्ययन में, हम MIL-53(AI) मेटल-ऑर्गेनिक फ्रेमवर्क की अंतर्निहित संरचनात्मक गतिकी का उपयोग करके एक अत्यधिक दक्ष एवं चयनात्मक जलीय-चरण विषम उत्प्रेरक MIL-53-Co(OH) विकसित करते हैं। इसमें MOF नोड्स पर एंकर किए गए परमाणु-स्तर पर प्रकीर्णित Co^{2+} -OH सक्रिय प्रजातियाँ उपस्थित हैं, जो CO_2 के एथेनॉल में होमोलोगेशन के लिए उत्तरदायी हैं। सौम्य अभिक्रिया परिस्थितियों (130 °C, 20 bar, $\text{H}_2/\text{CO}_2 = 3$) में MIL-53-Co(OH) 92% CO_2 रूपांतरण, 93% एथेनॉल चयनात्मकता तथा $10,133 \mu\text{mol gcat}^{-1} \text{h}^{-1}$ की एथेनॉल उत्पादकता प्रदर्शित करता है। कठोर MIL-68(AI) फ्रेमवर्क तथा श्वसन-दबित MIL-53 एनालॉग्स के साथ किए गए तुलनात्मक अध्ययनों से स्पष्ट होता है कि जाली (lattice) की लचीलापन एक निर्णायक कारक है, जो एथेनॉल उत्पादकता को कम से कम 3.5-गुना बढ़ाता है तथा CH_3OH के निर्माण को प्रभावी रूप से दबाता है। संयुक्त प्रायोगिक, संरचनात्मक और संगणकीय अध्ययनों से पता चलता है कि प्रतिवर्ती संकीर्ण-छिद्र (np) $\rightleftharpoons$ विशाल-छिद्र (lp) श्वसन व्यवहार समय-समय पर $\text{Al}_2(\mu_3\text{-O-Co(OH)})$ नोड की ज्यामिति को परिवर्तित करता है, जिससे इन-सिटू CH_3OH सक्रियण और उसके बाद CO समावेशन (insertion) का समन्वय होता है और C-C बंध निर्माण को बढ़ावा मिलता है। np $\rightarrow$ lp संक्रमण के दौरान, क्षणिक जाली विस्तार $\text{Al}-(\mu_3\text{-O-Co(OH)})$ -Al हिंग को शिथिल करता है, जिससे Co-H बंध और CH_3OH के C-O बंध के बीच σ -बंध मेटाथेसिस की सक्रियण बाधा में उल्लेखनीय कमी आती है—जो उत्प्रेरक चक्र का एक प्रमुख प्राथमिक चरण है।

समग्र रूप से, यह कार्य दर्शाता है कि सक्रिय-स्थल अभियांत्रिकी की एक रणनीति के रूप में MOF की संरचनात्मक गतिकी का दोहन कठिन रासायनिक रूपांतरणों के लिए अत्यधिक दक्ष एवं चयनात्मक विषम उत्प्रेरकों के डिज़ाइन हेतु एक शक्तिशाली और सामान्यीकृत दृष्टिकोण प्रदान करता है।

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List of Acronyms/Abbreviation

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
UiO	Universitetet i Oslo	DUT	Dresden University of Technology
<i>n</i> -BuLi	n-butyllithium	TON	Turnover Number
INT	Intermediate	TS	Transition state
DMPO	5,5-dimethyl-1-pyrroline N- oxide	R _f	Retention Factor
PCM	Polarizable Continuum Model	IEFPCM	Integral Equation Formalism Polarizable Continuum Model

Chapter 1: Introduction to Metal-Organic Frameworks

Abstract: 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 isorecticular 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.

1.1. Heterogeneous Catalysts and Functional Porous Materials

Catalysis underpins the growth and sustainability of modern chemical industries by enabling the efficient and selective conversion of raw materials into fuels, chemicals, and value-added products. Among the different catalytic paradigms, heterogeneous catalysis occupies a dominant position in industrial practice owing to its mechanical stability, ease of separation from reaction media, reusability, and suitability for continuous processing.¹⁻⁵ Increasing demands for higher efficiency, improved selectivity, and long-term operational stability have consequently stimulated intensive efforts toward the development of advanced solid catalyst systems. Traditional heterogeneous catalysts generally rely on solid supports such as zeolites, carbon-based materials (including carbon nanotubes), and mesoporous silica to anchor catalytically active metal species. In many cases, these supports give rise to multi-site catalytic architectures, where metal centers are present in a variety of coordination and electronic environments.^{6,7} Such site heterogeneity results in a broad distribution of redox characteristics and Lewis acid strengths, leading to variable substrate-catalyst interactions. As a result, mechanistic understanding at the molecular level becomes complicated, while practical issues such as suboptimal selectivity, high reaction temperatures, and ambiguity regarding the true active species frequently persist.

In response to these challenges, single-site heterogeneous catalysts (SSHCs) have attracted growing attention.^{8,9} These systems are characterized by atomically or molecularly isolated active centers that are uniformly distributed on a solid support. The uniformity of the active sites ensures consistent binding interactions with reactant molecules, thereby minimizing energetic disparities and enabling catalytic transformations under comparatively mild conditions. SSHCs often exhibit superior selectivity and catalytic efficiency relative to conventional multi-site catalysts. Moreover, their well-defined nature permits the application of advanced spectroscopic and microscopic techniques, allowing detailed interrogation of active-site structures and reaction mechanisms. Accordingly, the rational engineering of solid supports capable of stabilizing isolated catalytic sites has emerged as a key focus in heterogeneous catalysis research.

Porous materials are particularly well suited to this purpose, as their internal cavities and high surface areas promote effective host-guest interactions, molecular confinement, and site isolation. Based on pore dimensions, porous solids are commonly classified as microporous (<2 nm), mesoporous (2-50 nm), or macroporous (>50 nm). Owing to these features, porous materials have found extensive use in ion exchange, adsorption, separation, and catalytic

applications.^{10,11} Among them, zeolites represent one of the earliest and most thoroughly investigated classes of microporous materials. Initially discovered as naturally occurring aluminosilicate minerals and later synthesized artificially, zeolites consist of crystalline Si–O–Al frameworks containing well-defined sub-nanometric channels (Figure 1.1).¹² Their controlled pore architecture, adjustable acidity, and ion-exchange capacity have rendered them indispensable in petrochemical processing, biomass upgrading, and environmental catalysis. Despite their widespread industrial relevance, zeolites possess inherent limitations, notably their small pore apertures, which restrict the diffusion of bulky reactants, and their limited flexibility for atomic-level modification of pore surfaces. These shortcomings prompted the development of ordered mesoporous silicas in the early 1990s, which feature larger pore sizes and enhanced mass-transport properties. Although mesoporous materials significantly broadened the scope of heterogeneous catalysis to include reactions involving larger molecules,¹³ their lower crystallinity and less precisely defined structures often hinder accurate structure-activity correlations and in-depth mechanistic analyses.

To address the limitations associated with both microporous zeolites and mesoporous silicas, a new family of crystalline porous materials, collectively termed reticular materials, has emerged. This class primarily encompasses metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), which provide unparalleled control over pore topology, chemical functionality, and active-site environments.^{14,15} MOFs are hybrid organic-inorganic materials assembled from metal ions or metal clusters connected by organic linkers through coordination bonds, whereas COFs are fully organic porous networks constructed via strong covalent bonds between light elements such as carbon, nitrogen, and oxygen. Although COFs offer low density and structural order, their relatively limited thermal stability and, in certain cases, the absence of permanent porosity constrain their broader application in heterogeneous catalysis.¹⁶

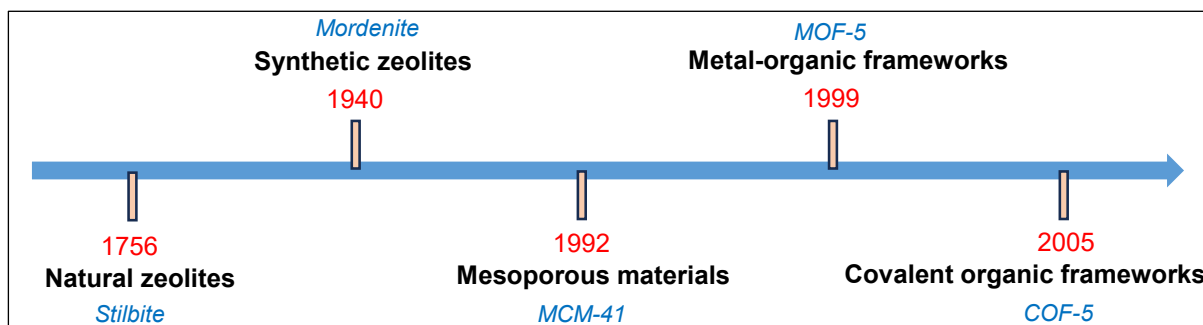


Figure 1.1. Key milestones in the development of functional porous materials.

By contrast, MOFs have emerged as highly versatile platforms for heterogeneous and single-site catalysis due to their exceptionally high surface areas, modular and isorecticular

architectures, and amenability to post-synthetic modification. These characteristics enable precise tuning of the spatial arrangement, electronic properties, and accessibility of isolated active sites, establishing MOFs as highly promising candidates for the development of next-generation single-site heterogeneous catalyst systems.

1.2. Metal-Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) constitute a distinctive class of crystalline porous solids that have progressed from simple coordination compounds into highly sophisticated, architecturally precise networks over the past few decades. This rapid evolution has profoundly influenced materials chemistry by merging classical coordination chemistry with modern reticular design principles. MOFs are constructed from metal ions or metal clusters interconnected by multitopic organic linkers through coordination bonds, resulting in extended three-dimensional frameworks with long-range order (Figure 1.2).^{17,18} The inorganic components, commonly referred to as metal nodes, often consist of single metal ions or oxo- or hydroxo-bridged clusters that function as secondary building units (SBUs), while the organic linkers serve as structural connectors that define the geometry and dimensionality of the lattice.¹⁹ The deliberate selection of metal nodes and linkers allows precise control over framework topology, pore size, and connectivity, enabling the formation of structures ranging from microporous to mesoporous regimes.

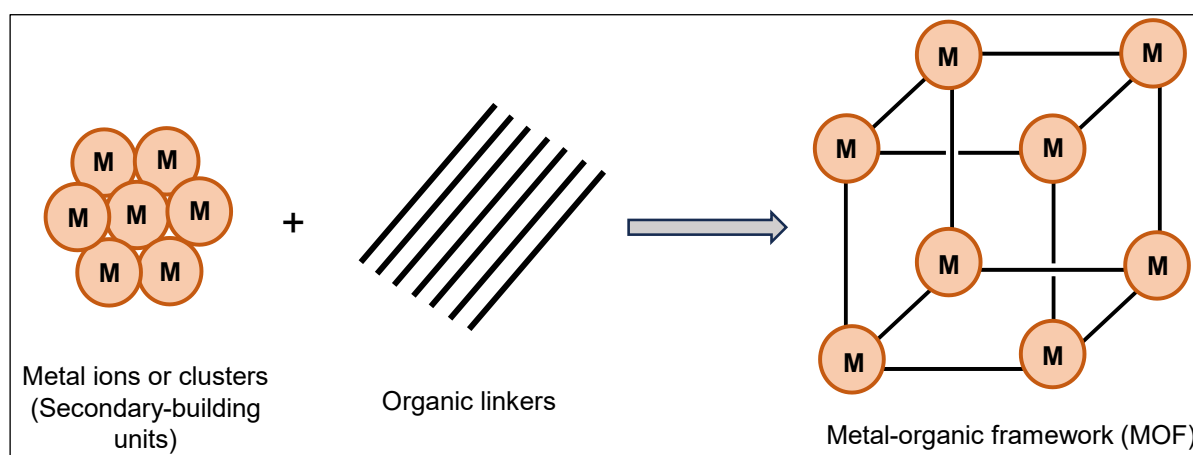


Figure 1.2. Schematic illustration of a MOF and its fundamental components.

A defining advantage of MOFs lies in their exceptional tunability. Variations in linker length, rigidity, and functional group substitution, as well as changes in metal identity or coordination environment, provide a powerful means to regulate pore architecture, surface chemistry, and electronic properties. This modularity enables systematic tailoring of MOFs for

targeted chemical functions, distinguishing them from conventional heterogeneous supports such as zeolites, mesoporous silica, and activated carbon, which offer comparatively limited structural and chemical flexibility. Furthermore, the highly porous nature of MOFs permits molecular-level design strategies, wherein framework properties can be modified either during synthesis or after framework construction. Post-synthetic modification (PSM) represents a particularly versatile approach to tuning MOF functionality without compromising the integrity of the crystalline framework. PSM strategies include the incorporation of additional metal species at coordinatively unsaturated sites, ligand functionalization, metal or linker exchange, and the grafting of catalytically active moieties onto pre-existing frameworks. These transformations enable precise adjustment of chemical reactivity and catalytic behavior while retaining the ordered porous structure.²⁰ As a result, MOFs have been extensively explored as customizable platforms for heterogeneous and single-site catalysis,^{21–23} as well as for applications in gas storage,²⁴ separation,²⁵ sensing,^{26,27} and industrially relevant chemical transformations^{28,29}. Collectively, the structural modularity, design precision, and post-synthetic adaptability of MOFs underscore their unique position among porous materials and highlight their potential for the rational development of next-generation functional catalysts.

1.3. Initial Advancements in Metal-Organic Frameworks

Although coordination polymers and extended metal-ligand networks can be traced back to the nineteenth century, the conceptual origin of modern metal-organic frameworks (MOFs) is widely attributed to the pioneering work of Richard Robson in the late twentieth century. Robson's vision emerged from an unconventional starting point during his tenure at the University of Melbourne, where he was tasked with developing physical models to aid undergraduate teaching. While constructing three-dimensional models using wooden spheres and rods to represent atomic connectivity, Robson conceived the idea of assembling extended architectures not from individual atoms, but from larger molecular building blocks. This insight marked a decisive conceptual shift toward the deliberate design of infinite coordination networks. After several years of reflection, Robson translated this idea into practice by synthesizing crystalline frameworks in which metal ions were linked by multitopic organic ligands, producing diamond-like architectures with large internal cavities occupied by solvent molecules and counterions. These results, achieved in collaboration with crystallographer Bernard Hoskins and later Brendan Abrahams, laid the foundation for what would later be recognized as coordination polymers and early MOF-like materials. Importantly, Robson

anticipated key features that would define the field, including permanent porosity, ion-exchange behavior, and the potential incorporation of catalytic sites within extended frameworks.^{30,31}

Despite their conceptual importance, many of Robson's early frameworks suffered from limited structural stability, prompting further developments aimed at achieving robust and functional porous materials. Significant progress in this direction was realized through the work of Susumu Kitagawa in Japan, who systematically addressed the challenge of framework stability while preserving porosity. Initially exploring copper(I)-based coordination chemistry, Kitagawa recognized the advantages of closed-shell metal ions for constructing extended crystalline structures. His discovery of porous coordination networks in the early 1990s, including two-dimensional materials containing guest molecules within well-defined cavities, represented a critical turning point. Although these early structures exhibited limited stability due to weak metal-ligand interactions, Kitagawa persisted in refining his design strategy. By employing metal ions with stronger coordination bonds, such as cobalt(II), in combination with neutral organic linkers, he succeeded in creating frameworks that were both structurally robust and permanently porous. These materials demonstrated reversible gas adsorption under ambient conditions, providing the first compelling evidence that coordination frameworks could function as practical porous solids.^{32,33} Kitagawa further articulated a generational classification of MOFs, progressing from aesthetically intriguing but unstable networks to chemically robust, flexible, and ultimately multifunctional frameworks, thereby establishing a long-term vision for the field.

In parallel, Omar M. Yaghi played a decisive role in transforming MOFs into a broadly applicable materials platform through the introduction of reticular chemistry, a design philosophy based on assembling rigid molecular building units into predetermined crystalline networks. Beginning in the mid-1990s, Yaghi demonstrated that metal ions and organic linkers could be systematically combined to produce highly stable, permanently porous frameworks.^{34,35} His seminal contributions included the coining of the term metal-organic framework and the synthesis of landmark materials such as MOF-5, which exhibited unprecedented surface area, thermal stability, and permanent porosity even after complete guest removal.³⁶ These discoveries established MOFs as viable materials for gas storage, separation, and catalysis, and catalyzed widespread academic and industrial interest. The subsequent development of isorecticular frameworks, wherein pore size and functionality could be predictably tuned without altering underlying topology, further underscored the power of reticular design principles.

Collectively, the foundational contributions of Robson, Kitagawa, and Yaghi transformed MOFs from conceptual coordination networks into a mature class of functional materials characterized by design precision, structural diversity, and practical utility. Their work laid the intellectual and experimental groundwork for the rapid expansion of MOF research across chemistry, materials science, and chemical engineering.

1.4. Nobel Prize Recognition of Metal-Organic Frameworks

The profound scientific and technological impact of metal-organic frameworks was formally recognized at the highest international level when the 2025 Nobel Prize in Chemistry was awarded for the development of metal-organic frameworks. This recognition honored the pioneering and complementary contributions of Richard Robson, Omar M. Yaghi, and Susumu Kitagawa. The Nobel Prize highlighted how the deliberate assembly of metal nodes and organic linkers enabled unprecedented control over structure, porosity, and function, ultimately leading to wide-ranging applications in catalysis, gas storage, separation, and energy-related technologies. This milestone underscored the central role of MOFs in modern chemistry and affirmed their status as one of the most influential material classes of the twenty-first century.

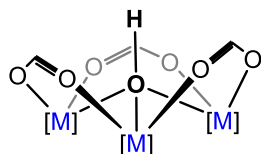
1.5. Secondary Building Units (SBUs) in Metal-Organic Frameworks

Secondary building units (SBUs) constitute the fundamental inorganic components of metal-organic frameworks (MOFs) and play a decisive role in the construction of periodic and potentially porous architectures through their connection with multitopic organic linkers. As preorganized metal-containing entities, SBUs govern the underlying topology of MOFs by defining the spatial arrangement and connectivity of the framework. These units are generated through the coordination of metal ions or metal clusters with inorganic or organic ligands, forming rigid and well-defined structural motifs that serve as the backbone of the crystalline network. Consequently, the geometry, dimensionality, and structural stability of a MOF are strongly influenced by the nature of its SBUs.^{37,38}

The structural characteristics of an SBU including its shape, charge, nuclearity, and coordination environment—determine how it interacts with organic linkers and, in turn, dictate key material properties such as framework topology, pore architecture, and mechanical robustness. By controlling these parameters, it is possible to rationally design MOFs with tailored porosity and functionality. SBUs can be classified according to their dimensionality

and structural motif, ranging from zero-dimensional (0D) discrete metal clusters to one-dimensional (1D) chain-like units, two-dimensional (2D) sheet-based motifs, and three-dimensional (3D) extended inorganic substructures. A wide variety of SBUs have been reported to date, giving rise to the rich structural diversity of MOFs (Figure 1.3).

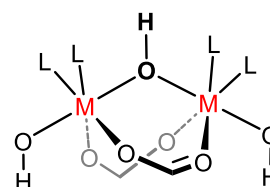
M⁴⁺ Hydroxyl Clusters



$M_6O_4(OH)_4$ with 6, 8, or 12 carboxylates

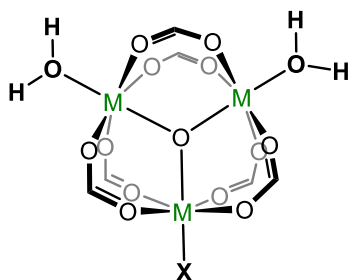
$M = Zr^{4+}, Hf^{4+}, Ce^{4+}$

M³⁺ Hydroxyl Clusters



$M = Cr^{3+}, Fe^{3+}, Al^{3+}$

M³⁺ Aqua Clusters

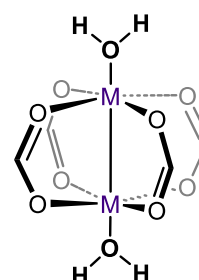


$M_3O(H_2O)_2X$

$M = Cr^{3+}, Ga^{3+}, In^{3+}, Fe^{3+}$

$X = F^-, Cl^-, OH^-$

M²⁺ Aqua Clusters



$M_2(H_2O)_2$

$M = Cu^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}$

Figure 1.3. Examples of various types of SBUs involved in the synthesis of MOF.

Beyond their structural function, SBUs play a crucial role in defining the chemical and physical characteristics that govern MOF performance. The identity of the metal species within an SBU directly influences properties such as electronic structure, charge distribution, and resistance to thermal or chemical degradation. Frameworks constructed from high-valent metal centers, including zirconium (Zr^{4+}) and aluminum (Al^{3+}), typically exhibit strong metal-ligand bonds, which impart exceptional thermal and hydrolytic stability.³⁹ These attributes render such MOFs particularly suitable for demanding applications where chemical robustness is essential, including gas storage, separation, and water treatment. In contrast, SBUs incorporating redox-active metals, such as iron (Fe^{3+}) or cobalt (Co^{2+}), introduce electronically accessible metal centers that can participate directly in redox processes, thereby enabling catalytic functionality.⁴⁰ Additionally, the presence of coordinatively unsaturated or open metal sites within SBUs can significantly enhance adsorption behavior by strengthening interactions with

guest molecules. The properties of SBUs can be further tuned through strategies such as metal substitution, ligand functionalization, or post-synthetic modification, providing a versatile platform for the rational design of MOFs tailored to specific chemical applications.^{41,42}

1.6. Organic Linkers in Metal-Organic Frameworks

Organic linkers are essential components of MOFs, as they play a decisive role in controlling framework stability, porosity, and overall functionality. Acting as molecular connectors, these linkers bridge metal nodes to generate extended coordination architectures. Commonly employed linkers are derived from polycarboxylates, imidazoles, phosphonates, and other multitopic ligands, whose structural characteristics strongly influence the properties of the resulting framework.^{43,44} The diversity of reported organic linkers has led to an expansive landscape of MOF architectures (Figure 1.4). Parameters such as linker length, rigidity, and chemical functionality directly affect pore dimensions, internal surface area, and the accessibility of active sites within the MOF.

Rigid aromatic linkers, including 1,4-benzenedicarboxylate (BDC) and 2,6-naphthalenedicarboxylate (NDC), often enhance thermal and chemical stability due to their π -conjugated backbones, leading to robust framework architectures. In contrast, more flexible aliphatic linkers can impart structural adaptability, enabling dynamic or stimuli-responsive behavior under external triggers such as guest adsorption or changes in temperature. Moreover, the incorporation of functional groups such as $-\text{NH}_2$, $-\text{NO}_2$, $-\text{OH}$, or $-\text{SH}$ into organic linkers introduces chemically addressable sites that facilitate post-synthetic modification, strengthen host-guest interactions, or directly participate in catalytic processes.^{45,46} Through deliberate linker selection and molecular design, MOF properties can be precisely tailored, making these materials highly versatile platforms for applications in gas storage, catalysis, and molecular separations.

1.7. Diverse Methods for Synthesis of MOF

Metal-organic frameworks (MOFs) represent a highly versatile class of porous materials that can be prepared through a wide range of synthetic strategies, each enabling precise control over crystal structure, morphology, and functional characteristics. Over the years, numerous synthesis routes including solvothermal, mechanochemical, electrochemical, sonochemical,

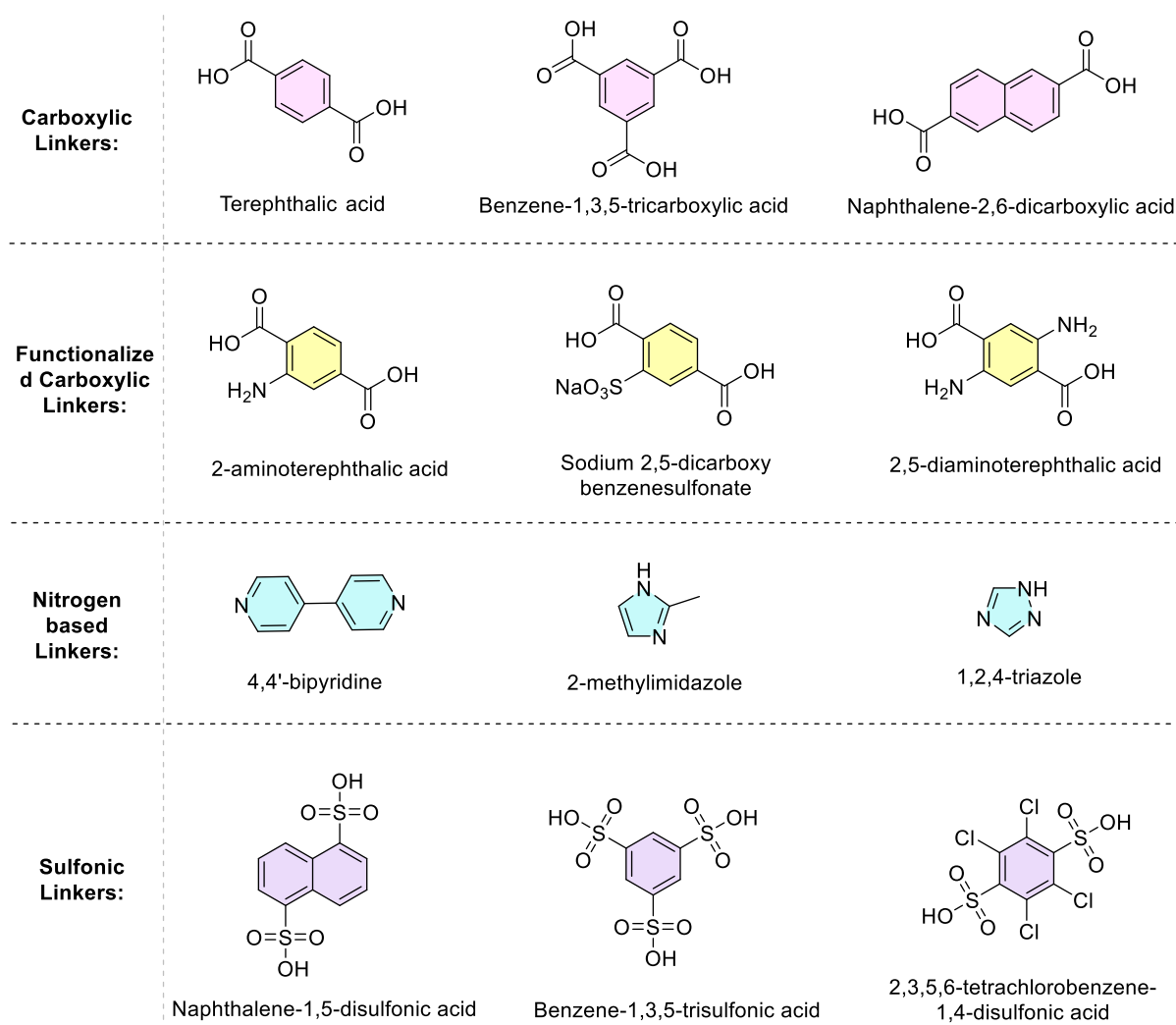


Figure 1.4. Examples of organic linkers illustrating the structural diversity used in MOF synthesis.

microwave-assisted, spray-drying, diffusion-based, and vapor deposition methods—have been developed to tailor MOF properties for specific applications.

1.7.1. Solvothermal Method

The solvothermal method involves heating a mixture of metal salts and organic linkers in aprotic or protic solvents, most commonly formamide-based solvents such as *N,N*-dimethylformamide (DMF), *N,N*-diethylformamide (DEF), and dimethyl sulfoxide (DMSO).⁴⁷ Under sealed conditions, controlled temperature and pressure promote nucleation and crystal growth, leading to the formation of MOFs with high yields and good crystallinity. Owing to its operational simplicity and reproducibility, the solvothermal approach remains one of the most widely used techniques for MOF synthesis.

Advantages

- One-step synthesis of MOFs
- Formation of highly crystalline frameworks with well-defined order
- Operation at relatively moderate temperatures

Disadvantages

- Higher likelihood of by-product formation due to solvent or precursor decomposition
- Longer reaction times compared to alternative synthesis methods

1.7.2. Microwave-Assisted Method

Microwave-assisted synthesis is widely employed for the rapid preparation of MOFs, particularly for achieving reduced particle sizes and accelerated crystallization. In this method, heating occurs through the interaction of electromagnetic radiation with polar solvent molecules or ionic species, resulting in efficient dielectric heating.⁴⁸ Consequently, thermal energy is generated directly within the reaction medium rather than being transferred from an external heat source. Typically, a mixture of metal precursors and organic linkers dissolved in a suitable solvent is sealed in a Teflon-lined vessel and exposed to microwave irradiation for a controlled period. The applied microwave frequency induces molecular rotation and collision, leading to a rapid increase in temperature and promoting fast nucleation and crystallization of MOFs with well-defined structures.

Advantages

- Extremely rapid MOF crystallization
- Formation of phase-pure materials with high chemical purity
- Uniform particle morphology due to homogeneous heating

Disadvantages

- Limited reproducibility in yields arising from uneven microwave-solvent interactions
- Challenging scalability and limited applicability for large-scale industrial production

1.7.3. Electrochemical Method

The electrochemical method involves the application of an external potential to drive the formation of MOFs directly at the electrode-solution interface. In this approach, metal electrodes are immersed in an electrolyte solution containing dissolved organic linkers.⁴⁹ Upon

application of a controlled voltage, metal ions are generated electrochemically from the anode and subsequently react with the organic ligands in the vicinity of the electrode surface, leading to the nucleation and growth of MOF materials. A distinguishing feature of this method is that metal ions are supplied in situ through electrochemical dissolution rather than from pre-added metal salts, enabling precise control over the rate of metal ion generation. This allows real-time regulation of MOF formation by adjusting electrochemical parameters such as voltage and current.

Advantages

- Fine control over MOF synthesis through real-time adjustment of applied potential
- Mild reaction conditions, often at ambient temperature and pressure
- Shorter synthesis times compared to conventional solvothermal methods

Disadvantages

- Variable or poor crystallinity of the resulting MOF structures
- Generally low yields, limiting suitability for bulk material production

1.7.4. Mechanochemical Method

The mechanochemical method is a solvent-free approach for the synthesis of MOFs that relies on mechanical energy to drive chemical reactions between metal precursors and organic linkers. In this technique, metal salts and organic ligands are subjected to continuous grinding using a mortar and pestle or a ball mill, where repeated impact and friction promote bond cleavage and formation, ultimately yielding a three-dimensional crystalline porous framework.⁵⁰ Chemical transformations in mechanochemical synthesis occur as a direct consequence of mechanical activation, eliminating the need for external heating or solvents. This method was first reported for MOF synthesis in 2006 and has since attracted considerable attention due to its environmentally benign nature and operational simplicity.

Advantages

- Operates under ambient temperature conditions and requires short reaction times
- Eliminates the use of solvents, making the process environmentally friendly
- Generates fewer and less hazardous by-products

Disadvantages

- Often results in frameworks with lower crystallinity
- Reduced pore size and pore volume compared to solvothermally synthesized MOFs

1.8. MOF Architecture and Design for Catalysis

In the early stages of metal-organic framework research, efforts were primarily directed toward the synthesis of novel structures exhibiting diverse topologies and tunable porosity, while their catalytic potential received comparatively limited attention. With growing understanding of their structural versatility, it became evident that MOFs offer unique advantages as catalysts or catalyst supports, owing to their well-defined active sites, high surface areas, and tailorable chemical environments. The key advantages of MOF-based materials in catalysis are discussed below.

1.8.1. High Porosity and Tunable Pore Dimensions

Metal-organic frameworks possess exceptionally high porosity along with adjustable pore sizes, which facilitate unhindered access to catalytically active sites.^{51,52} The presence of well-defined and interconnected channels enhances the diffusion of reactants and products, thereby improving reaction rates and selectivity. Moreover, precise control over pore geometry enables size- and shape-selective catalysis, allowing MOFs to preferentially stabilize specific transition states or exclude undesired substrates.

1.8.2. Developing Single-Site Catalysts

Single-site catalysts feature well-defined, spatially isolated, and structurally uniform active centers that are homogeneously dispersed within a solid matrix, allowing for high catalytic precision, reproducibility, and mechanistic clarity. MOFs provide an ideal platform for constructing such catalysts owing to their crystalline order, tunable porosity, and modular chemistry.^{53,54} By selectively functionalizing either the metal nodes or organic linkers, MOFs enable effective isolation of catalytic sites, minimizing site–site interactions and undesired side reactions. This structural control not only enhances activity and selectivity but also affords improved stability, accessibility of active sites, and opportunities for rational catalyst design based on structure–performance relationships.

1.8.3. Shape Selectivity and Controlled Product Formation

The precisely defined and hierarchically organized pore architecture of MOFs enables shape-selective catalysis by regulating the diffusion and orientation of reactant molecules toward the active sites.^{55,56} Such molecular sieving effects ensure that only substrates of suitable size and geometry can access the catalytic centers, thereby exerting fine control over reaction pathways. This confinement enhances the selective formation of desired products, suppresses competing side reactions, and effectively prevents over-functionalization, leading to improved selectivity, efficiency, and product purity.

1.8.4. High Stability for Robust Catalysis

Many MOFs demonstrate outstanding thermal, chemical, and mechanical stability, which is crucial for maintaining consistent catalytic activity under demanding reaction conditions.⁵⁷ Their rigid and well-defined frameworks preserve structural integrity during prolonged operation, resisting framework collapse, metal leaching, and deactivation. As a result, MOF-based catalysts enable durable, recyclable, and long-term catalytic performance with minimal loss of activity or selectivity.

1.8.5. Isolated Active Sites for Enhanced Selective Catalysis

MOFs provide spatially well-defined and uniformly isolated catalytic centers embedded within their porous architectures, effectively preventing site aggregation and mutual deactivation.⁵⁸ This isolation creates unique microenvironments that can stabilize reactive or solution-inaccessible species, allowing controlled activation of substrates. Consequently, such precise active-site confinement leads to high catalytic efficiency, improved selectivity, and better control over reaction pathways.

1.8.6. Isoreticularity in Metal-Organic Frameworks

Isoreticular synthesis is a defining feature of metal-organic frameworks, enabling systematic tuning of framework porosity and functionality while preserving the underlying topology. Through this strategy, the chemical and physical properties of MOFs can be deliberately modulated by controlling the nature of the porous architecture. Specifically, isoreticular design involves varying the length and functional groups of the organic linkers; increasing linker size directly leads to frameworks with enlarged pore apertures and accessible voids, thereby

offering precise control over pore dimensions and framework functionality without disrupting structural connectivity.^{59–61}

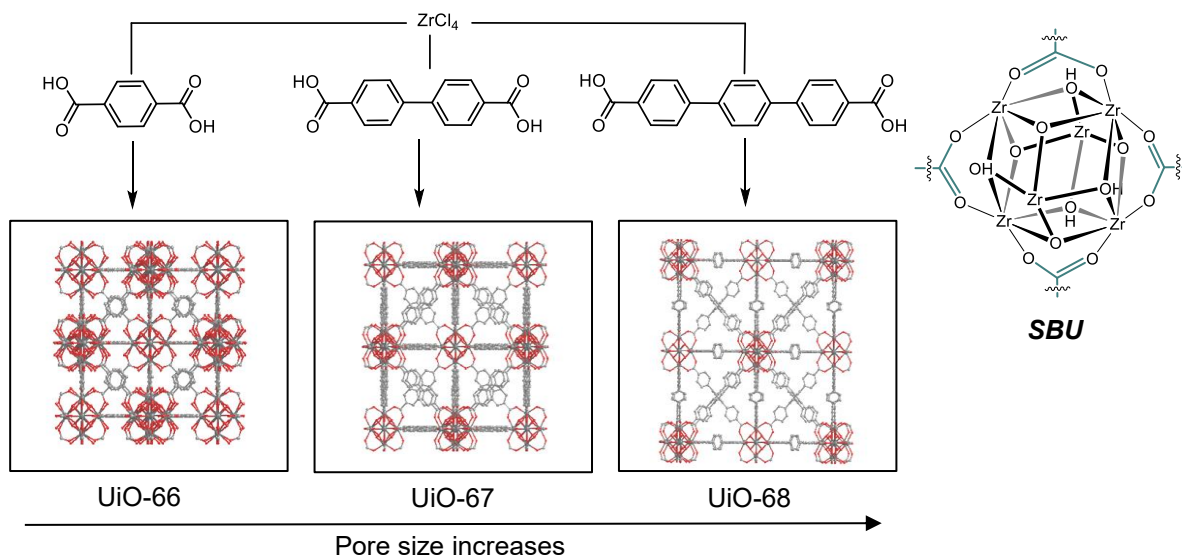


Figure 1.5. Isorecticular zirconium-based UiO-MOFs illustrating systematic pore expansion through linker elongation.

A classical and well-established demonstration of isorectricularity is found in the UiO (University of Oslo) family of MOFs, which comprises a series of zirconium-based frameworks sharing an identical face-centered cubic (fcc) topology but differing in linker length (Figure 1.5). These materials are built from robust $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters that act as secondary building units (SBUs) and are interconnected by linear dicarboxylate linkers. Systematic elongation of the organic linker within this series leads to a gradual expansion of pore size while preserving the original UiO framework topology. UiO-66 employs the shortest linker, 1,4-benzenedicarboxylate (BDC), giving rise to the most compact framework; UiO-67 incorporates the longer [1,1'-biphenyl]-4,4'-dicarboxylate (BPDC) linker, which increases pore dimensions while preserving Zr_6 cluster connectivity; and UiO-68 uses the even more extended [1,1':4,1''-terphenyl]-4,4''-dicarboxylate (TPDC) linker, resulting in a further expansion of the pore system. Despite substantial differences in linker length, the Zr_6 -based SBUs remain unchanged across UiO-66, UiO-67, and UiO-68, ensuring retention of the same fcc topology. Because the $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters coordinate to carboxylate groups located at opposite termini of the linkers, variations in linker size do not disrupt the underlying structural connectivity. This UiO series clearly illustrates how isorecticular expansion can be achieved through systematic linker elongation, enabling precise tuning of pore dimensions without altering the fundamental framework architecture. Beyond the UiO family, this design principle is broadly applicable to

many MOF systems, highlighting the versatility of isorecticular synthesis in rational framework engineering.

1.8.7. Functionality in Metal-Organic Frameworks

Metal-organic frameworks (MOFs) are distinguished by their exceptional tunability, which originates from their modular construction using metal-based secondary building units (SBUs) and organic linkers. This rational assembly enables fine control over the physicochemical characteristics of MOFs, making them highly versatile materials for applications such as gas storage and separation, catalysis, drug delivery, and chemical sensing. The functional behavior of MOFs is governed not only by the inherent properties of the individual ligands and SBUs but also by their cooperative interactions within the framework. Organic linkers, commonly bearing carboxylate, azolate, or related coordinating groups, can be systematically modified to regulate pore dimensions, surface functionality, and framework flexibility. At the same time, SBUs, comprising metal ions or clusters that define the framework nodes, can be tailored through variations in metal identity, oxidation state, and coordination environment, thereby affecting framework robustness, porosity, and electronic features. This complementary and dual-level tunability enables the deliberate design of MOFs with specific, targeted functions, including selective adsorption, enhanced catalytic performance, and stimuli-responsive behavior, through strategic modification of one or both structural components.

1.8.7.1. SBU modifications

Modifications of secondary building units (SBUs) play a crucial role in tailoring the structural and functional properties of metal-organic frameworks (MOFs), providing precise control over their performance characteristics (Figure 1.6). Incorporation of heterometals into inorganic clusters or the construction of mixed-metal nodes enables systematic tuning of redox behavior, catalytic activity, and thermal stability.^{62,63} In addition, post-synthetic approaches such as defect-site metal grafting and manipulation of μ_x -OH groups allow site-specific functionalization of SBUs.^{64–66} These strategies facilitate the introduction of customized active centers without the need to rebuild the framework, thereby maintaining structural integrity while significantly broadening the functional scope of MOFs.

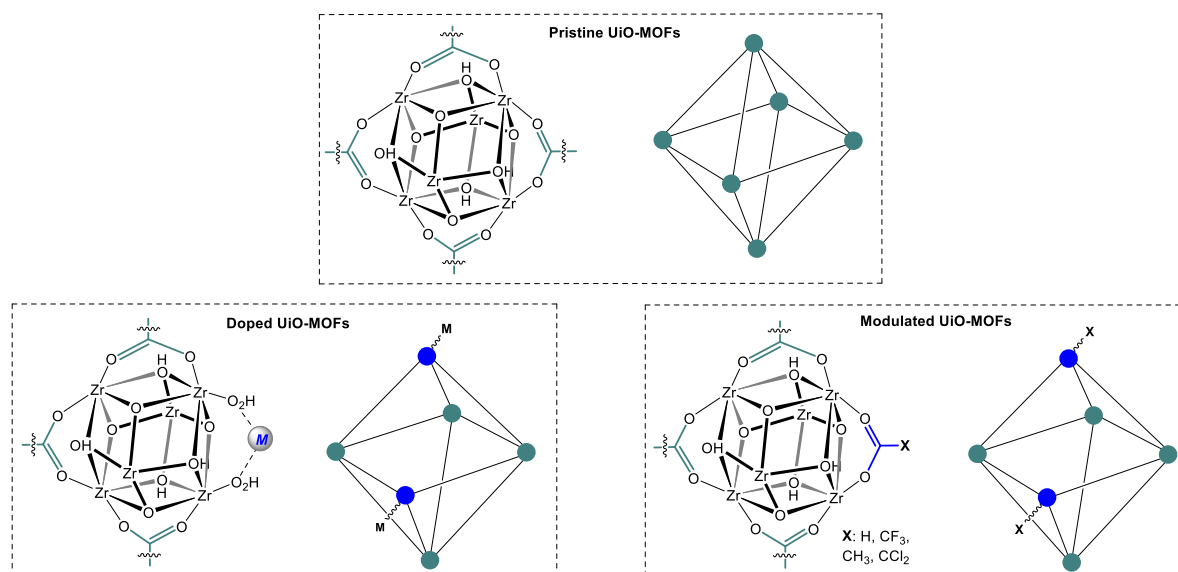


Figure 1.6. Schematic illustration of functionalities introduced through secondary building unit (SBU) modification.

1.8.7.2. Linker modifications

Organic ligands in MOFs act as highly versatile platforms for incorporating functional groups, controlling framework topology, and tuning host-guest interactions.

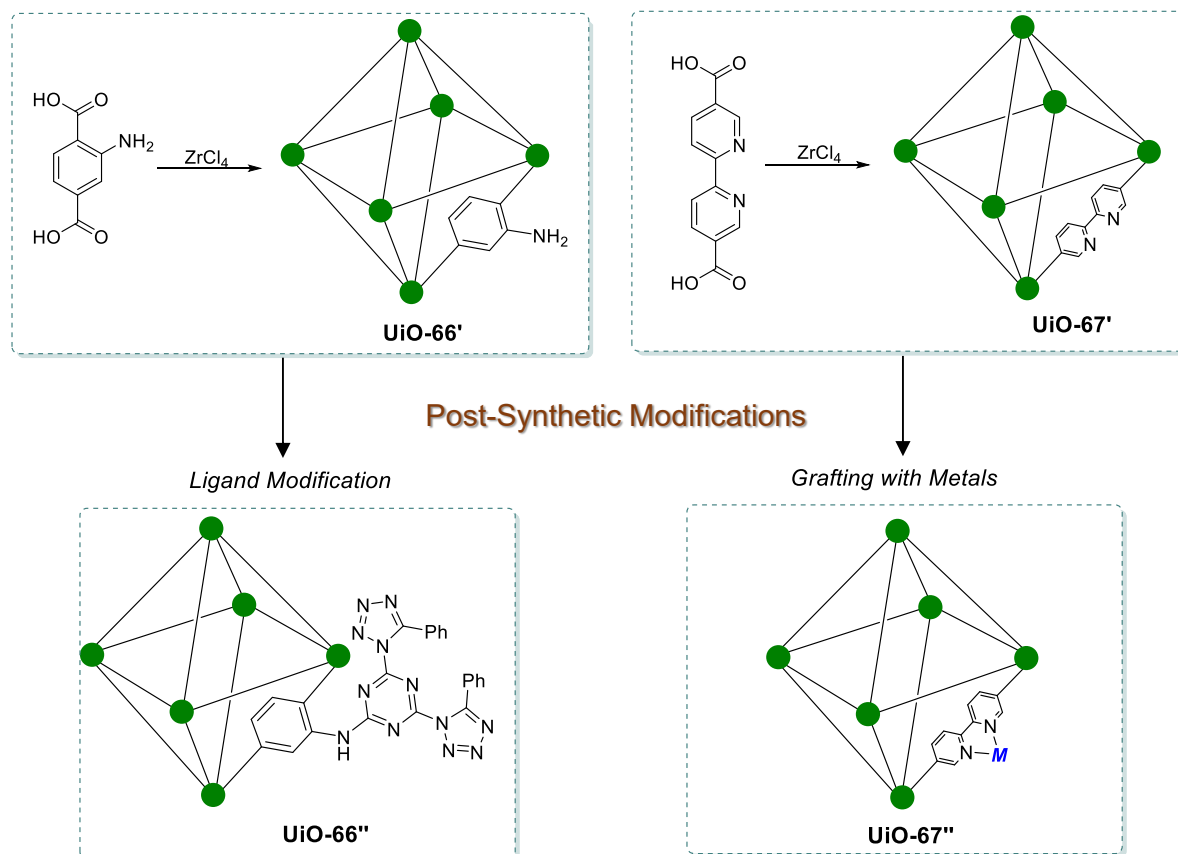


Figure 1.7. Representative functionalities introduced through organic linkers in MOFs.

Pre-synthetic ligand functionalization involves the deliberate design of linkers bearing specific substituents such as amino, hydroxyl, or sulfonate groups—prior to framework construction (Figure 1.7), allowing functionality to be encoded directly into the MOF structure.^{67,68} In addition, post-synthetic modification (PSM) greatly enhances ligand adaptability, as a wide range of organic transformations can be carried out on the linkers without compromising the integrity of the framework. Consequently, ligand engineering represents a key strategy for customizing MOFs with multifunctional properties, enabling their application across a broad spectrum of fields.

1.9. Applications of Metal-Organic Frameworks

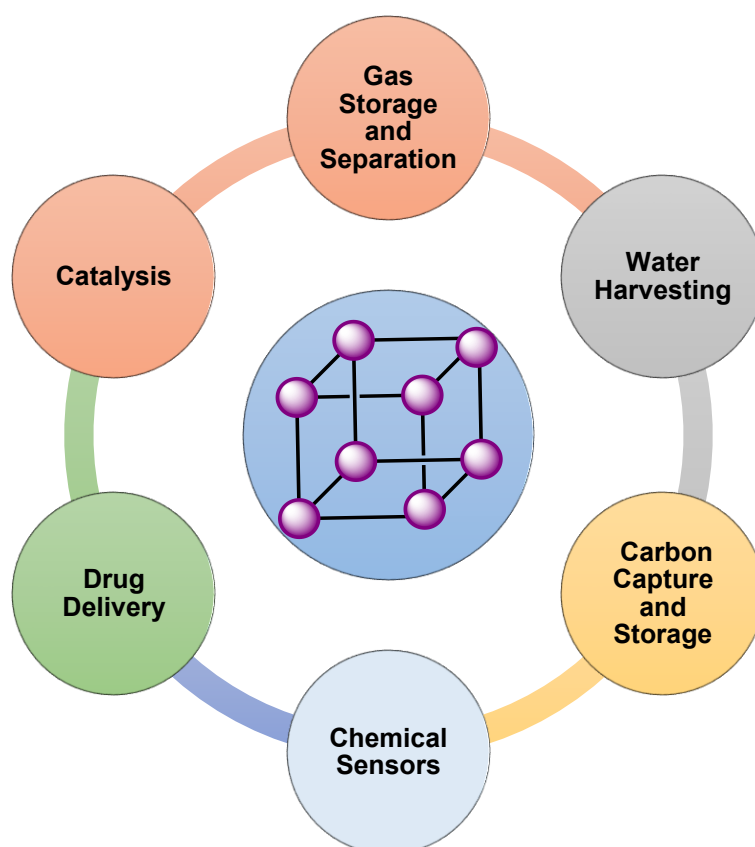


Figure 1.8. Overview of distinct applications of metal-organic frameworks.

1.9.1. Gas Storage and Separation

MOFs offer significant advantages for gas storage and separation owing to their high porosity, structural robustness, excellent thermal and chemical stability, and tunable pore environments.^{69–73} The principle of selective gas adsorption relies on variations in framework

architecture, which influence pore size, shape, and surface chemistry, allowing MOFs to preferentially adsorb specific gas molecules from mixtures. MOFs have demonstrated exceptional performance in storing and separating gases such as hydrogen, methane, and natural gas. For example:

- MOF-210 achieves a hydrogen storage capacity of 17.6 wt% at 77 K, attributed to its exceptionally high surface area of 6,240 m²/g.^{74,75}
- UiO-66-NH₂ enhances methane storage to 230 cm³(STP)/cm³ at 65 bar, exceeding the capacity of activated carbon by approximately 30%.⁷⁶

1.9.2. Carbon Capture and Storage (CCS)

MOFs are emerging as powerful materials for carbon capture technologies owing to their ultrahigh surface areas, adjustable pore environments, and strong affinity for CO₂.^{77–79} Their tunable pore chemistry enables selective adsorption of CO₂ even in the presence of competing gases. For example:

- HKUST-1 (Cu-BTC) exhibits a CO₂ uptake of 23.5 wt% under flue gas-relevant conditions (40 °C, 1 bar), highlighting its potential for post-combustion carbon capture.^{80,81}
- Zirconium-based NU-1000 MOF shows a CO₂ adsorption capacity of 4.2 mmol g⁻¹ at ambient conditions with approximately 90% selectivity over nitrogen, making it particularly attractive for direct air capture applications.⁸²

1.9.3. Water Harvesting

MOFs offer promising solutions to critical challenges such as water scarcity and the high energy demand of conventional cooling and purification systems by enabling efficient adsorption-driven processes under mild conditions.⁸³ For example:

- MOF-303, an aluminum-based framework, can harvest up to 0.7 L of water per kg of MOF per day from arid air with only 20% relative humidity using solar energy, as demonstrated by researchers at UC Berkeley.⁸⁴
- CAU-10-H exhibits exceptional performance in water purification, achieving up to 99% removal efficiency of perfluorinated compounds (PFCs) from industrial wastewater, thereby addressing persistent environmental pollution.^{85,86}

1.9.4. Drug Delivery

Owing to their highly porous architectures, MOFs exhibit a strong capability to encapsulate and retain guest molecules within their frameworks. A key criterion in the selection of effective drug carriers is high loading capacity, making MOFs particularly attractive due to their ability to accommodate and transport substantial amounts of therapeutic agents. As a result, MOFs are increasingly being explored in biomedical applications such as drug delivery, antimicrobial treatments, and biosensing.^{87–89} For example:

- MIL-100(Fe) has demonstrated exceptional performance as a drug carrier, achieving anticancer drug (e.g., busulfan) loadings of up to 1.4 g_{drug}/g_{MOF} along with pH-responsive release behavior, thereby enhancing targeted delivery to tumor environments and improving therapeutic efficacy.^{90,91}
- HKUST-1 and MIL-53 MOFs have been reported to exhibit antiviral activity against SARS-CoV-2 by disrupting the viral envelope, achieving an approximately 50% reduction in viral titers, highlighting their potential in antimicrobial coatings and protective applications.⁹²

1.9.5. Chemical Sensors

Optimizing the performance of chemical sensors requires careful attention to factors such as selectivity, sensitivity, stability, reusability, and response time. MOFs have emerged as a highly promising class of porous materials that inherently possess many of these desirable attributes, making them well suited for chemical sensing applications.^{93–95} The sensing response of MOFs toward specific analytes is largely governed by the strength of host-guest interactions and the diffusion behavior of analyte molecules within the porous network. Strong and selective binding, combined with efficient mass transport through the framework, directly influences detection sensitivity and response kinetics. For example:

- Zn(bptc) porous framework exhibits selective adsorption toward polar molecules and substrates with π -conjugated systems, driven by strong host-guest interactions such as hydrogen bonding and π - π stacking, enabling high selectivity in chemical sensing applications.^{96,97}
- MOFs with unsaturated metal sites, such as Cu²⁺, Co²⁺, and Ni²⁺ centers, demonstrate reversible and selective sensing of gaseous analytes (e.g., NO and CO₂) through

coordination and electrostatic interactions,^{98,99} while frameworks like HKUST-1 show excellent humidity-sensing performance by reversibly adsorbing up to ~40 wt% water.¹⁰⁰

1.9.6. MOFs as Heterogeneous Catalysts

Among the wide range of reported applications of MOFs, one of the most significant and intensively explored areas is their use as heterogeneous catalysts. Two intrinsic features make MOFs particularly well suited for heterogeneous catalysis: their high porosity and long-range crystallinity. The porous architecture enables efficient diffusion of reactants and products, ensuring effective contact between substrate molecules and the catalytically active sites embedded within the framework. At the same time, the periodic and well-defined crystalline structure of MOFs allows precise determination of atomic positions, coordination environments, and oxidation states of the metal centers, providing valuable insights into structure–activity relationships. The ordered nature of MOFs also ensures spatial isolation of active sites, thereby suppressing site aggregation and minimizing catalyst deactivation. Catalytic functionality in MOFs can be introduced through three main strategies (Figure 1.9)

- (i) grafting active catalytic sites onto metal nodes (SBUs),^{101,102}
- (ii) anchoring catalytically active species onto the organic linkers,¹⁰³ and
- (iii) encapsulating catalytic moieties within the pores of the MOF framework.^{104,105}

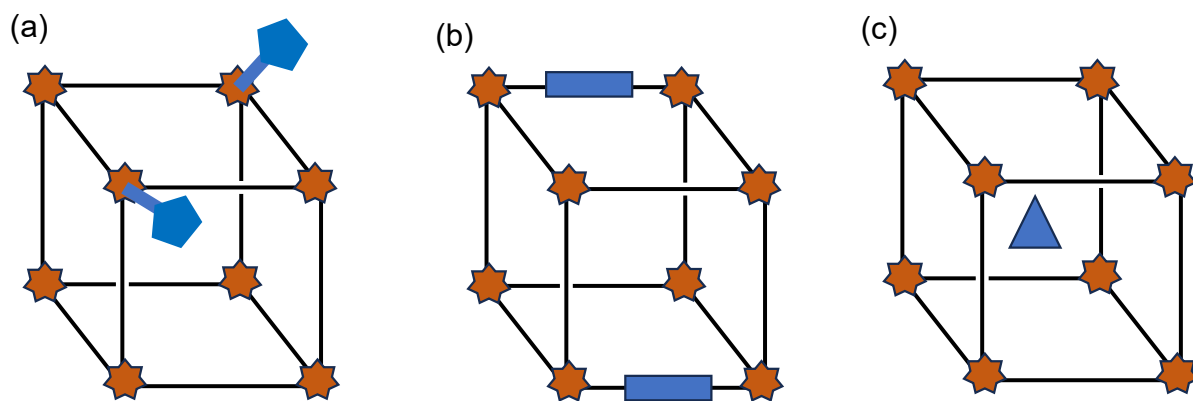


Figure 1.9. Schematic representation of different sites for introducing catalytic functionalities in MOFs: (A) at metal nodes (SBUs), (B) catalytically functionalized organic linkers, and (C) encapsulated catalytic species within the MOF pores.

1.9.6.1. Catalysis reactions at metal nodes (SBUs)

MOFs incorporating catalytically active SBUs have shown considerable promise in a wide range of catalytic transformations due to their tunable electronic environments and robust

structural frameworks. In this context, Zhang *et al.* reported the efficient utilization of metal nodes in a copper-based MOF for redox reactions. Specifically, they developed a Cu-MOF capable of selectively oxidizing toxic carbon monoxide (CO). This framework was synthesized using copper nitrate ($\text{Cu}(\text{NO}_3)_2$) as the metal precursor and 1H-pyrazole-4-carboxylic acid as the organic linker, yielding a crystalline material with the composition $[\text{Cu}(\mu_3\text{-OH})(\text{PyCA})_3(\text{H}_3\text{O})]\cdot 2\text{C}_2\text{H}_5\text{OH}\cdot 4\text{H}_2\text{O}$.¹⁰⁶ The well-defined copper SBUs within this MOF act as the active catalytic sites, highlighting the effectiveness of node-based catalysis in MOF systems.

Beyond copper, SBU based on metals such as iron (Fe), cobalt (Co), and vanadium (V) have also been shown to function as effective catalytic centers for a variety of oxidation reactions. For instance, the iron-based MOF MIL-100(Fe), which contains Fe-oxo SBUs, has demonstrated notable catalytic activity in the oxidation of diphenylmethane (DPM) and triphenylmethane (TPM) using tert-butyl hydroperoxide (TBHP) as the oxidant, underscoring the versatility of metal-node-driven catalysis in MOF systems.¹⁰⁷ Another illustrative example highlights the use of Al metal ions as catalytic centers for reduction reactions. In this case, the aluminum-based MOF $\text{Al}_2(\text{BDC})_3$ exhibited efficient catalytic activity toward the reduction of multiple carbon-carbon bonds when hydrazine was employed as the reducing agent (Scheme 1.1), demonstrating the potential of Al-based SBUs in MOF-mediated reduction processes.¹⁰⁸



Scheme 1.1. $\text{Al}_2(\text{BDC})_3$ MOF catalysed hydrogenation of olefins.

1.9.6.2. Catalysis reactions at organic linkers

Catalytic sites can be introduced at organic linkers by heterogenizing homogeneous catalyst molecules onto the linker backbone of the MOF. Such anchoring or grafting of homogeneous active sites onto the ligand framework combines the advantages of homogeneous catalysis (high activity and selectivity) with those of heterogeneous systems (stability, recyclability, and ease of separation). Among the various strategies available for incorporating catalytically active species onto organic linkers, two principal approaches are:

a) **De novo approach:** In this strategy, the catalytically active moiety is grafted onto the organic linker prior to MOF assembly, and the functionalized linker is subsequently used to construct the framework.

b) **Post-synthetic modification approach:** In this method, the catalytically active species is introduced onto the organic linkers after the MOF has been synthesized, typically through post-synthetic modification of the preformed framework.

MOFs constructed from pyridyl- or bipyridyl-containing linkers, as demonstrated by Mistry *et al.*, possess both Lewis acidic and basic sites, enabling efficient tandem deacetalization–Knoevenagel condensation reactions under mild conditions.¹⁰⁹ In another example, post-synthetic modification of UiO-type MOFs with TEMPO radicals affords catalysts capable of promoting aerobic alcohol oxidation at room temperature, where the tethered TEMPO moieties function as redox-active centers (Figure 1.10).¹¹⁰ Equally noteworthy is the incorporation of imidazolium functionalities into UiO-type MOF linkers, either through direct synthesis or post-synthetic exchange. These moieties not only improve CO₂ adsorption but also actively catalyze the cycloaddition of CO₂ with epoxides, leading to the efficient formation of cyclic carbonates.¹¹¹

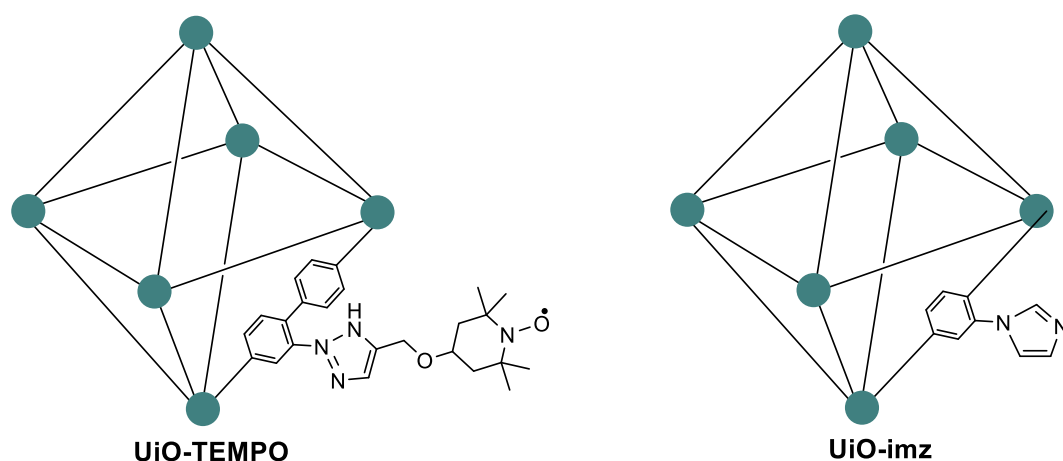


Figure 1.10. Schematic illustration of linker-functionalized MOFs highlighting the incorporation of catalytic sites within the organic linkers.

1.9.6.2. Catalysis reactions at encapsulated nanoparticles

MOFs have emerged as highly effective supports for metal nanoparticles (NPs), giving rise to NP@MOF architectures that combine the high surface area and tunable porosity of MOFs with the distinctive catalytic properties of NPs. The spatial confinement of NPs within the MOF matrix suppresses particle aggregation and enables regulated interactions with reactant molecules, thereby enhancing catalytic activity and selectivity. For example, several studies have reported the successful encapsulation of palladium, gold, and copper nanoparticles within MOF pores or channels, resulting in catalysts that display high activity in reactions such as CO oxidation and hydrogenation.^{112–117}

1.10. Outline of Thesis

MOFs constitute a highly versatile class of porous materials with wide-ranging applications, as briefly introduced in this chapter. A defining feature of MOFs is their ability to undergo chemical functionalization and post-synthetic modification without loss of structural integrity, enabling precise tuning of their properties. Although MOFs have been extensively investigated for gas storage, separation, and sensing, their deployment as robust and efficient catalysts for industrially relevant transformations remains an active area of research.

This thesis focuses on the rational design of MOF-based catalysts through the incorporation of catalytically active sites at both the metal nodes and the organic linkers of the framework. Transition-metal centers, including Fe, Ni, Cu, Ir, and Co, are introduced via metalation strategies to generate well-defined single-site catalytic systems. These materials are explored for a range of important chemical transformations, such as methane borylation, CO₂ hydrogenation, alkene oxidation, and oxidative bromination reactions. A key aspect of this work is the single-site nature of the developed catalysts, which enables detailed structural and mechanistic investigations. Accordingly, beyond the synthesis and catalytic evaluation of the MOFs, this thesis provides an in-depth characterization of the active sites and a molecular-level understanding of the catalytic processes. Multiple spectroscopic techniques, complemented by theoretical studies, are employed to elucidate reaction pathways and structure-activity relationships.

Overall, the central objective of this thesis is to develop sustainable, single-site heterogeneous MOF-based catalysts for diverse chemical transformations, while establishing clear mechanistic insights through comprehensive spectroscopic and theoretical analyses. While the catalytic reactions in this thesis were performed at a laboratory scale to establish fundamental design principles and mechanistic understanding, the catalysts are based on robust Zr-based UiO and Al-based MIL/DUT-type materials. These frameworks are known for their scalable solvothermal synthesis and thermal stability. Furthermore, the demonstrated structural integrity and recyclability over multiple cycles provide the necessary foundation for industrial viability. I acknowledge that future transition to fixed-bed or continuous-flow reactors will require further studies into material shaping (e.g., pelletization) and mechanical stress resistance, which remain a primary focus for future development toward large-scale sustainable processes.

Chapter 2: Materials and Methods

Abstract: 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.

2.1. Starting Materials, Solvents and Reagents

All starting materials, solvents and reagents employed in the reactions described in the subsequent chapters were obtained from commercial suppliers and used as received unless otherwise stated. Most substrates required for MOF catalyst synthesis were purchased directly from commercial sources. Specifically, 4,4'-benzenedicarboxylic acid (BDC) and 4,4'-biphenyldicarboxylic acid (BPDC) were obtained from Alfa Aesar. Aluminium(III) chloride, iron(III) chloride, iridium(III) chloride, iron(III) nitrate, aluminium oxide, sodium borohydride, *n*-butyllithium, and sodium triethylborohydride were procured from Sigma-Aldrich. Zirconium(IV) chloride, cobalt(II) chloride and nickel(II) bromide were supplied by GLR Innovations, while copper(II) chloride and sodium sulphite, were purchased from CDH Chemicals. When certain materials or reagents were not commercially available, they were synthesised in lab according to well-established literature procedures, as detailed in the relevant chapters.

Solvents were purchased from reputable suppliers to ensure the required level of purity for all experiments. *N,N*-Dimethylformamide (DMF), tetrahydrofuran (THF), acetonitrile, and ethylene glycol were obtained from CDH Chemicals. Toluene, cyclohexane were acquired from Avra Synthesis. Ultrapure deionised water was produced using a Milli-Q EQ 7000 purification system. Tetrahydrofuran was dried over calcium hydride and subsequently distilled over a sodium/benzophenone ketyl prior to use.

2.2. Glassware Cleaning

Prior to use, all glassware was subjected to a rigorous cleaning protocol. Initially, the glassware was pre-washed with hexane to remove residual grease, followed by sequential rinsing with acetone and soap solution. The glassware was then thoroughly rinsed with tap water. Subsequently, it was immersed in a pre-prepared alkaline base bath for 8-10 h. After removal from the base bath, the glassware was extensively washed with tap water to remove residual alkali and briefly rinsed with dilute hydrochloric acid to neutralize any remaining basicity. This was followed by successive rinses with tap water, distilled water, and a final rinse with acetone to ensure complete removal of contaminants.

The cleaned glassware was dried in an oven preheated to 110 °C and allowed to cool under vacuum or in the glovebox antechamber immediately prior to use. The alkaline base bath was prepared by dissolving 1 kg of potassium hydroxide (KOH) flakes in a mixture of 5 L of

isopropanol and 1 L of water. The solution was stored in a sealed plastic container, replenished with isopropanol as required, and replaced once it developed a dark red coloration.

2.3. High-Pressure Reaction Handling

All high-pressure reactions were carried out in specialized pressure reactors, specifically the PP-100-6624-00 model from Amar Equipment and the 4793(VGR)-T-SS-3000-DVD model from Parr Instrument Company. The reactors were directly pressurized from gas cylinders through calibrated pressure gauges capable of monitoring pressures in the range of 0-3000 psi (0-200 bar).

Strict handling, inspection, and cleaning protocols were followed to ensure operational integrity and user safety, particularly in view of the explosion hazards associated with gas mixtures. Reactions were conducted in pressure-rated vessels equipped with safety relief valves and housed within sealed polycarbonate fume hoods to enable continuous visual monitoring.

Prior to each experiment, the reactor assembly was carefully inspected for signs of wear, leaks, or residual contaminants. All seals, gaskets, and valves were examined and replaced when necessary. The system was subsequently purged with an inert gas (nitrogen) to remove atmospheric oxygen and moisture. After completion of the reaction, the reactor was depressurized in a controlled manner in accordance with established safety procedures. Post-reaction cleaning involved rinsing all internal surfaces, including tubing and fittings, with acetone using non-abrasive methods to prevent particulate contamination, followed by thorough washing with deionized water. The reactor was then dried under vacuum or by continuous inert gas flow until completely free of residual solvents. A final leak test was performed prior to reassembly, after which the reactor was stored in a clean, dust-free environment to ensure readiness for subsequent high-pressure gas reactions.

2.4. Air-Sensitive Reaction Handling

All reactions involving air- and moisture-sensitive materials were performed in glovebox (Vigor SG1200/750TS-F) under a high-purity nitrogen atmosphere. Prior to experimentation, the glovebox interior was thoroughly cleaned and decontaminated, with oxygen and moisture levels consistently maintained below 3 ppm. Reagents, solvents, and equipment were transferred into the glovebox through an antechamber using multiple evacuation and nitrogen refill cycles to minimize atmospheric contamination. Throughout all experimental operations,

strict precautions were taken to preserve the inert environment, with continuous monitoring of oxygen and moisture levels. Solvent removal within the glovebox was carried out using a high-vacuum pump equipped with a liquid nitrogen cold trap to prevent back-diffusion of volatile impurities.

2.5. Instrumental Methods

A comprehensive suite of analytical techniques was employed to characterize the synthesized metal-organic framework (MOF) catalysts. The specific methodologies and corresponding instrumental parameters used in this study are detailed in the following sections.

2.5.1. Powder X-Ray Diffraction (PXRD)

The MOF samples were air-dried and subsequently analysed by powder X-ray diffraction (PXRD) to determine their crystalline structure and assess phase purity. PXRD measurements were performed at room temperature using a Bruker Advance diffractometer equipped with Ni-filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Diffraction data were collected over a 2θ range of 4° – 70° with a step size of 0.05° and a counting time of 1 s per step. The experimental diffraction patterns were systematically compared with simulated patterns to confirm the monophasic nature of the bulk materials. Furthermore, peak positions and relative intensities were examined for consistency across measurements, and any deviations were carefully analysed to exclude the presence of secondary crystalline phases.

2.5.2. Brunauer-Emmett-Teller (BET) Analysis

To determine the surface area and pore volume, the MOF samples were initially dried at room temperature under vacuum. The samples were then subjected to a freeze-drying protocol to preserve the framework structure: they were soaked in benzene, frozen at -10°C , and subsequently dried slowly under vacuum at the same temperature to minimize structural distortion. Prior to analysis, a final degassing step was performed at 80°C for 24 h to remove residual solvent and ensure complete surface cleanliness. Textural properties were evaluated using a BELLSORP MAX II surface area and porosity analyzer (Microtrac) under ultra-high vacuum conditions, following standard Brunauer–Emmett–Teller (BET) procedures. The resulting adsorption isotherms were carefully analysed to verify the expected microporous nature of the materials, thereby providing reliable measurements of surface area and pore volume.

2.5.3. Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared (IR) spectra were recorded for samples that were dried overnight under dynamic vacuum at 90 °C and subsequently stored in a glovebox to prevent atmospheric contamination. A small quantity of the dried sample was thoroughly mixed with dry KBr inside the glovebox and pressed into a homogeneous pellet, ensuring exclusion of moisture during sample preparation. The pellets were analysed in transmission mode using a Nicolet Protege 460 FT-IR spectrometer (Bruker) under a controlled nitrogen atmosphere. Prior to spectral acquisition, the instrument was purged with dry nitrogen for 20 min to minimize background interference.

2.5.4. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed using a PerkinElmer TGA 7 instrument to evaluate the thermal stability and decomposition behaviour of the samples. Finely ground samples were loaded into the instrument and analysed under a continuous flow of nitrogen to maintain an inert atmosphere throughout the experiment. The temperature was increased from 40 to 800 °C at a constant heating rate of 10 °C min⁻¹, enabling systematic monitoring of mass loss associated with solvent removal and framework decomposition. In selected cases, MOF samples dispersed in tetrahydrofuran (THF) were analysed directly in their solvated state to assess the influence of residual solvent on thermal behaviour. This approach provided additional insight into solvent evaporation processes and the intrinsic thermal stability of the MOF frameworks.

2.5.5. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

Elemental compositions were determined by inductively coupled plasma–optical emission spectroscopy (ICP-OES) using an Agilent 5110 system. Prior to analysis, MOF samples were vacuum-dried and subsequently digested using a mixture of hydrofluoric acid (HF) and nitric acid (HNO₃). The resulting solutions were diluted in a 5% (v/v) HNO₃ matrix and analysed using a six-point calibration curve in the concentration range of 0.1–20 ppm, affording correlation coefficients (R^2) greater than 0.9990. Measurement accuracy and reproducibility were ensured through repeated analyses and calibration against reference standards.

2.5.6. Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS)

Morphological and compositional analyses were performed using a Zeiss FE-SEM Ultra Plus 55 operated at an accelerating voltage of 20 kV. Prior to imaging, MOF powders were vacuum-dried, and small amounts (1-2 mg) were uniformly dispersed onto carbon tape. High-resolution field-emission scanning electron microscopy (FE-SEM) enabled detailed examination of surface morphology, while energy-dispersive X-ray spectroscopy (EDS) was employed to obtain qualitative and quantitative elemental composition information.

2.5.7. X-Ray Photoelectron Spectroscopy (XPS)

XPS was performed using a Physical Electronics 5000 VersaProbe III equipped with an Al-K α X-ray source ($h\nu = 1486.6$ eV) to investigate the surface composition and chemical states of the samples. Binding energies were calibrated to the C1s peak at 284.8 eV, and peak deconvolution was carried out using CasaXPS software to accurately resolve overlapping signals. This detailed surface analysis provided crucial insights into the electronic environments and oxidation states of the constituent elements.

2.5.8. Electron Paramagnetic Resonance (EPR)

Electron paramagnetic resonance (EPR) measurements were carried out in the X-band region using a Bruker A300-9.5/12/S/W spectrometer. Solid MOF samples were vacuum-dried, mounted in EPR tubes, and analysed at room temperature. The acquired spectra were simulated using Bruker EPR Simfonia software, allowing deconvolution of overlapping signals and reliable identification of the radical species present.

2.5.9. X-Ray Absorption Spectroscopy (XAS)

XAS measurements, including both XANES and EXAFS, were conducted at the Energy-Scanning EXAFS beamline (BL-9) at the *Indus-2* Synchrotron Source in Indore, India. Measurements were taken at room temperature over an energy range of 4-25 keV. The beamline setup featured a Rh/Pt-coated collimating mirror, a Si(111) double crystal monochromator with horizontal focusing, and a Rh/Pt-coated post mirror for vertical focusing. Data collection was performed in transmission mode using two ionization chambers, and energy calibration was achieved using standard metal foils. Sample pellets were prepared by

mixing the powder with cellulose and pressing into 15 mm discs to ensure proper absorption edge jumps. Data analysis was performed using Demeter software, with concurrent measurements of metallic foil standards for calibration.

2.6. Analytical Techniques

2.6.1. Nuclear Magnetic Resonance (NMR)

^1H NMR and ^{13}C NMR spectra were recorded on a *Bruker* NMR DRX spectrometer operating between 300 and 500 MHz. This procedure ensured that the spectra provided accurate insights into the product distribution and conversion efficiency, facilitating reliable analysis of the catalytic process. The well-resolved spectral peaks allowed for precise integration and quantification of the reaction products, while additional data processing such as baseline correction and phase adjustment further enhanced the clarity and reproducibility of the measurements.

2.6.2. Gas Chromatograph (GC)

After cooling the reactor to room temperature, the gaseous sample was collected in a Tedlar bag and analyzed using an *Agilent* 8890 GC system equipped with a thermal conductivity detector (TCD) and configured with a PoraPlot Q column in series with a molecular sieves column. For the liquid phase, a 1 mL aliquot of the cold solution was transferred into a centrifuge tube, centrifuged for 1 minute to remove particulates, and the resulting clear solution was quickly transferred into a GC vial and spiked with 5 μL of an internal standard. The liquid products were then analyzed by two complementary gas chromatography methods—one employing an *Agilent* 8890 GC with a flame ionization detector and an *Agilent* DB-WAX column, and another utilizing an *Agilent* 7890B GC fitted with a mass spectrometric detector. Detailed operating conditions and calibration protocols for these analyses are thoroughly elaborated in the respective chapters.

2.7. Theoretical Studies

Theoretical studies were conducted using density functional theory (DFT) calculations implemented in the Gaussian software suite. Electronic structures were optimized at the unrestricted level using hybrid functionals such as B3LYP, with tailored basis sets (e.g., split-

valence, effective core potentials) selected for specific atoms to balance accuracy and computational efficiency. Solvent effects were incorporated via the Polarizable Continuum Model (PCM) in its integral equation formalism (IEFPCM), with solvent parameters and temperatures adjusted according to the system under study. Geometries were optimized in the solvated state, followed by frequency calculations to confirm stationary points as minima or transition states and to derive thermochemical corrections. Spin state energetics were systematically evaluated for metal-containing species, with the most stable multiplicities selected for further analysis. Internal energies were corrected to account for coordinated solvent molecules where applicable. All calculations included validation of key intermediates and transition states through comparative energy evaluations across plausible spin states and coordination environments. Further methodological specifics are detailed in subsequent chapters.

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

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Abstract: 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.

3.1. Introduction

Chemoselective oxidation of alkenes to epoxides, diols or carbonyls is an essential industrial method to synthesize valuable intermediates of pharmaceuticals and fine chemicals.^{118–125} In particular, the oxidation of styrene and its derivatives to the corresponding benzaldehydes or ketones is of great interest due to their wide application in the perfumery and food processing industries, synthesis of epoxy resins, plasticizers, drugs, sweeteners, and other fine chemicals.^{126–132} The common oxidants used for such transformations are peroxyacids,¹³³ manganese dioxide,¹³⁴ selenium dioxide,¹³⁵ potassium dichromate, osmium tetroxide¹³⁶ and ozone,¹³⁷ which results in a significant amount of undesired and harmful byproducts, making the oxidation processes industrially unsuitable. Developing sustainable methods using cheap and reusable catalysts and molecular oxygen (O₂) or H₂O₂ as an environmentally friendly oxidant is a task of high significance to overcome these drawbacks.

Several homogeneous catalysts based on heteropolyacids,¹³⁸ metal complexes with Schiff bases,^{139–142} porphyrins, salen, polyoxo- or N-ligands, and polyoxometalates^{143–147} have been developed for oxidation of styrene by O₂, H₂O₂ and *tert*-butylhydroperoxide (TBHP). However, due to the poor selectivity, difficulty in separation and recycling of the homogeneous catalyst, it is a matter of the utmost urgency to develop highly active, selective, and reusable heterogeneous catalysts for economical and eco-friendly oxidation of alkenes. Many heterogeneous catalysts, including metal oxides,^{148–154} polyoxometalates (POMs),^{155–158} and zeolites-, silica- or carbon materials-supported metal nanoparticles^{159–179} have been developed for the oxidation of styrene. However, the poor selectivity of many of these catalysts in converting styrene to benzaldehyde impels further development of catalysts.

Metal-organic frameworks (MOFs), constructed from metal- ions or -clusters nodes connected with bridging ligands, have recently emerged as the solid crystalline supports for facile synthesis of highly chemoselective heterogeneous catalysts due to their high porosity, reticular synthesis and tunability.^{17,41,180–206} The metal-oxo cluster nodes of MOFs have been employed as the weak-field oxide support to synthesize robust single-site earth-abundant metal catalytic species via active-site isolation.^{64,207–210} Herein, we report an easily synthesizable, single-site copper(II) catalyst supported on DUT-5(Al) MOF for the chemoselective oxidation of a wide range of alkenes including styrene and its derivatives to the corresponding carbonyl compounds or vicinal diols using H₂O₂ as an oxidizing agent with excellent yield and selectivity.

3.2. Results & Discussion

3.2.1 Synthesis and Characterization of DUT-5-CuCl

DUT-5-CuCl was synthesized via post-synthetic metalation of the nodes of DUT-5 MOF. First, the solvothermal reaction between 4,4'-biphenyldicarboxylic acid (H_2bpd) and aluminum trichloride hexahydrate ($AlCl_3 \cdot 6H_2O$) in DMF at 120 °C for 48 h produced DUT-5-MOF as a white crystalline solid.^{211,212} Then, the metalation of the nodes of DUT-5-MOF was performed via deprotonation of its μ_2 -OH by n -BuLi in THF, followed by the addition of a THF solution of $CuCl_2$ to afford DUT-5-CuCl. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis of the digested DUT-5-CuCl revealed 30% Cu-loading with respect to μ_3 -OLi, corresponding to a formula of $Al(O)(bpd)(Li)_{0.70}(CuCl)_{0.30}$. The crystallinity and structure of DUT-5 MOF upon metalation remained intact as revealed by the similarity of the PXRD pattern of DUT-5-CuCl with that of pristine DUT-5 (Figure 3.1b). X-ray photoelectron spectroscopy (XPS) spectrum of DUT-5-CuCl displayed $2p_{3/2}$ and $2p_{1/2}$ binding energy peaks at 933 eV and 953 eV, suggesting a +2 oxidation state of the copper ion (Figure 3.1c).

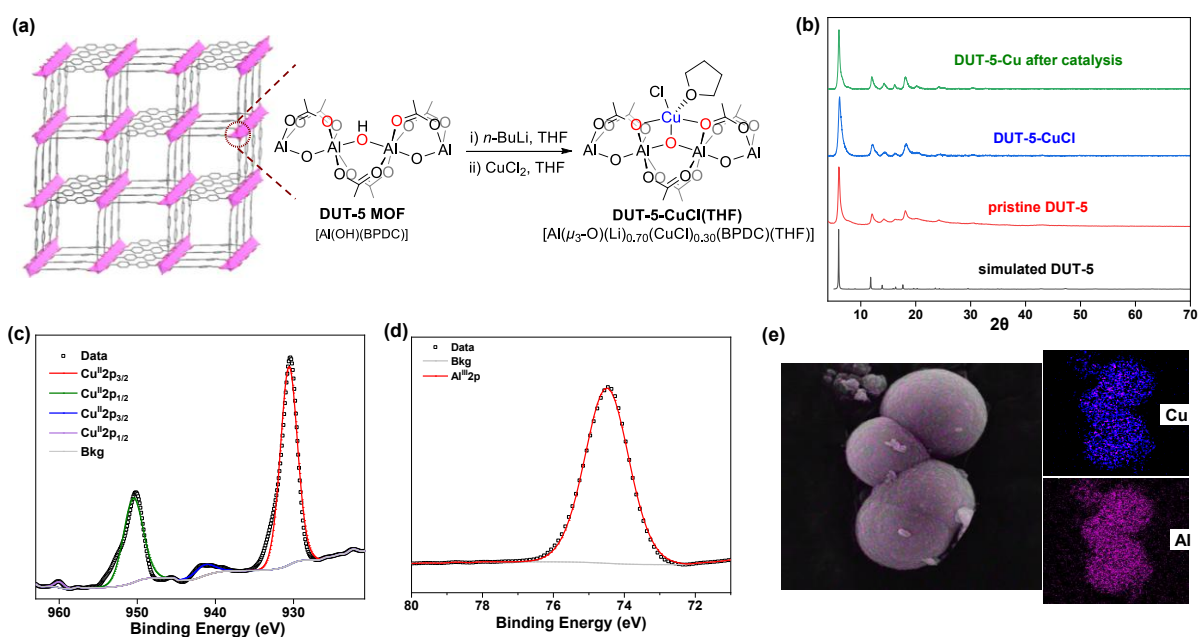


Figure 3.1. (a) Synthesis of DUT-5-CuCl(THF) via metalation of SBUs of DUT-5 MOF. (b) PXRD patterns of the simulated DUT-5 MOF (black), pristine DUT-5 MOF (red), DUT-5-CuCl (blue) and DUT-5-Cu after oxidation of styrene (green). (c) Cu 2p XPS spectrum of DUT-5-CuCl. (d) Al 2p XPS spectrum of DUT-5-CuCl. (e) SEM image of DUT-5-CuCl particles and the SEM-EDX mapping of Al and Cu of the respective particles.

The similar energies of the Cu-K-edge peaks of DUT-5-CuCl and CuCl₂ in X-ray absorption near-edge structure (XANES) also support the existence of Cu⁺² ion in DUT-5-CuCl (Figure 3.2a). The +3-oxidation state of aluminium ion in the SBUs was unchanged during the metalation as indicated by the binding energies of aluminium of DUT-5-CuCl in the XPS spectrum (Figure 3.1d). Thermogravimetric analysis (TGA) of DUT-5-CuCl showed that the framework is thermally robust up to 400 °C (Figure 3.5). Scanning electron microscopy (SEM)-energy dispersive X-ray (EDX) mapping of DUT-5-CuCl indicated that Al and Cu are uniformly distributed throughout the spherical MOF-particles (Figure 3.1e). The coordination environment of Cu⁺² ion in DUT-5-CuCl was determined by extended X-ray absorption fine structure (EXAFS) at the Cu K-edge fitted with its density functional theory (DFT)-optimized structure. The DFT-optimized model of the Cu-functionalized node of DUT-5-CuCl, calculated using the B3LYP method and a basis set of 6-311G(d,p) on Gaussian 09 software suite, showed that copper ion is coordinated with μ_3 -O⁻, two neutral carboxylate oxygens of the bridging linkers, one chloride ion, and one THF molecule to give the $[(\mu_3\text{-O})(\text{O}_{\text{carboxylate}})_2\text{CuCl}(\text{THF})]$ species [Figure 3.11a]. The EXAFS feature of the Cu centers in DUT-5-CuCl fitted well with this model, suggesting a nearly identical local coordination environment of the Cu ion at the node of DUT-5 MOF (Figure 3.2b).

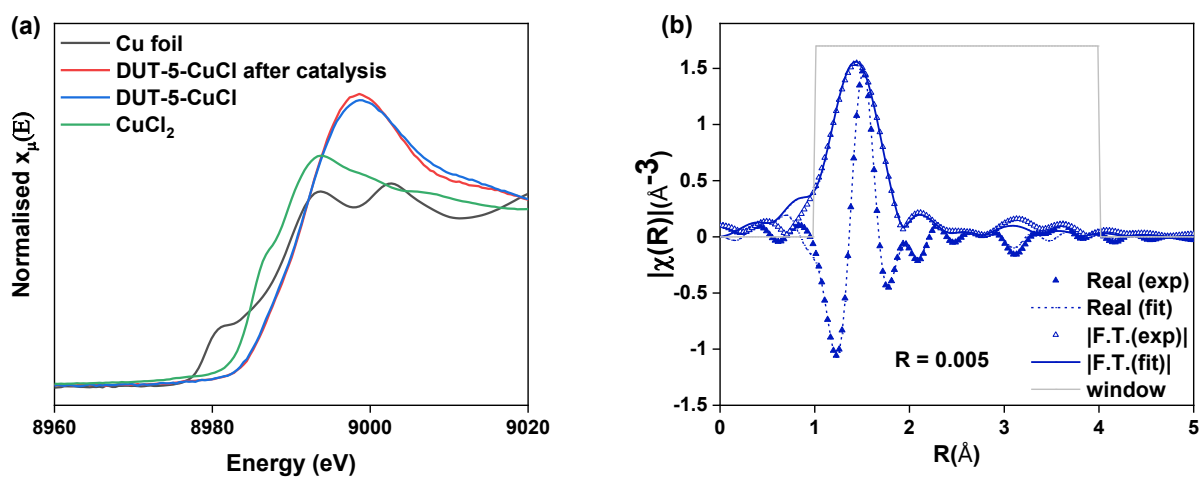


Figure 3.2. (a) Cu K-edge XANES spectra of Cu foil, CuCl₂, DUT-5-CuCl, and DUT-5-Cu after catalysis. (b) EXAFS spectra and fits in R-space at the Cu K-edge of DUT-5-CuCl(THF) with the magnitude and real component of the Fourier transformation shown as hollow and solid triangles in blue color, respectively. The fitting range in R-space is 1.0–4.0 Å (within the gray line).

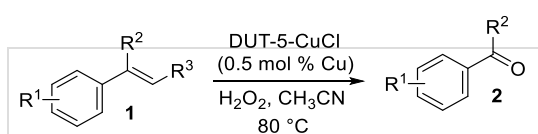
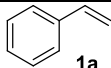
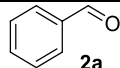
3.2.2. Catalytic Alkene Oxidation

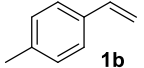
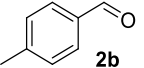
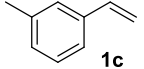
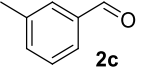
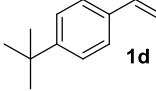
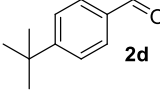
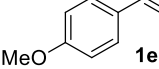
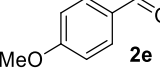
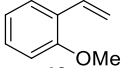
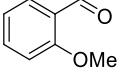
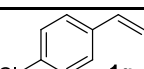
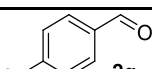
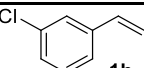
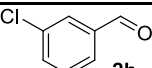
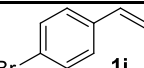
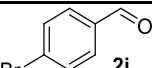
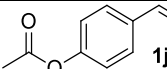
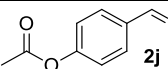
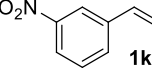
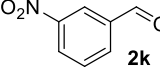
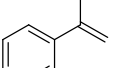
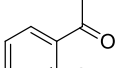
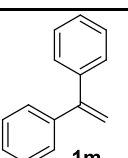
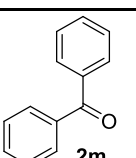
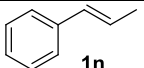
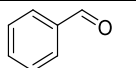
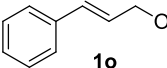
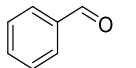
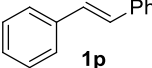
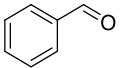
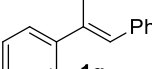
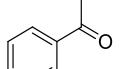
DUT-5-CuCl is an active catalyst for the oxidation of styrene and its derivatives using H₂O₂ as an oxidizing agent. The oxidation reaction was first optimized using styrene (**1a**) as an alkene

substrate (1.25 mmol), H₂O₂ as the oxidant (4 equiv. with respect to substrate) with variable solvents, temperature and mol% of the catalyst (Table 3.1). At a 0.5-1.0 mol% Cu-loading, the reaction between **1a** and H₂O₂ in the presence of DUT-5-CuCl in CH₃CN at 50-80 °C for 7-24 h produced benzaldehyde (**2a**) as the sole product (Table 3.1). The yield of **2a** diminished when less than 4.0 equiv. of H₂O₂ with respect to styrene was used (entries 4 and 5, Table 3.1). The oxidation reaction in solvents such as methanol, DMF and water gave **2a** in lesser yields (entries 10-12, Table 3.1). In addition, lower conversion and selectivity were observed for the reactions at a lower temperature of 50 °C or below (entry 6, Table 3.1). The highest turn-over frequency and selectivity were obtained when the oxidation reaction was performed in acetonitrile as a solvent with 0.5 mol% DUT-5-CuCl and 4 equiv. of H₂O₂ with respect to the styrene substrate at 80 °C for 7 h (entry 8, Table 3.1).

Under the optimized reaction conditions, several alkyl-substituted styrenes, such as 4-methylstyrene (**1b**), 3-methylstyrene (**1c**) and 4-tert-butylstyrene (**1d**), were oxidized to the corresponding substituted benzaldehydes (**2b-d**) in 78-91% yields (entries 2-4, Table 3.1). Styrenes bearing electron-donating functional groups such as 4-methoxystyrene (**1e**) and 2-methoxystyrene (**1f**), and electron-withdrawing functional groups such as 4-chlorostyrene (**1g**), 3-chlorostyrene (**1h**), 4-bromostyrene (**1i**), 4-acetoxystyrene (**1j**) and 3-nitrostyrene (**1k**) were also selectively converted to the corresponding carbonyl compounds (**2e-k**) in 58-88% yields (entries 5-11, Table 3.1). At a 0.5 mol% Cu-loading, DUT-5-CuCl also efficiently catalysed the oxidation of various di- and tri-substituted alkenes. 1,1'-Disubstituted alkenes such as α -methylstyrene (**1l**), α -phenylstyrene (**1m**) and 1,2-disubstituted alkenes such as trans- β -methylstyrene (**1n**) were transformed into acetophenone (**2l**), benzophenone (**2m**) and benzaldehyde, respectively, in 93%, 95% and 81% yield, respectively (entries 12-14, Table 3.1). In addition, cinnamyl alcohol (**1o**), stilbene (**1p**) and α -methyl stilbene (**1q**) were also converted into the corresponding carbonyl compounds in good yields (entries 15-17, Table 3.1).

Table 3.1. DUT-5-CuCl catalyzed oxidation of styrene derivatives.^[a]

				
Entry	Substrate	Product	Time	% Conversion (% Yield)
1			7 h	94 (81)

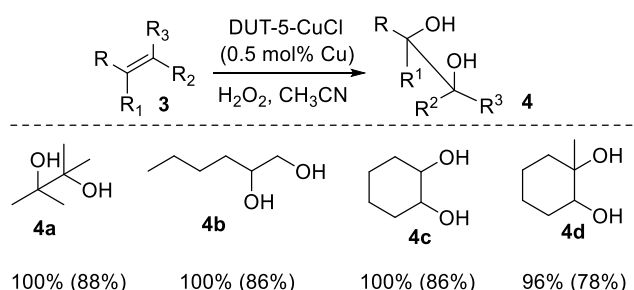
2			4 h	92 (91)
3			4 h	91 (89)
4			4 h	92 (78)
5			4 h	98 (86)
6			3 h	96 (88)
7			4 h	100 (58)
8			6 h	95 (65)
9			4 h	100 (71)
10			4 h	91 (65)
11			5 h	92 (72)
12			7 h	100 (93)
13			7 h	100 (95)
14			4 h	100 (81)
15			6 h	95 (85)
16			4 h	95 (75)
17			4 h	100 (84)

[a] Reaction conditions: DUT-5-CuCl (2 mg, 0.5 mol % Cu), substrate (1.25 mmol), H₂O₂ (0.5 mL), CH₃CN (3.0 mL), 80 °C, isolated yield in the parenthesis.

Styrene oxidation ceased upon removing the solid DUT-5-Cu from the reaction mixture, suggesting that the catalytic moiety is embedded within the MOF (Figure 3.7). Adding a drop of metallic mercury did not affect the rate of the catalytic reaction, confirming that any in situ formed Cu-nanoparticle or leached Cu-particulates were not responsible for the catalysis; instead, solid DUT-5-Cu MOF was the actual catalyst for alkene oxidation (Figure 3.8). DUT-5-CuCl MOF could be recycled and reused at least 5 times in the oxidation of α -methylstyrene (Figure 3.9). The leaching of Cu and Al after run 1 was 0.07% and 0.8%, respectively, while after run 4 was 0.05% and 1.5%, respectively (Table 3.3). The PXRD pattern of DUT-5-Cu recovered after the styrene oxidation showed the MOF's robustness under the reaction conditions (Figure 3.1b).

We next explored the DUT-5-CuCl catalyzed oxidation of aliphatic and cyclic alkenes using H_2O_2 under the similar reaction conditions employed for styrene oxidation. Unlike the oxidation of styrene derivatives to the corresponding carbonyls, the oxidation of aliphatic and cyclic alkenes produced diols (Scheme 3.1). At a 0.5 mol% Cu-loading, DUT-5-CuCl catalyzed oxidation of aliphatic alkenes such as 2,3-dimethylbut-2-ene (**3a**) and 1-hexene (**3b**) gave to the corresponding 1,2-diols, 2,3-dimethylbutane-2,3-diol (**4a**) and hexane-1,2-diol (**4b**) in 100% conversion and 88% and 86% yields, respectively. Cyclic alkenes such as cyclohexene (**3c**), 1-methylcyclohexene (**3d**) were selectively converted to cyclohexane-1,2-diol (**4c**) and 1-methylcyclohexane-1,2-diol (**4d**), respectively, in excellent yields (Scheme 3.1).

Scheme 3.1. DUT-5-CuCl catalyzed oxidation of aliphatic and cyclic alkenes.^[a]



^[a]Reaction conditions: 0.5 mol % Cu with respect to DUT-5-CuCl, substrate (1.25 mmol), H_2O_2 (0.5 mL), CH_3CN (3.0 mL), 18 h, 80 °C, isolated yield in the parenthesis.

3.3. Mechanism Exploration of DUT-5-CuCl Catalyzed Oxidation of Styrene

We next investigated the mechanism of DUT-5-CuCl catalyzed oxidation of styrene to benzaldehyde by the determination of reaction intermediates, characterization of the catalyst after catalysis, and the computational studies. The similar energies of the Cu-K-edge peaks of

recovered DUT-5-Cu after oxidation of styrene and DUT-5-CuCl in XANES indicate +2 oxidation state Cu ion in DUT-5-Cu after catalysis (Figure 3.2a). The identification of the Cu-species within DUT-5-Cu after catalysis was performed by EXAFS studies. The EXAFS data of the recovered MOF fitted well with the DFT optimized structure of DUT-5-Cu(OH)(NCCH₃), which indicates that the Cu⁺² ion is coordinated with μ_3 -O⁻, two neutral carboxylate oxygens of the bridging linkers, one hydroxyl, and one CH₃CN molecule at the nodes of DUT-5 MOF (Figures 3.3b-c). DUT-5-Cu(OH)(NCCH₃) as the resting state of the catalyst suggests that DUT-5-Cu(OH) is likely to be a catalytic intermediate in the oxidation of styrene in CH₃CN. To identify the reaction intermediates, the reaction mixture in incomplete conversion was analyzed by GC-MS. The reaction of styrene and H₂O₂ at 80 °C in CH₃CN in the presence of 0.5 mol% DUT-5-CuCl gave a mixture of benzaldehyde (81%), styrene oxide (3%) and 1-phenylethane-1,2-diol (2%) in 90% conversion. Similarly, a mixture of 4-chlorobenzaldehyde (58%), 4-chlorostyrene oxide (7%) and 1-(4-chlorophenyl)ethane-1,2-diol (7%) were obtained from the oxidation of 4-chlorostyrene in 78% conversion. We thus infer that the reaction of styrene and H₂O₂ produced epoxy, which subsequently hydrolyzes to give 1,2-diol. The diol is then converted to benzaldehyde. To further verify whether the catalysis occurring via radical pathway, a test for the oxidation of styrene with H₂O₂ in the presence of Na₂SO₃ as the radical scavenger was performed, which showed no role of the radical scavenger on the rate of oxidation (section 3.5.7).

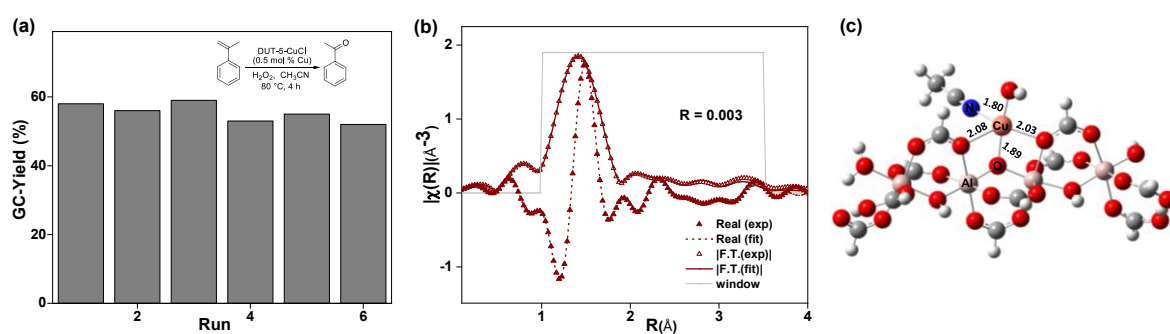


Figure 3.3. (a) % GC yield of acetophenone in the recycling and reuse experiments of DUT-5-CuCl for oxidation of α -methylstyrene. (b) EXAFS spectra and fits in R-space at the Cu K-edge of DUT-5-Cu recovered after oxidation of styrene with the magnitude and real component of the Fourier transformation shown as hollow and solid triangles in red color, respectively. The fitting range in R-space is 1.0–3.5 Å (within the gray line). (c) DFT optimized structure of DUT-5-Cu(OH)(NCCH₃) unit.

Based on the above experimental data, we propose that DUT-5-CuCl reacts with H₂O₂ to give copper-hydroperoxide species (INT-1) (Figure 3.4a). Then, the insertion of alkene into Cu-O bond of INT-1 forms INT-2, which is subsequently transformed to INT-3 upon rearrangement. The hydrolysis of the coordinated epoxide in INT-3 via nucleophilic attack of

water at the most substituted carbon furnished INT-4. Then, INT-4 is transformed into DUT-5-Cu(OH) (INT-5) with liberation of 1,2-diol. Finally, INT-5 reacts with H_2O_2 and regenerates INT-1. In the case of 1-phenylethane-1,2-diol product, benzaldehyde is formed via facile cleavage of the C–C bond of 1-phenylethane-1,2-diol, presumably due to resonance stabilization of the carbocation intermediate by the aromatic ring. However, the lack of resonance stabilization in the carbocation intermediates formed from aliphatic 1,2-diol makes the C–C bond cleavage less favourable, and thus, only 1,2-diol products were obtained from the oxidation of aliphatic and cyclic alkenes.

3.4. Computational Studies of DUT-5-CuCl Catalyzed Oxidation of Styrene

To further understand the reaction pathway, we computed the whole catalytic cycle by DFT method (B3LYP) and a basis set of 6-311G (d,p) on Gaussian 09 software (Figure 3.4b). The DFT calculation revealed that the insertion of alkene into Cu–O bond of INT-1 require an activation free energy of 9.2 kcal/mol, and the transformation of INT-1 to INT-2 is endergonic by 3.9 kcal/mol. In the next step, the conversion of INT-2 to INT-3 is exergonic by 44.2 kcal/mol. The hydrolysis of epoxide in INT-3, followed by liberation of diol generates INT-5, which is exergonic by 14.3 kcal/mol. Finally, the coordination of H_2O_2 to the Cu center of INT-5 and regeneration of INT-1 is exergonic by 5.8 kcal/mol. The DFT-calculated energy profile diagram suggests the insertion of alkene in TS-1 is the rate-determining step of the catalytic cycle (Figure 3.4b).

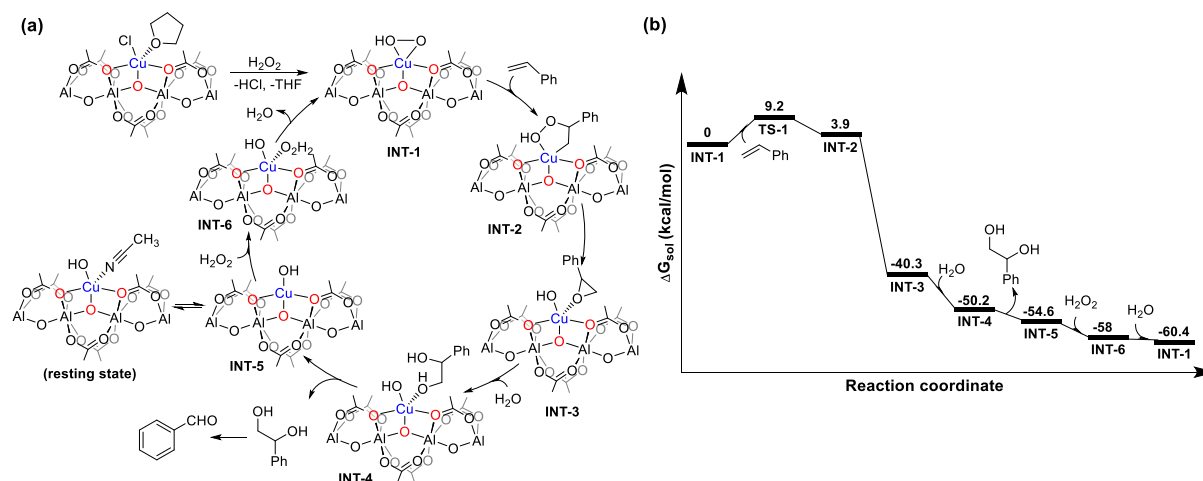


Figure 3.4. (a) Proposed catalytic cycle of DUT-5-CuCl catalyzed oxidation of styrene. (b) DFT-calculated Gibbs free enthalpy reaction profile diagram.

3.5. Experimental Section

3.5.1. Synthesis and Characterization of DUT-5 and DUT-5-CuCl

3.5.1.1. Synthesis of DUT-5^{213,214}

4, 4'-Bipenyldicarboxylic acid (0.05 g, 0.206 mmol), and aluminum chloride hexahydrate (0.032 g, 0.135 mmol) were dissolved in 3 mL DMF in a vial and the resultant mixture was stirred for 2 h. The solution was transferred to a hydrothermal bomb with a Teflon liner and kept it in a preheated oven at 120 °C for 48 h. After cooling to the room temperature, the white solid was collected *via* centrifugation, which was washed with DMF several times. The resulting solid was dried at room temperature to give the DUT-5 as a white solid.

3.5.1.2. Synthesis of DUT-5-CuCl

n-BuLi (0.047 mL, 1.65 M in cyclohexane) was added to the slurry of DUT-5 (0.015 g, 0.052 mmol) in 1 mL THF in a vial, and the mixture was stirred for 2 h at room temperature inside the glovebox. The brown solid was washed with THF several times to remove the excess *n*-BuLi. A THF solution of CuCl₂ (9.8 mg, 0.0732 mmol) was added to the brown solid of lithiated-DUT-5 and the mixture was stirred overnight at room temperature. The DUT-5-CuCl was centrifuged out of the suspension, and the resultant light green solid was washed with THF several times. The DUT-5-CuCl has 28% solvent weight as analyzed by TGA, and 30% copper-loading with respect to the μ_2 -OH moiety as analyzed by ICP-OES.

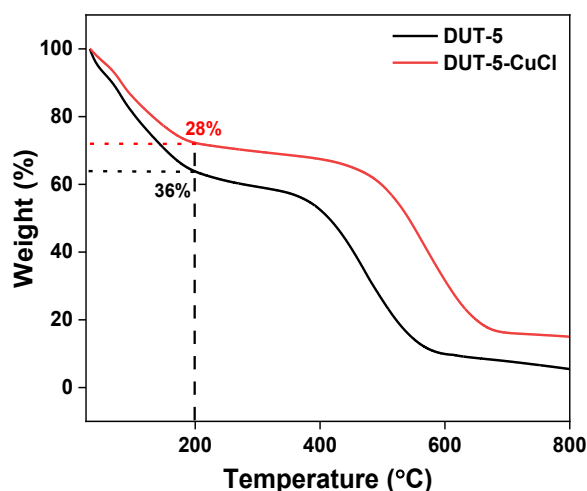


Figure 3.5. TGA curve of freshly prepared DUT-5 and DUT-5-CuCl. A solvent weight loss of 36% in DUT-5 (black) and 28% in DUT-5-CuCl (red) was observed from 40 °C to 200 °C.

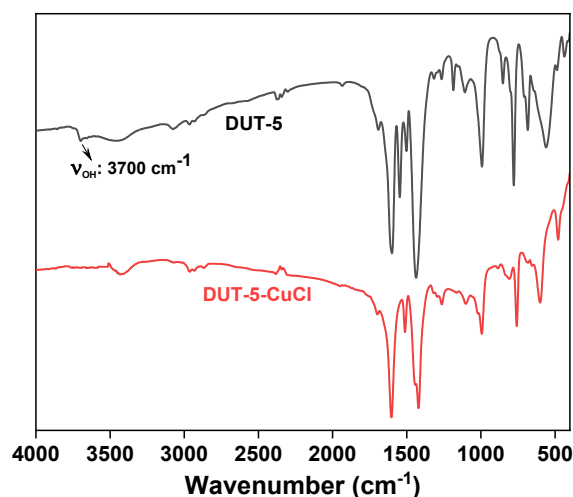


Figure 3.6. IR (KBr) spectrum of DUT-5 (black) and DUT-5-CuCl (red).

3.5.2. DUT-5-CuCl Catalysed Oxidation of Styrene and Styrene Derivatives

3.5.2.1. General procedure for DUT-5-CuCl catalysed oxidation of styrene derivatives

Solid MOF DUT-5-CuCl (0.5 mol% Cu) in 3 mL CH₃CN was transferred into a 25 mL Schlenk tube placed in oil bath and equipped with a water-cooled reflux condenser. Then 30% w/v H₂O₂ in water along with styrene substrate were added dropwise under continuous stirring for 7 to 24 h. After the reaction was completed, the solid MOF was centrifuged out from the suspension, followed by several washing with CH₃CN and can be reused. The remaining organic extract in the suspension were concentrated in vacuo to yield corresponding carbonyl compounds as the pure product.

3.5.2.2. Typical procedure for DUT-5-CuCl catalysed oxidation of styrene

DUT-5-CuCl (0.5 mol% of Cu) in 3 mL of acetonitrile (CH₃CN) was transferred into a 25 mL Schlenk tube. To the mixture, styrene (143 μ L, 1.25 mmol) was added. Then H₂O₂ (0.5 mL) was added dropwise under continuous stirring for 7 h. The Schlenk tube was placed in oil bath at temperature of 80 °C and equipped with a water-cooled reflux condenser. After the reaction was completed, the solid MOF was removed by centrifugation from the suspension, followed by several washing with CH₃CN and can be reused. The combined organic extracts were concentrated in vacuo, followed by column chromatography using hexane and ethyl acetate (50:1, R_f: 0.6) as an eluent to yield benzaldehyde as the pure product.

3.5.2.3. General procedure for the DUT-5-CuCl catalyzed oxidation of aliphatic and cyclic alkenes using H₂O₂

Solid MOF DUT-5-CuCl (0.5 mol% Cu) in 3 mL CH₃CN was transferred into a 25 mL Schlenk tube placed in oil bath and equipped with a water-cooled reflux condenser. Then 30% w/v H₂O₂ in water along with alkene substrate were added dropwise under continuous stirring for 12 to 24 h. After the reaction was completed, the solid MOF was removed by centrifugation from the suspension, followed by several washing with CH₃CN and can be reused. The remaining organic extract in the suspension were concentrated in vacuo to yield corresponding diols as the pure product. The product was analyzed by a gas chromatography–mass spectrometry (GC–MS).

3.5.2.4. Typical procedure for the DUT-5-CuCl catalyzed oxidation of tetramethylethylene using H₂O₂

DUT-5-CuCl (0.5 mol% of Cu) in 3 mL of acetonitrile (CH₃CN) was transferred into a 25 mL Schlenk tube. To the mixture, tetramethylethylene (149.2 μ L, 1.25 mmol) was added. Then H₂O₂ (0.5 mL) was added dropwise under continuous stirring for 18 h. The Schlenk tube was placed in oil bath at temperature of 80 °C and equipped with a water-cooled reflux condenser. After the reaction was completed, the solid MOF was centrifuged out from the suspension, followed by several washing with CH₃CN and can be reused. The combined organic extracts were concentrated in vacuo, followed by column chromatography using hexane and ethyl acetate (50:1, R_f: 0.6) as an eluent to yield 2,3-dimethylbutane-2,3-diol as the pure product.

Table 3.2. Optimization reaction conditions for the oxidation of styrene.

Entry	DUT-5-CuCl (mol%)	H ₂ O ₂ (30% w/v in water)	Temp. (°C)	Time (h)	Solvent	Conversion (%)	Selectivity (%)
1	1	4 equiv.	70	7	CH ₃ CN	47	72
2	1	4 equiv.	70	20	CH ₃ CN	68	52
3	1	3 equiv.	70	7	CH ₃ CN	43	58
4	1	2 equiv.	70	7	CH ₃ CN	32	55
5	1	4 equiv.	50	24	CH ₃ CN	18	95
6	1	4 equiv.	80	7	CH ₃ CN	84	66
7	0.5	4 equiv.	80	7	CH ₃ CN	94	81
8	0.5	4 equiv.	80	14	CH ₃ CN	98	70

9	0.5	4 equiv.	80	7	MeOH	55	33
10	0.5	4 equiv.	80	7	DMF	15	84
11	0.5	4 equiv.	80	7	H ₂ O	5	100
12	0.5	4 equiv.	80	7	---	4	100

3.5.3. Test for “Heterogeneity” of DUT-5-CuCl in Oxidation of α -methylstyrene

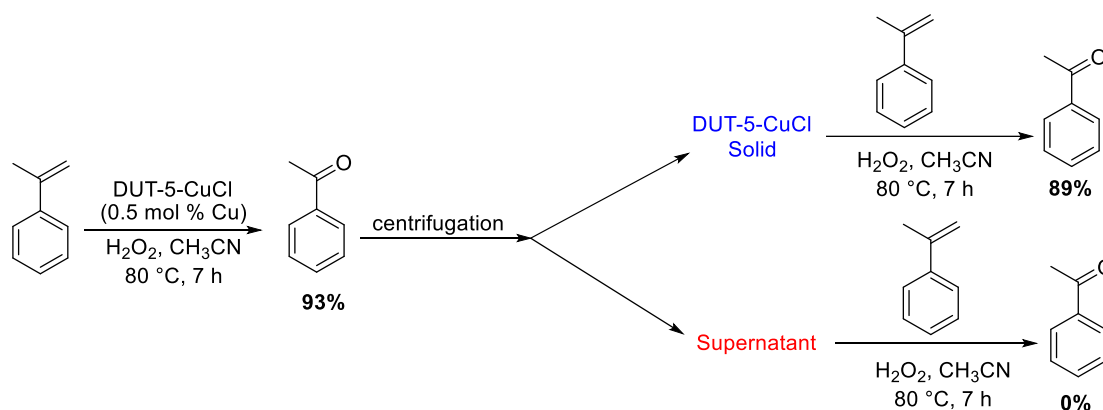


Figure 3.7. Heterogeneity test of DUT-5-CuCl for oxidation of α -methylstyrene.

DUT-5-CuCl (0.5 mol% of Cu) in 3 mL of acetonitrile (CH_3CN) was transferred into a 25 mL Schlenk tube. To the mixture, α -methylstyrene (162.5 μL , 1.25 mmol) was added. Then H_2O_2 (0.5 mL) was added dropwise under continuous stirring for 7 h. The Schlenk tube was placed in oil bath at temperature of 80°C and equipped with a water-cooled reflux condenser. After the reaction was completed, the solid MOF was removed from suspension to separate the solid and the supernatant and washed with CH_3CN multiple times. The conversion analysed by taking aliquots from the organic extract gave 93% acetophenone.

Two reactions were set up separately in two different Schlenk tubes, one with the solid and the other one with the supernatant recovered from the previous reaction. The extracted solid and supernatant were added into two separate tubes, and α -methylstyrene (162.5 μL , 1.25 mmol), 0.5 mL H_2O_2 , and 3 mL of CH_3CN were added to each tubes. Then both the Schlenk tubes were placed in oil bath at temperature of 80°C and equipped with a water-cooled reflux condenser for 7 h. The reactions were analysed with the GC-MS, which showed that the reaction with the solid MOF gave 89% yield, while the reaction with supernatant gave 0% conversion. This experiment excludes the potential of any leached Cu-species responsible for catalysis and confirms that solid DUT-5-CuCl was the actual catalyst for the oxidation of α -methylstyrene.

3.5.4. Hg Test

A catalytic oxidation of α -methylstyrene was carried out in the presence of a drop of Hg to investigate the role of any leached Cu-nanoparticles in the solution responsible for catalysis. Hg is known to form an amalgam with metallic copper, thus removing any in-situ-borne metallic copper during catalysis. The details of the experiments are as follows:

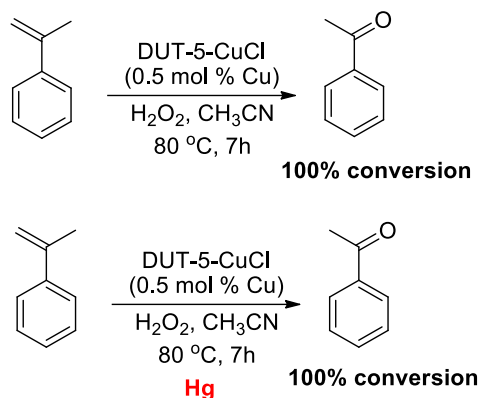


Figure 3.8. Hg test in the oxidation of α -methylstyrene with DUT-5-CuCl.

DUT-5-CuCl (0.5 mol% of Cu) was charged into two separate vials and washed with THF multiple times. The MOF as a slurry in 3 mL acetonitrile was transferred into two separate 25 mL Schlenk tubes. Then, α -methylstyrene (162.5 μL , 1.25 mmol) and 0.5 mL H_2O_2 were added to both the Schlenk tubes. In one of the reaction mixtures, a drop of mercury was added. The Schlenk tubes were then stirred at $80\text{ }^\circ\text{C}$ for 7 h. After the completion of the reaction, the solid MOF was removed from suspension and washed with CH_3CN multiple times. The catalytical conversion was 100% for both the reactions analysed by GC-MS. We thus conclude that any leached Cu-particles were not responsible for the catalytical activity, and DUT-5-CuCl was the actual catalyst.

3.5.5. Recycling of DUT-5-CuCl for the Oxidation of α -methylstyrene

In order to monitor the intrinsic initial activity of each run and also to check the stability of the MOF-catalyst, the recycle and reuse experiment using DUT-5-CuCl was conducted at incomplete conversion (~ 50 - 60%) for same reaction time (4 h). The catalytic activity of DUT-5-CuCl remained the same till run 5, and the leaching of Cu and Al was very low (Table 3.3). The detailed procedure of the recycling experiments is given below.

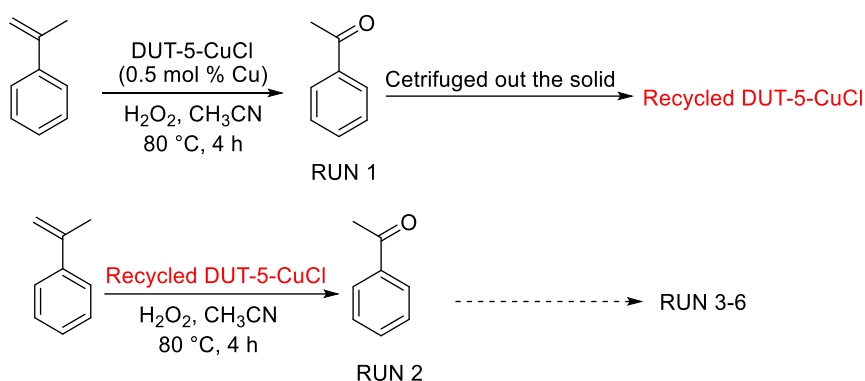


Figure 3.9. Recycle and reuse of DUT-5-CuCl in oxidation of α -methylstyrene.

Solid MOF DUT-5-CuCl (0.5 mol% of Cu) in 3 mL of CH_3CN was transferred into a 25 mL Schlenk tube. To the mixture, α -methylstyrene (162.5 μL , 1.25 mmol) was added. Then H_2O_2 (0.5 mL) was added dropwise under continuous stirring for 4 h. The Schlenk tube was placed in oil bath at temperature of $80\text{ }^\circ\text{C}$ and equipped with a water-cooled reflux condenser. After the reaction was completed, the solid MOF was removed by centrifugation from the suspension, followed by several washing with CH_3CN and recycled. The recovered MOF-catalyst was again added to the Schlenk tube. Then, 3 mL of CH_3CN , α -methylstyrene (162.5 μL , 1.25 mmol) and 0.5 mL H_2O_2 were added to it. Then the reaction mixture was stirred at temperature of $80\text{ }^\circ\text{C}$ for 4 h. After the reaction was completed, the solution was analysed in the same way as mentioned previously in run 1. The recycling and reuse experiments were performed 5 times in total.

Table 3.3. % GC-Yield of acetophenone, the leaching of Al and Cu at various runs of the recycling of DUT-5-CuCl in the oxidation of α -methylstyrene.

No. of Run	Time	%GC-Yield	%Leaching (Cu, Al)
Run-1	4 h	58	0.07, 0.8
Run-2	4 h	56	
Run-3	4 h	59	
Run-4	4 h	53	0.05, 1.5
Run-5	4 h	55	
Run-6	4 h	52	

3.5.6. Investigation of the Effect of Pore Sizes on the Rate of Catalysis

The effect of pore sizes on the rate of catalytic reaction was investigated by comparing the rate of oxidation reactions of styrene derivatives catalyzed by DUT-5-CuCl with that of MIL-

53(Al)-CuCl under identical reaction conditions. MIL-53(Al)-CuCl has the same topology but smaller pore sizes compared to DUT-5-CuCl.

3.5.6.1 Synthesis and characterizations of MIL-53(Al)-CuCl

MIL-53(Al) was synthesized according to the reported procedure.²¹⁴ 1,4-Benzene dicarboxylic acid (0.050 g, 0.300 mmol) and aluminium chloride hexahydrate (0.048 g, 0.198 mmol) were dissolved in 3 ml DMF and kept it on stirring for 2 h. Then the reaction mixture was sealed in a Teflon liner and kept it in a pre-heated oven at 120 °C for 48 h. The mixture was cooled and solid was separated from the suspension *via* centrifugation, which was washed thoroughly with DMF several times. The obtained solid was dried at room temperature to give the white solid as MIL-53(Al). MIL-53(Al) was then treated with *n*-BuLi in THF, to which a solution of CuCl₂ in THF was added to give a light green-coloured MOF of MIL-53(Al)-CuCl.

3.5.6.2. Comparison of the catalytic activities of DUT-5-CuCl and MIL-53(Al)-CuCl in the oxidation of styrene under identical conditions.

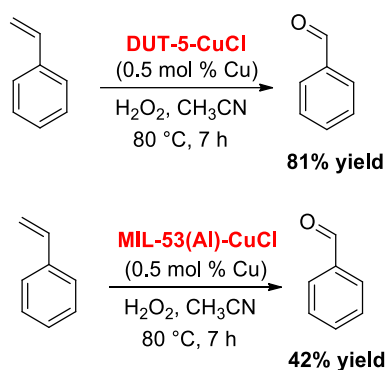


Figure 3.10. The oxidation of styrene catalyzed by DUT-5-CuCl and MIL-53(Al)-CuCl under identical reaction conditions.

Solid MOF DUT-5-CuCl (0.5 mol% of Cu) and MIL-53(Al)-CuCl (0.5 mol% of Cu) each in 3 mL of acetonitrile (CH₃CN) were transferred into two separated 25 mL Schlenk tubes. To both the mixtures, styrene (143 μL, 1.25 mmol) was added. Then H₂O₂ (0.5 mL) was added dropwise under continuous stirring 7 h. Both the Schlenk tubes were placed in oil bath at temperature of 80 °C and equipped with a water-cooled reflux condenser. After reactions were completed, the solid MOF was removed by centrifugation from the suspension, followed by several washing with CH₃CN and recycled. The yield of benzaldehyde were 81% and 42% with DUT-5-CuCl and MIL53(Al)-CuCl respectively. This experiment indicates that the larger pore size MOF (DUT-5-CuCl) has comparatively higher efficiency than the smaller pore size

MIL-53(Al)-CuCl MOF due to the facile diffusion of substrates into the larger pores of DUT-5-CuCl.

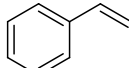
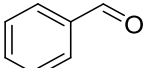
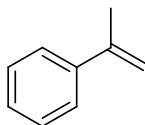
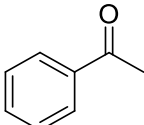
3.5.7. Radical Scavenging Experiment with DUT-5-CuCl

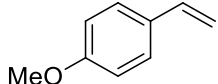
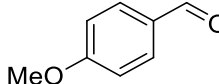
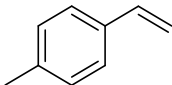
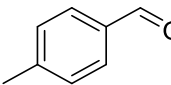
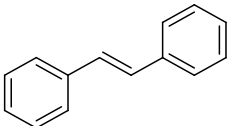
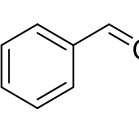
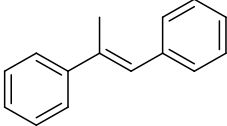
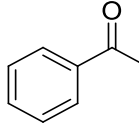
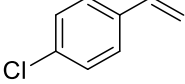
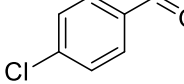
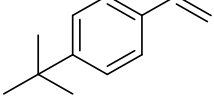
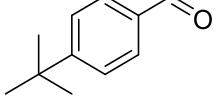
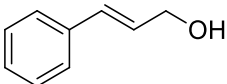
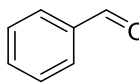
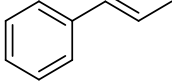
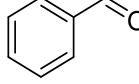
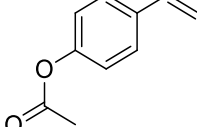
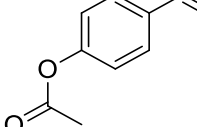
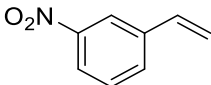
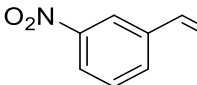
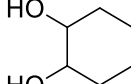
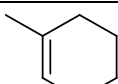
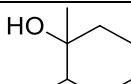
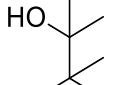
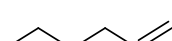
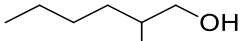
To investigate any role of $\cdot\text{OH}$ in DUT-5-CuCl catalysed α -methylstyrene to acetophenone conversion, we had performed the catalysis in presence of a known $\cdot\text{OH}$ radical scavenger such as Na_2SO_3 , and then catalytic activity and selectivity were compared to those of reactions done in absence of Na_2SO_3 . The experimental details are given below: Solid MOF DUT-5-CuCl (0.5 mol% of Cu) as a slurry in 1 mL CH_3CN was charged into a 5 mL vial. The MOF slurry was then transferred to a 25 mL Schlenk tube. To the mixture 2 mL CH_3CN , 162.5 μL (1.25 mmol) α -methylstyrene and 0.5 mL H_2O_2 were added. Then, Na_2SO_3 (315 mg, 2.5 mmol), $\cdot\text{OH}$ scavenger was added to the Schlenk tube to study its effect on the catalytical reaction. Then, the Schlenk tube was heated at 80 $^\circ\text{C}$ and equipped with a water-cooled reflux condenser. After 4 h, the reaction mixture was taken out and analysed by GC-MS. The yield of acetophenone in the reaction was 57%, which is similar to that obtained without scavenger (58%) under identical reaction conditions. We conclude that the presence of the radical scavenger (Na_2SO_3) does not affect the rate of the oxidation of α -methylstyrene to acetophenone catalysed by DUT-5-CuCl, which illustrates that $\cdot\text{OH}$ radicals do not participate in the mechanism.

3.6. Analysis of Products by GC-MS

The conversions and yields of the reactions were determined by Agilent 7890B gas chromatograph equipped with a mass detector (Agilent 5977B GC/MSD) and HP-5MS Ultra Inert 30 m-250 μm -0.25 μm column for GC-MS. GC-MS conditions: Inj: 220 $^\circ\text{C}$; Det: 250 $^\circ\text{C}$; Column temp: 40 $^\circ\text{C}$ followed by a ramp of 5 $^\circ\text{C}/\text{min}$ to 200 $^\circ\text{C}$; Column flow: 1.0 mL/min.

Table 3.4. The GC-MS retention times of the substrates and the products.

Entry	Substrate	Retention time	Product	Retention time
1		7.65		9.63
2		10.23		13.05

3		15.11		18.08
4		10.63		13.24
5		29.04		9.64
6		29.28		13.04
7		12.93		14.43
8		17.218		19.65
9		19.45		9.63
10		11.45		9.64
11		18.96		20.67
12		19.346		20.627
13		3.54		12.52
14		4.89		13.57
15		3.03		6.94
16		2.72		6.80

3.7. DFT Calculations

All quantum chemical calculations were done using the density functional theory (DFT) functional B3LYP/6-311G+g(d,p) as implemented in the Gaussian 09 software suite.^{215–219} Electronic structure complexes were optimized at the unrestricted level. All calculations were performed in the solvated state. We used the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) as the default SCRF method by using THF as the solvent for DUT-5-CuCl at room temperature (25 °C) and acetonitrile (CH₃CN) as the solvent for other molecules in this DFT calculation at 80 °C. Each structure was first optimized, and then frequency calculation was performed to confirm its geometry and to obtain the thermochemical data. DUT-5-CuCl was calculated with one or two THF molecules coordinated to Cu, and DUT-5-Cu(OH) was calculated with zero or one CH₃CN molecule coordinated to Cu. Internal energies were compared directly after accounting for the difference in the number of coordinated CH₃CN molecules.

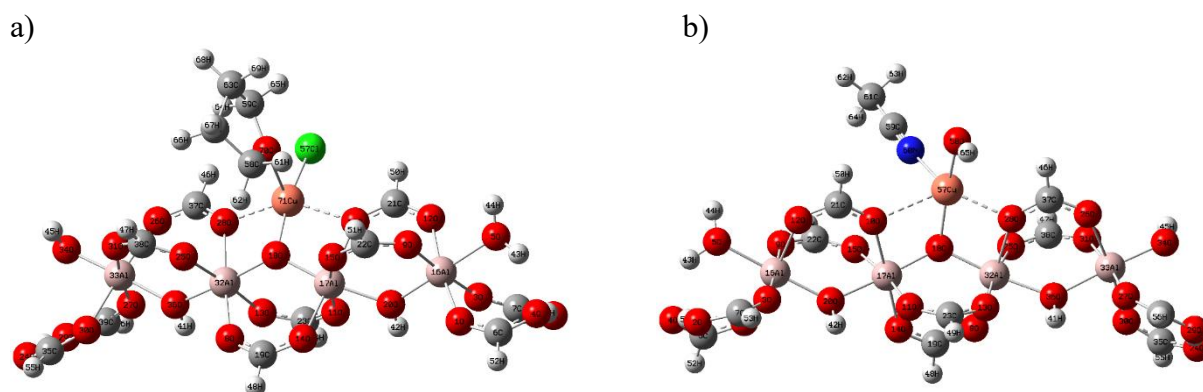
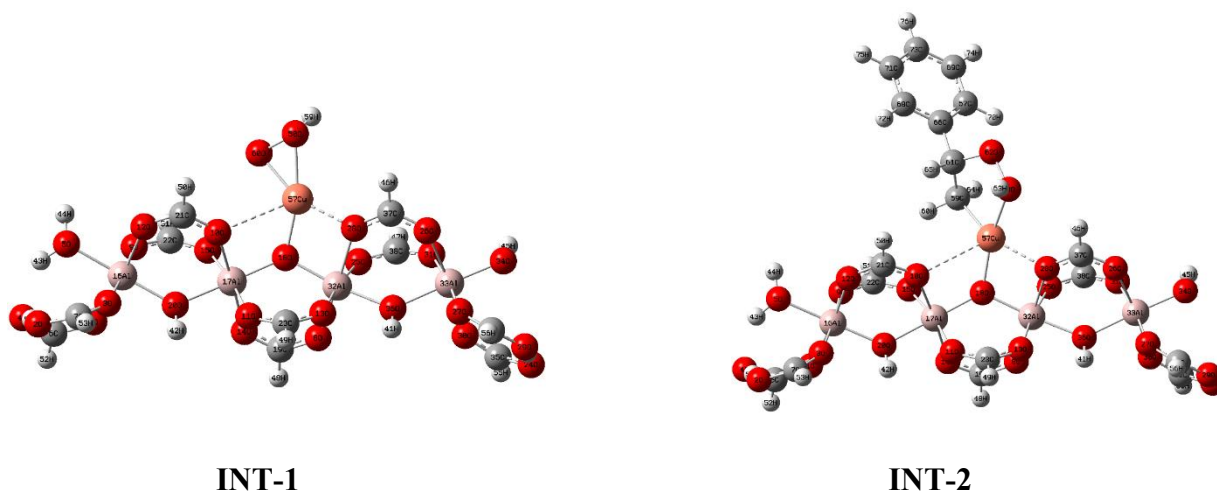


Figure 3.11. DFT-optimized structures of a) DUT-5-Cu(Cl)(THF) b) DUT-5-Cu(OH)(CH₃CN).



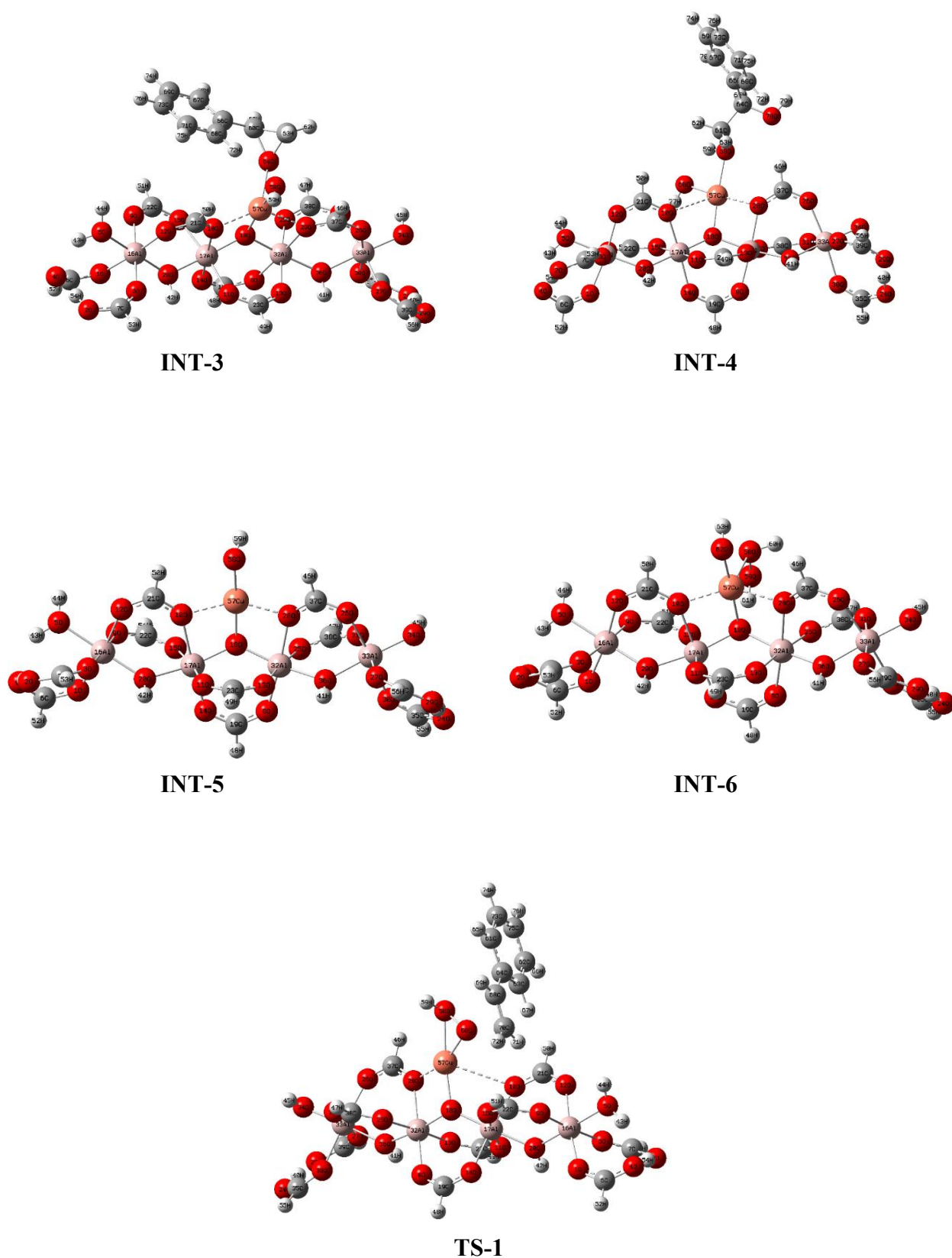


Figure 3.12. DFT-optimized structures of intermediates and transition states of the catalytic cycle in DUT-5-CuCl catalysed oxidation of styrene using H_2O_2 .

3.7.1. Cartesian coordinates of the DFT-optimized structures.

Cartesian coordinates of DUT-5-Cu(Cl)(THF)

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	O	23.221257	12.362069	17.218987
2	O	20.262341	11.108350	18.788542
3	O	21.024344	13.232265	18.693672
4	O	21.947259	10.554563	16.852640
5	O	20.827213	12.801701	15.999915
6	C	23.052653	11.116548	17.034558
7	C	20.344640	12.330639	19.194009
8	O	26.210810	18.427596	19.164546
9	O	22.926584	14.459077	15.570847
10	O	21.762167	17.103863	17.299144
11	O	23.101112	16.833588	19.892300
12	O	20.668551	15.196056	16.925154
13	O	23.795761	18.910975	20.437313
14	O	25.510627	16.346543	18.622142
15	O	24.229639	16.169963	16.234043
16	Al	22.043584	13.849610	17.126108
17	Al	23.718799	16.613788	18.037835
18	O	23.827562	18.382487	17.789446
19	C	26.367386	17.190184	19.012159
20	O	23.093921	14.864293	18.268363
21	C	20.714293	16.444257	17.020842
22	C	23.822670	15.335215	15.395354
23	C	23.231115	17.815430	20.677943
24	O	27.767031	24.488420	21.465336
25	O	25.656588	20.361901	17.326075
26	O	23.235751	22.717027	19.060636
27	O	24.539574	22.919263	21.439698
28	O	22.980219	20.655952	18.228921
29	O	25.575581	24.515204	22.650959
30	O	27.147484	22.812273	20.084455
31	O	25.727915	22.568009	17.781847
32	Al	24.714093	19.590552	18.791341
33	Al	25.170206	22.870198	19.637370
34	O	25.185696	24.633117	19.428714
35	C	27.978923	23.576087	20.585481
36	O	25.210846	20.982853	19.890488
37	C	22.550460	21.824556	18.549457
38	C	25.949281	21.561321	17.068443
39	C	24.662267	23.703271	22.434866
40	H	26.787176	24.501067	21.843060
41	H	25.016857	20.793978	20.815108
42	H	22.949808	14.681918	19.203872
43	H	21.041930	11.846795	15.935514
44	H	20.505404	13.143538	15.157460
45	H	25.453068	24.910759	18.550277
46	H	21.494322	22.022751	18.338351
47	H	26.445075	21.737461	16.105441
48	H	27.359259	16.789946	19.250888
49	H	22.801396	17.691696	21.680023
50	H	19.798342	17.017012	16.852156
51	H	24.279623	15.365157	14.400604
52	H	23.965150	10.507078	17.039713
53	H	19.735630	12.533837	20.076301
54	H	20.863866	10.904523	18.003719
55	H	29.029146	23.499139	20.284831
56	H	23.861204	23.624957	23.186708
57	Cl	20.383323	19.290669	18.829871
58	C	20.507162	18.897902	14.842284
59	C	21.250121	21.150133	15.503038
60	C	20.096188	19.869383	13.745294
61	H	19.603224	18.418233	15.295664
62	H	21.140176	18.076295	14.423117
63	C	20.495199	21.270172	14.186879
64	H	22.292193	21.542999	15.393795
65	H	20.750446	21.760073	16.296967
66	H	20.602919	19.606057	12.782734

67	H	18.993930	19.813418	13.562674
68	H	21.135384	21.758553	13.410089
69	H	19.587321	21.911632	14.316029
70	O	21.275595	19.680212	15.897535
71	Cu	22.099987	19.034077	17.561121

Cartesian coordinates of DUT-5-Cu(OH)(CH₃CN)

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	O	22.750385	12.247748	17.404215
2	O	20.083463	10.901928	19.357489
3	O	20.762572	13.049220	19.193056
4	O	21.477457	10.414158	17.194113
5	O	20.199660	12.662442	16.545542
6	C	22.583521	11.001637	17.218953
7	C	20.191190	12.119496	19.771393
8	C	25.878627	18.281548	19.116780
9	O	22.196469	14.370074	15.863431
10	O	21.258596	16.941426	17.799493
11	O	22.861573	16.676448	20.167189
12	O	20.128417	15.033837	17.522086
13	O	23.635737	18.730144	20.691741
14	O	25.099873	16.224321	18.594359
15	O	23.538195	16.105208	16.371084
16	Al	21.543354	13.711917	17.512707
17	Al	23.239528	16.517559	18.239795
18	O	23.347311	18.288155	18.015976
19	C	26.004006	17.047912	18.906836
20	O	22.724891	14.727474	18.514587
21	C	20.191728	16.281214	17.629123
22	C	23.039614	15.270561	15.582362
23	C	23.089718	17.630604	20.961734
24	O	27.876892	24.180335	21.354775
25	O	25.128730	20.281390	17.422824
26	O	22.979808	22.595704	19.586852
27	O	24.624169	22.671413	21.762326
28	O	22.640853	20.563488	18.713474
29	O	25.893485	24.172852	22.869354
30	O	27.011376	22.584041	20.014226
31	O	25.250812	22.468303	17.954412
32	Al	24.342113	19.450041	18.965602
33	Al	24.974782	22.680195	19.881402
34	O	25.001426	24.456736	19.751883
35	C	27.929386	23.307751	20.410039
36	O	25.034730	20.790673	20.048534
37	C	22.248596	21.716385	19.107082
38	C	25.377316	21.491096	17.175984
39	C	24.935530	23.388973	22.765469
40	H	26.969730	24.181218	21.877675
41	H	24.971800	20.554704	20.980304
42	H	22.716379	14.525607	19.456978
43	H	20.409354	11.714410	16.419563
44	H	19.741983	13.019676	15.775197
45	H	25.217636	24.760525	18.867518
46	H	21.176391	21.908594	18.990150
47	H	25.737342	21.712834	16.163213
48	H	27.014296	16.635562	19.012774
49	H	22.776360	17.479463	22.002492
50	H	19.266473	16.861132	17.565736
51	H	23.356467	15.323206	14.535223
52	H	23.500206	10.416692	17.070990
53	H	19.715208	12.290472	20.737993
54	H	20.567399	10.729433	18.487508
55	H	28.917629	23.231380	19.945050
56	H	24.271426	23.278172	23.637082
57	Cu	21.589721	18.991091	17.956816
58	O	19.899237	19.607021	17.903021
59	C	21.276516	19.943017	15.064293

60	N	21.399416	19.569485	16.199305
61	C	21.118952	20.421903	13.609150
62	H	20.297001	19.911158	13.152601
63	H	20.934294	21.475795	13.598514
64	H	22.016084	20.211487	13.065294
65	H	19.515341	19.528615	18.755806

Cartesian coordinates of INT-1

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	O	23.129181	12.396705	17.096435
2	O	20.750298	10.745359	19.202225
3	O	21.216405	12.952288	19.043283
4	O	22.042270	10.441440	16.934162
5	O	20.489674	12.541384	16.436634
6	C	23.082042	11.143291	16.900572
7	C	20.779921	11.962026	19.637002
8	O	25.842079	18.565654	18.607848
9	O	22.227998	14.452939	15.622346
10	O	21.172241	16.917758	17.765749
11	O	23.015683	16.783781	19.919085
12	O	20.259052	14.886314	17.467591
13	O	23.766008	18.847063	20.438732
14	O	25.099327	16.496517	18.102145
15	O	23.327613	16.369273	16.055379
16	Al	21.787573	13.729658	17.312978
17	Al	23.200804	16.708530	17.959854
18	O	23.203847	18.498065	17.781146
19	C	25.997992	17.350362	18.336718
20	O	22.914747	14.859118	18.233249
21	C	20.196226	16.131175	17.644482
22	C	22.900916	15.475083	15.294212
23	C	23.288591	17.721058	20.720185
24	O	28.114463	24.247901	20.955918
25	O	24.829528	20.592612	17.099115
26	O	23.082092	22.789890	19.565903
27	O	24.908878	22.728297	21.596739
28	O	22.551161	20.765557	18.741363
29	O	26.291791	24.167716	22.649266
30	O	27.121062	22.688520	19.657946
31	O	25.199162	22.723485	17.735994
32	Al	24.252369	19.675672	18.680258
33	Al	25.087462	22.834957	19.691720
34	O	25.146136	24.612258	19.656543
35	C	28.078166	23.390424	19.996271
36	O	25.098354	20.943021	19.746469
37	C	22.272534	21.931893	19.180749
38	C	25.152310	21.792620	16.895880
39	C	25.305972	23.413920	22.591958
40	H	27.246177	24.266791	21.545609
41	H	25.142727	20.653636	20.663677
42	H	23.038055	14.640718	19.163123
43	H	20.803167	11.625801	16.279087
44	H	19.955139	12.857311	15.698807
45	H	25.231356	24.966387	18.768948
46	H	21.205538	22.190010	19.198346
47	H	25.411141	22.052480	15.861019
48	H	27.031088	16.982760	18.307463
49	H	23.079433	17.526016	21.780335
50	H	19.193348	16.571538	17.679277
51	H	23.118695	15.581898	14.225817
52	H	24.043606	10.658397	16.687285
53	H	20.365228	12.067818	20.641593
54	H	21.177172	10.632372	18.292905
55	H	29.027053	23.305743	19.455296
56	H	24.700291	23.298134	23.505527
57	Cu	21.445068	19.172606	17.759399
58	O	19.637685	19.807326	17.333596
59	H	18.747761	20.119876	17.123927
60	O	20.446521	19.651897	16.092824

Cartesian coordinates of INT-2

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	O	25.049706	13.867025	16.599070
2	O	23.387979	10.691299	16.702618
3	O	22.836975	12.614707	17.747654
4	O	24.939778	12.147428	15.165034
5	O	22.716666	13.613368	15.206272
6	C	25.572024	13.001956	15.828094
7	C	22.807887	11.386405	17.622421
8	O	24.458161	18.553365	21.753018
9	O	23.540004	16.027865	16.103141
10	O	21.272131	16.457720	18.500868
11	O	22.689398	15.563616	20.931627
12	O	21.351724	14.723784	17.093548
13	O	22.245151	17.083738	22.542086
14	O	24.901571	17.028854	20.147012
15	O	23.752037	17.532487	17.762985
16	Al	23.246488	14.356802	16.939274
17	Al	23.190646	16.650422	19.387316
18	O	22.335036	18.083932	20.043492
19	C	25.223881	17.825942	21.071205
20	O	23.644335	14.999398	18.631188
21	C	20.731146	15.593369	17.744320
22	C	23.799623	17.177191	16.563216
23	C	22.307901	15.913714	22.084167
24	O	22.958102	22.488367	26.872444
25	O	22.864377	20.595416	20.981346
26	O	19.732340	20.240166	23.123857
27	O	20.963676	19.813288	25.515496
28	O	20.513677	19.114225	21.353890
29	O	21.187293	20.850668	27.506190
30	O	23.141456	21.661354	24.780414
31	O	21.824566	21.971415	22.431004
32	Al	22.548277	18.835698	21.673510
33	Al	21.368626	20.977232	24.054718
34	O	20.469484	22.362531	24.718893
35	C	23.519591	22.365833	25.721699
36	O	22.374926	19.513027	23.384893
37	C	19.570435	19.569382	22.095998
38	C	22.471023	21.722325	21.384161
39	C	20.793679	19.930095	26.770850
40	H	22.153109	21.833809	27.022542
41	H	22.381410	18.810178	24.043940
42	H	23.674374	14.317925	19.312574
43	H	23.406501	13.072810	14.766233
44	H	22.246623	14.154559	14.560312
45	H	20.539482	23.149280	24.173817
46	H	18.550000	19.340383	21.771290
47	H	22.716427	22.577224	20.741590
48	H	26.292615	17.884775	21.306316
49	H	22.018954	15.104563	22.763984
50	H	19.642184	15.619564	17.650408
51	H	24.089192	17.936630	15.829359
52	H	26.666581	13.029204	15.756123
53	H	22.253347	10.778882	18.338823
54	H	23.939655	11.251372	16.069976
55	H	24.431026	22.963087	25.617052
56	H	20.240373	19.102649	27.241634
57	Cu	20.491869	17.934510	19.702084
58	O	19.233529	16.975165	20.190378
59	C	19.759460	18.921293	18.547775
60	H	20.354142	19.075085	17.671647
61	C	18.449074	18.287997	18.145376
62	O	17.986944	17.339945	19.420274
63	H	19.338124	16.291010	20.855654
64	H	19.559815	19.876103	18.987525
65	H	18.626073	17.689714	17.276107
66	C	17.484984	19.461223	17.889108
67	C	16.199529	19.438841	18.430934
68	C	17.896883	20.546265	17.115434
69	C	15.326006	20.500992	18.198525
70	H	15.874836	18.582914	19.040200

71	C	17.023553	21.609276	16.883679
72	H	18.910049	20.564150	16.688463
73	C	15.738229	21.586749	17.424949
74	H	14.312566	20.483132	18.625044
75	H	17.348733	22.464840	16.273974
76	H	15.049332	22.424130	17.241888

Cartesian coordinates of INT-3

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	O	23.031079	12.383138	16.977005
2	O	20.598699	10.865297	19.102722
3	O	21.169039	13.044786	18.948995
4	O	21.824532	10.500290	16.816801
5	O	20.401542	12.705366	16.346777
6	C	22.902603	11.136279	16.767735
7	C	20.688839	12.074738	19.543767
8	O	26.031912	18.503207	18.609574
9	O	22.258732	14.519517	15.554166
10	O	21.378665	16.992026	17.640304
11	O	23.185789	16.735263	19.857083
12	O	20.311705	15.043574	17.398890
13	O	23.912964	18.806777	20.378811
14	O	25.300498	16.427902	18.090241
15	O	23.563114	16.299035	16.001973
16	Al	21.776022	13.787729	17.230865
17	Al	23.406019	16.646297	17.900932
18	O	23.418692	18.425404	17.723908
19	C	26.191747	17.282693	18.351793
20	O	22.993459	14.827941	18.161970
21	C	20.330431	16.289150	17.538899
22	C	23.035837	15.464540	15.231973
23	C	23.439227	17.676713	20.659084
24	O	27.958005	24.423018	20.855319
25	O	25.056762	20.512592	17.046676
26	O	23.001337	22.667445	19.452663
27	O	24.818852	22.758011	21.485095
28	O	22.677030	20.646581	18.547944
29	O	26.111777	24.284526	22.528690
30	O	27.051395	22.826413	19.542592
31	O	25.129682	22.687463	17.633790
32	Al	24.439561	19.604725	18.623036
33	Al	25.008618	22.833977	19.582702
34	O	24.948229	24.612779	19.506539
35	C	27.967769	23.579814	19.882902
36	O	25.163219	20.945241	19.685623
37	C	22.270484	21.769389	19.008364
38	C	25.231647	21.738587	16.817623
39	C	25.182872	23.461264	22.480614
40	H	27.099054	24.368610	21.451650
41	H	25.189376	20.681321	20.611635
42	H	23.073228	14.600246	19.095092
43	H	20.640192	11.771577	16.174467
44	H	19.865567	13.062437	15.628621
45	H	25.075768	24.950059	18.617095
46	H	21.184998	21.916044	18.987050
47	H	25.495017	22.003940	15.785772
48	H	27.224081	16.913704	18.360484
49	H	23.221661	17.483206	21.717117
50	H	19.379178	16.828156	17.570711
51	H	23.260555	15.560022	14.164242
52	H	23.827684	10.597635	16.525965
53	H	20.289340	12.197570	20.551448
54	H	21.014344	10.738671	18.190570
55	H	28.915557	23.560924	19.335167
56	H	24.600121	23.296799	23.400600
57	Cu	21.633941	19.049508	17.832985
58	O	19.893904	19.597891	17.940755
59	H	19.367610	19.375994	18.712361
60	C	21.928265	19.043216	14.669398
61	C	22.303495	20.458160	15.001734
62	H	23.363608	20.760698	14.940583

63	H	21.626549	21.277359	14.702122
64	O	21.874680	19.519610	16.091904
65	H	22.741930	18.391488	14.428359
66	C	20.566285	18.858631	13.974748
67	C	20.419726	17.901855	12.969973
68	C	19.479194	19.647852	14.350129
69	C	19.186495	17.734872	12.340308
70	H	21.277161	17.280335	12.673727
71	C	18.245262	19.480265	13.721053
72	H	19.594483	20.401866	15.142152
73	C	18.098787	18.524065	12.716183
74	H	19.071063	16.981183	11.547891
75	H	17.388208	20.102392	14.017518
76	H	17.126511	18.392184	12.219613

Cartesian coordinates of INT-4

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	O	23.031079	12.383138	16.977005
2	O	20.598699	10.865297	19.102722
3	O	21.169039	13.044786	18.948995
4	O	21.824532	10.500290	16.816801
5	O	20.401542	12.705366	16.346777
6	C	22.902603	11.136279	16.767735
7	C	20.688839	12.074738	19.543767
8	O	26.031912	18.503207	18.609574
9	O	22.258732	14.519517	15.554166
10	O	21.378665	16.992026	17.640304
11	O	23.185789	16.735263	19.857083
12	O	20.311705	15.043574	17.398890
13	O	23.912964	18.806777	20.378811
14	O	25.300498	16.427902	18.090241
15	O	23.563114	16.299035	16.001973
16	Al	21.776022	13.787729	17.230865
17	Al	23.406019	16.646297	17.900932
18	O	23.418692	18.425404	17.723908
19	C	26.191747	17.282693	18.351793
20	O	22.993459	14.827941	18.161970
21	C	20.330431	16.289150	17.538899
22	C	23.035837	15.464540	15.231973
23	C	23.439227	17.676713	20.659084
24	O	27.958005	24.423018	20.855319
25	O	25.056762	20.512592	17.046676
26	O	23.001337	22.667445	19.452663
27	O	24.818852	22.758011	21.485095
28	O	22.677030	20.646581	18.547944
29	O	26.111777	24.284526	22.528690
30	O	27.051395	22.826413	19.542592
31	O	25.129682	22.687463	17.633790
32	Al	24.439561	19.604725	18.623036
33	Al	25.008618	22.833977	19.582702
34	O	24.948229	24.612779	19.506539
35	C	27.967769	23.579814	19.882902
36	O	25.163219	20.945241	19.685623
37	C	22.270484	21.769389	19.008364
38	C	25.231647	21.738587	16.817623
39	C	25.182872	23.461264	22.480614
40	H	27.099054	24.368610	21.451650
41	H	25.189376	20.681321	20.611635
42	H	23.073228	14.600246	19.095092
43	H	20.640192	11.771577	16.174467
44	H	19.865567	13.062437	15.628621
45	H	25.075768	24.950059	18.617095
46	H	21.184998	21.916044	18.987050
47	H	25.495017	22.003940	15.785772
48	H	27.224081	16.913704	18.360484
49	H	23.221661	17.483206	21.717117
50	H	19.379178	16.828156	17.570711
51	H	23.260555	15.560022	14.164242
52	H	23.827684	10.597635	16.525965
53	H	20.289340	12.197570	20.551448
54	H	21.014344	10.738671	18.190570

55	H	28.915557	23.560924	19.335167
56	H	24.600121	23.296799	23.400600
57	Cu	21.633941	19.049508	17.832985
58	O	19.893904	19.597891	17.940755
59	H	19.506185	20.107845	17.225758
60	O	21.277136	19.656515	16.143863
61	C	19.109946	19.267357	19.090127
62	H	18.385080	18.525856	18.826223
63	H	19.748046	18.884591	19.859034
64	C	18.390561	20.529501	19.601085
65	H	18.426878	21.289819	18.849089
66	C	16.922107	20.190599	19.917926
67	C	15.940026	20.364220	18.942302
68	C	16.573892	19.709977	21.180185
69	C	14.609953	20.057901	19.229175
70	H	16.214762	20.743879	17.947505
71	C	15.243605	19.402584	21.466991
72	H	17.347825	19.572908	21.949190
73	C	14.261634	19.576587	20.491802
74	H	13.835716	20.195319	18.460429
75	H	14.969409	19.023262	22.462182
76	H	13.212863	19.335077	20.717741
77	H	22.102470	19.822339	15.682424
78	O	19.037590	21.000060	20.786339
79	C	18.474849	21.642153	21.225247

Cartesian coordinates of INT-5

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	O	23.045437	12.376000	17.003714
2	O	20.592988	10.882526	19.132061
3	O	21.169901	13.058041	18.952952
4	O	21.843178	10.488643	16.860205
5	O	20.418170	12.684149	16.350345
6	C	22.920704	11.125719	16.813006
7	C	20.679858	12.098444	19.556241
8	O	26.018175	18.522788	18.537902
9	O	22.274062	14.490703	15.545294
10	O	21.349793	16.993131	17.674544
11	O	23.213632	16.731445	19.852967
12	O	20.315776	15.034637	17.371712
13	O	23.952583	18.791893	20.370076
14	O	25.285711	16.450104	18.033187
15	O	23.499354	16.327015	15.987338
16	Al	21.785022	13.780895	17.228416
17	Al	23.386010	16.660121	17.894349
18	O	23.377303	18.441415	17.709581
19	C	26.179227	17.307169	18.268932
20	O	22.995817	14.837113	18.150252
21	C	20.314844	16.277105	17.536063
22	C	23.011465	15.466183	15.220799
23	C	23.486015	17.663575	20.655069
24	O	27.966733	24.394446	20.923985
25	O	24.985098	20.539417	17.024126
26	O	23.028351	22.692048	19.402485
27	O	24.809410	22.743643	21.474708
28	O	22.654955	20.635135	18.601471
29	O	26.071294	24.275240	22.546288
30	O	27.078393	22.804557	19.588155
31	O	25.197167	22.700105	17.631411
32	Al	24.417494	19.611802	18.609042
33	Al	25.036617	22.832004	19.577312
34	O	24.996754	24.612025	19.513714
35	C	27.992831	23.548678	19.953757
36	O	25.171036	20.941783	19.665313
37	C	22.277484	21.791362	18.997354
38	C	25.229968	21.755090	16.805152
39	C	25.142406	23.453458	22.476374
40	H	27.093514	24.351922	21.501084
41	H	25.209980	20.670124	20.588672
42	H	23.100081	14.603029	19.079331
43	H	20.662975	11.748352	16.195959
44	H	19.898463	13.029721	15.614756

45	H	25.091900	24.951699	18.621109
46	H	21.196549	21.965490	18.957232
47	H	25.493302	22.015473	15.771969
48	H	27.213592	16.944237	18.245771
49	H	23.296424	17.461377	21.716886
50	H	19.354361	16.800110	17.560572
51	H	23.235481	15.565000	14.153179
52	H	23.849142	10.584816	16.589951
53	H	20.268440	12.236718	20.557099
54	H	21.018973	10.743298	18.227135
55	H	28.955642	23.517031	19.433373
56	H	24.531711	23.296184	23.379395
57	Cu	21.594997	19.056250	17.834632
58	O	19.871846	19.650612	17.957424
59	H	19.579321	20.054026	17.134443

Cartesian coordinates of INT-6

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	O	23.059680	12.369529	17.079533
2	O	20.625826	10.821848	19.187847
3	O	21.172013	13.007360	19.022008
4	O	21.887017	10.466124	16.911687
5	O	20.427336	12.623352	16.421844
6	C	22.956628	11.119117	16.882956
7	C	20.695708	12.037382	19.618175
8	O	25.917779	18.547467	18.585809
9	O	22.242682	14.459144	15.605322
10	O	21.260596	16.973953	17.744995
11	O	23.112694	16.748310	19.907816
12	O	20.289034	14.976847	17.445669
13	O	23.856251	18.812931	20.430571
14	O	25.185001	16.473289	18.078514
15	O	23.403672	16.337946	16.044402
16	Al	21.774334	13.753213	17.295335
17	Al	23.287905	16.677855	17.950804
18	O	23.279972	18.464929	17.781569
19	C	26.079317	17.333175	18.311186
20	O	22.944733	14.842288	18.215210
21	C	20.252047	16.217983	17.623175
22	C	22.952877	15.456307	15.281475
23	C	23.385496	17.683781	20.711781
24	O	28.014764	24.329342	20.984153
25	O	24.885049	20.566873	17.087193
26	O	23.040299	22.718905	19.510021
27	O	24.843969	22.740047	21.562870
28	O	22.577271	20.677182	18.700674
29	O	26.143083	24.248280	22.625425
30	O	27.085373	22.757871	19.654871
31	O	25.190032	22.712107	17.710325
32	Al	24.323496	19.646093	18.674883
33	Al	25.049591	22.836470	19.664345
34	O	25.042505	24.612273	19.609984
35	C	28.014960	23.487352	20.012667
36	O	25.123140	20.944027	19.732957
37	C	22.253140	21.841460	19.130337
38	C	25.180970	21.774056	16.878700
39	C	25.194290	23.450191	22.558679
40	H	27.142915	24.304432	21.569931
41	H	25.165464	20.665481	20.653836
42	H	23.058468	14.618174	19.145177
43	H	20.701448	11.694090	16.269004
44	H	19.901072	12.956731	15.685775
45	H	25.126025	24.963470	18.721228
46	H	21.178175	22.054765	19.147244
47	H	25.451548	22.030143	15.845867
48	H	27.114185	16.972222	18.276503
49	H	23.188196	17.482114	21.772441
50	H	19.269050	16.696119	17.671656
51	H	23.184453	15.553303	14.214989
52	H	23.895891	10.591530	16.673382
53	H	20.281006	12.162857	20.619704
54	H	21.054311	10.691778	18.283493

55	H	28.970800	23.441748	19.479588
56	H	24.579499	23.314564	23.462668
57	Cu	21.501191	19.100926	17.846847
58	O	20.832423	19.756481	16.274620
59	O	21.583769	19.762523	15.189335
60	H	19.935162	20.095985	16.239143
61	H	22.481162	19.423376	15.224904
62	O	20.013085	19.368580	18.877770
63	H	19.320391	19.764542	18.343927

60	O	20.367134	18.987333	16.119163
61	C	16.802768	21.295065	17.858204
62	C	17.351109	21.373772	20.592722
63	C	17.913190	20.375488	19.797090
64	C	17.639330	20.336339	18.429655
65	H	16.586606	21.264080	16.780495
66	H	17.567322	21.405368	21.670474
67	H	18.572490	19.619199	20.247450
68	C	18.260290	19.234184	17.551438
69	H	18.048784	19.205511	16.502943
70	C	19.073695	18.300479	18.102014
71	H	19.288876	18.324002	19.149890
72	H	19.502211	17.537128	17.486734
73	C	16.240137	22.293338	18.654049
74	H	15.549392	22.990338	18.227479
75	C	16.514601	22.333198	20.020907
76	H	16.134910	23.134282	20.620073

Cartesian coordinates of TS-1

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	O	23.124459	12.403740	17.037407
2	O	20.924210	10.666798	19.243921
3	O	21.322826	12.886544	19.097086
4	O	22.058006	10.437005	16.883821
5	O	20.444967	12.509467	16.534574
6	C	23.084276	11.155168	16.816047
7	C	20.945532	11.878051	19.696709
8	O	25.790088	18.529216	18.613046
9	O	22.095471	14.447415	15.628287
10	O	21.112028	16.850893	18.175477
11	O	23.182873	16.735006	19.968758
12	O	20.257869	14.844366	17.603687
13	O	23.756648	18.851233	20.493834
14	O	25.011253	16.534892	17.897307
15	O	22.956676	16.481114	16.072598
16	Al	21.773888	13.716636	17.345775
17	Al	23.080021	16.734016	18.003140
18	O	23.126507	18.520074	17.846541
19	C	25.922471	17.352533	18.183692
20	O	22.944403	14.847640	18.200284
21	C	20.170888	16.053210	17.970907
22	C	22.599214	15.563173	15.303729
23	C	23.392144	17.680554	20.773099
24	O	28.090709	24.169594	21.068767
25	O	24.779724	20.572897	17.143817
26	O	23.034844	22.788739	19.577812
27	O	24.843150	22.739429	21.622660
28	O	22.494883	20.779703	18.733121
29	O	26.209452	24.177854	22.697436
30	O	27.084513	22.672925	19.709717
31	O	25.181765	22.701164	17.771713
32	Al	24.223941	19.644546	18.739922
33	Al	25.061246	22.826199	19.724518
34	O	25.107123	24.601945	19.671805
35	C	28.050122	23.346051	20.082924
36	O	25.052231	20.936863	19.788675
37	C	22.221096	21.965673	19.147729
38	C	25.126729	21.765566	16.937066
39	C	25.221205	23.429742	22.621933
40	H	27.215882	24.184725	21.652395
41	H	25.088395	20.651789	20.707849
42	H	23.272930	14.559636	19.057026
43	H	20.775840	11.604011	16.350974
44	H	19.900180	12.830294	15.806294
45	H	25.248095	24.948995	18.788618
46	H	21.162085	22.249120	19.103888
47	H	25.400328	22.014316	15.903105
48	H	26.952930	16.997867	18.054752
49	H	23.244498	17.456306	21.837838
50	H	19.153956	16.434703	18.118605
51	H	22.724783	15.735513	14.228573
52	H	24.040327	10.688093	16.545783
53	H	20.585615	11.955073	20.724391
54	H	21.301574	10.582858	18.312314
55	H	29.003696	23.258723	19.551259
56	H	24.593185	23.325812	23.520988
57	Cu	21.571990	19.527791	17.467813
58	O	19.836757	20.229574	16.723270
59	H	19.928654	20.883013	16.013812

3.8. X-ray Absorption Spectroscopic Analysis

X-ray Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) measurements have been carried out at the Energy-Scanning EXAFS beamline (BL-9) at the Indus-2 Synchrotron Source at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.²²⁰ All the measurements were performed at room temperature. This beamline operates in the energy range of 4 keV to 25 keV. The beamline optics consist of a Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si(111) based double crystal monochromator (DCM). The second crystal of the DCM is a sagittal cylindrical crystal which is used for horizontal focusing of the beam while another Rh/Pt coated bendable post mirror facing downward is used for vertical focusing of the beam at the sample position. Two ionization chambers (300 mm length each) have been used for data collection in the transmission mode; one ionization chamber for measuring incident flux, the second one for measuring transmitted flux. For energy calibration, standard metal foils were used. Appropriate gas pressure and gas mixture have been chosen to achieve 10-20% absorption in the first ionization chamber and 70-90% absorption in the second ionization chamber to obtain a better signal-to-noise ratio. Pellets were made from powder samples for recording absorption spectra. Sample powder was mixed homogeneously with cellulose powder in appropriate proportion and pressed (2 Ton) into a 15 mm diameter disc. The amount of the sample was estimated such that to get a reasonable edge jump at a particular absorption edge of the element to be probed. Spectra were collected at the copper K-edge in transmission mode and were calibrated against the reference spectrum of metallic copper (8978.9 eV). Data were processed using Demeter software.²²¹ A metallic copper foil standard was used as a reference for energy calibration and was measured simultaneously with experimental samples.

3.8.1. XANES Analysis

The oxidation state of the Cu species within DUT-5-CuCl, and DUT-5-Cu after catalysis was determined by the comparison of the energies of their K-edge positions to those of CuCl₂. The positions of the Cu-K-edge of DUT-5-CuCl and DUT-5-Cu after catalysis aligned well with that of CuCl₂ (8986 eV). Therefore, we assign the oxidation state of copper in DUT-5-CuCl and DUT-5-Cu after catalysis as +2.

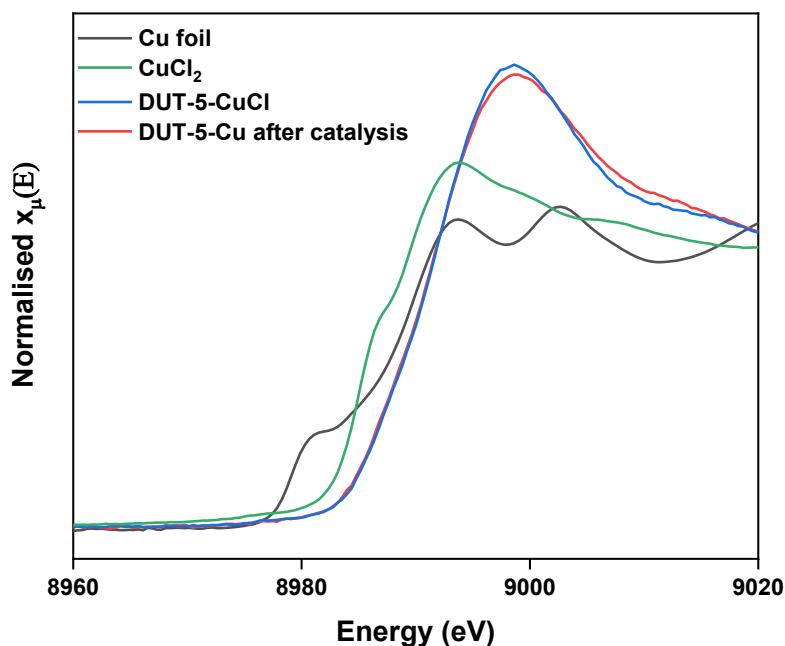


Figure 3.13. Cu K-edge XANES spectra of Cu foil, CuCl_2 , DUT-5-CuCl, and DUT-5-Cu after catalysis.

3.8.2. EXAFS Fitting using DFT Optimized Structures

The EXAFS spectra were calibrated against the reference spectra and aligned to the first peak in the smoothed first derivative of the absorption spectrum, the background noise was removed, and the spectra were processed to obtain a normalized unit edge step. The fitting parameters of DUT-5-Cu(Cl)(THF) and DUT-5-Cu(OH)(CH_3CN) after oxidation of styrene are summarized in Table 3.5 and Table 3.6, respectively.

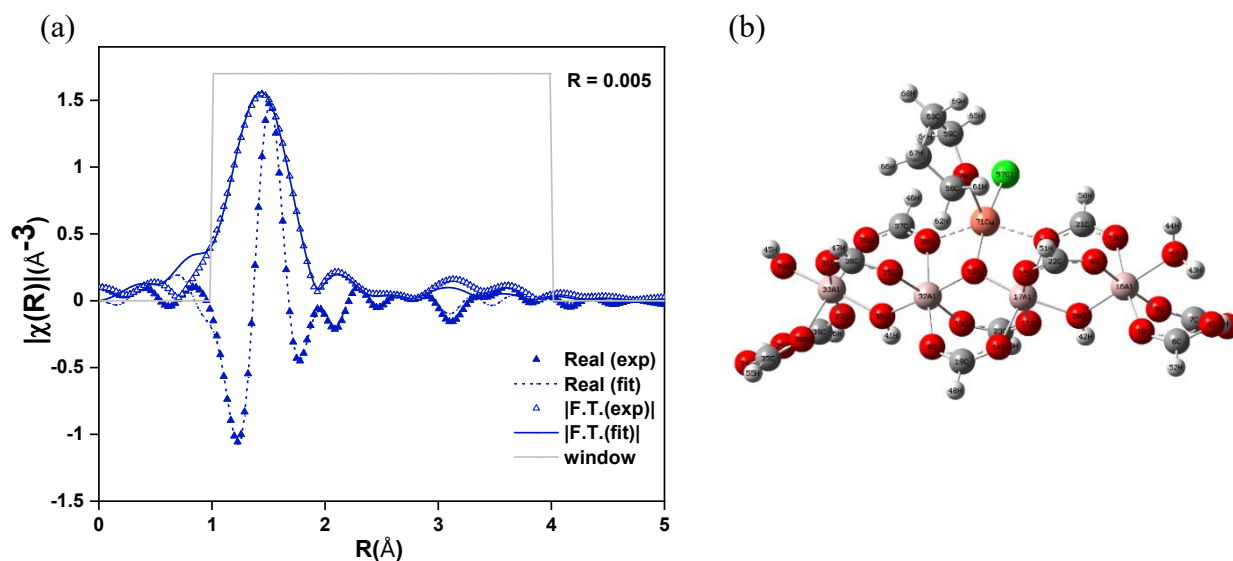


Figure 3.14. (a) EXAFS spectra and fits in R-space at the Cu K-edge of DUT-5-CuCl(THF) with the magnitude and real component of the Fourier transformation shown as hollow and solid triangles in blue color, respectively. The fitting range in R-space is 1.0–4.0 Å (within the gray line). (b) DFT-optimized structure of DUT-5-Cu(Cl)(THF).

Table 3.5. Summary of EXAFS fitting parameters of DUT-5-Cu(Cl)(THF).

Sample	DUT-5-Cu(Cl)(THF)	Fitting range	k 1.4-9.2 Å ⁻¹ R 1.0-4 Å
Independent points	14	R-factor	0.005
Variables	10	S_o^2	0.8
Reduced chi-square	22	ΔE_0 (eV)	-0.91
R(Cu-O18)	1.86±0.01	σ^2 (Cu-O18) (Å ²)	0.001±0.000
R(Cu-O28)	1.96±0.01	σ^2 (Cu-O28) (Å ²)	0.001±0.000
R(Cu-O10)	1.96±0.01	σ^2 (Cu-O10) (Å ²)	0.001±0.000
R(Cu-O70)	1.96±0.01	σ^2 (Cu-O70) (Å ²)	0.001±0.000
R(Cu-Cl57)	2.15±0.06	σ^2 (Cu-Cl57) (Å ²)	0.01±0.002
R(Cu-Al32)	2.94±0.06	σ^2 (Cu-Al32) (Å ²)	0.01±0.002
R(Cu-Al17)	2.94±0.06	σ^2 (Cu-Al17) (Å ²)	0.01±0.002
R(Cu-C37)	2.99±0.06	σ^2 (Cu-C37) (Å ²)	0.001±0.000
R(Cu-C21)	2.99±0.06	σ^2 (Cu-C21) (Å ²)	0.001±0.000
R(Cu-C58)	3.07±0.06	σ^2 (Cu-C58) (Å ²)	0.001±0.000
R(Cu-C59)	3.07±0.06	σ^2 (Cu-C59) (Å ²)	0.001±0.000
R(Cu-O13)	3.34±0.01	σ^2 (Cu-O13) (Å ²)	0.004±0.001
R(Cu-O11)	3.34±0.01	σ^2 (Cu-O11) (Å ²)	0.004±0.001
R(Cu-C23)	3.53±0.02	σ^2 (Cu-C23) (Å ²)	0.01±0.002
R(Cu-O25)	3.80±0.1	σ^2 (Cu-O25) (Å ²)	0.01±0.002
R(Cu-O15)	3.80±0.1	σ^2 (Cu-O15) (Å ²)	0.01±0.002

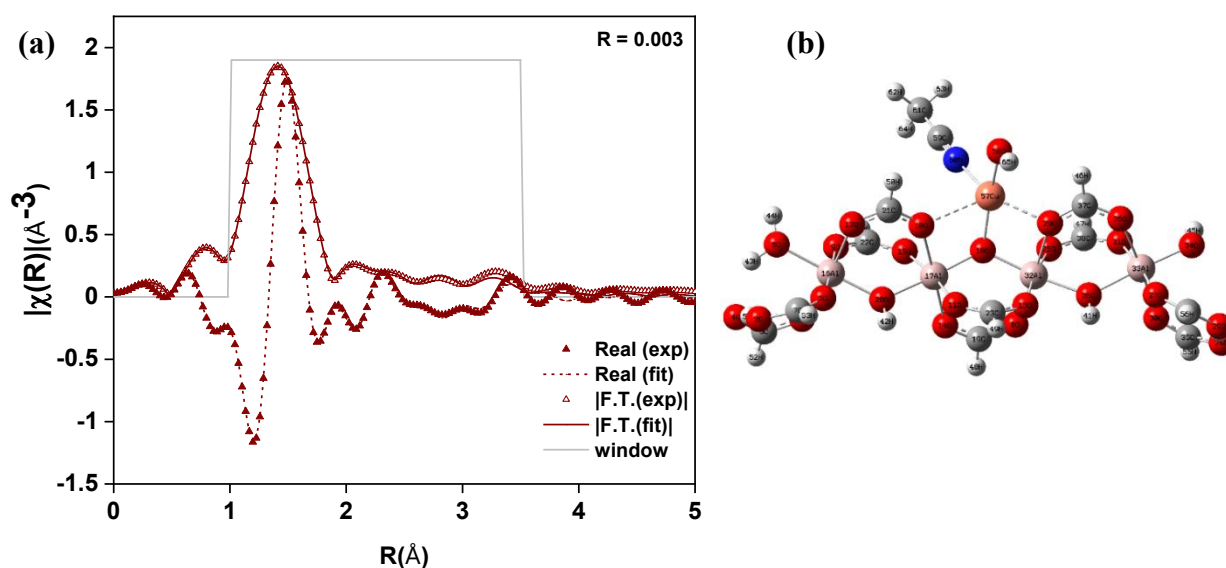


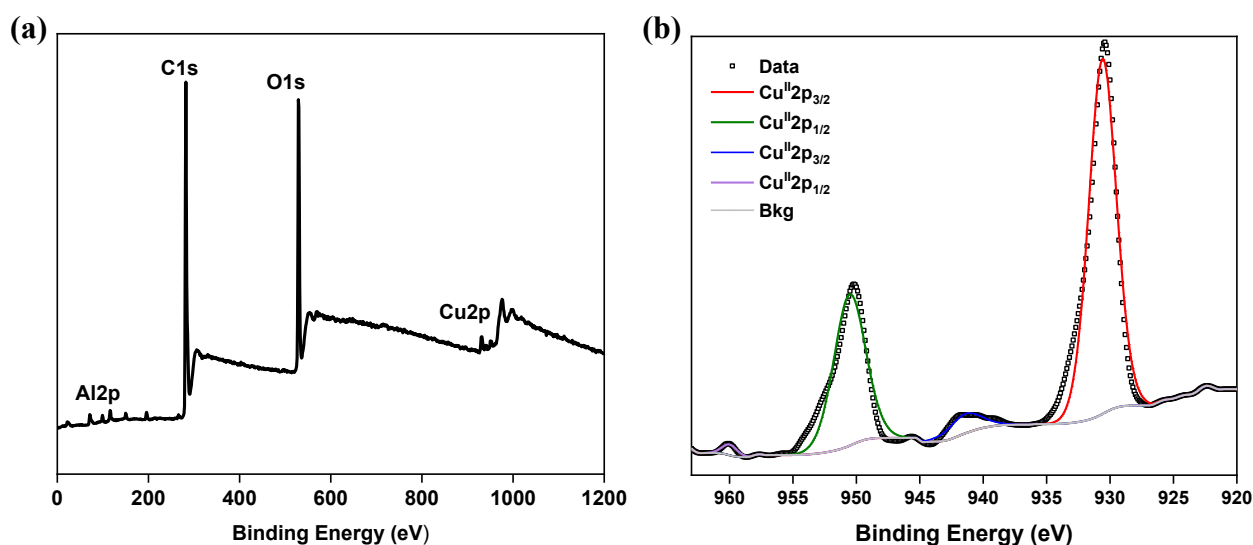
Figure 3.15. (a) EXAFS spectra and fits in R-space at the Cu K-edge of DUT-5-Cu recovered after oxidation of styrene with the magnitude and real component of the Fourier transformation shown as hollow and solid triangles in red color, respectively. The fitting range in R-space is 1.0–3.5 Å (within the gray line). (b) DFT-optimized structure of DUT-5-Cu(OH)(CH₃CN).

Table 3.6. Summary of EXAFS fitting parameters of DUT-5-Cu(OH)(CH₃CN).

Sample	DUT-5-Cu(OH)(CH ₃ CN)	Fitting range	k 1.0-9.0 Å ⁻¹ R 1.0-3.5 Å
Independent points	17	R-factor	0.003
Variables	16	S ₀ ²	1.1
Reduced chi-square	57	ΔE ₀ (eV)	-0.73
R(Cu-O58)	1.80±0.08	σ ² (Cu-O58) (Å ²)	0.01±0.005
R(Cu-O18)	1.89±0.08	σ ² (Cu-O18) (Å ²)	0.01±0.005
R(Cu-O28)	2.03±0.08	σ ² (Cu-O28) (Å ²)	0.01±0.005
R(Cu-O10)	2.08±0.08	σ ² (Cu-O10) (Å ²)	0.01±0.005
R(Cu-N60)	1.95±0.08	σ ² (Cu-N60) (Å ²)	0.004±0.001
R(Cu-H65)	2.28±0.08	σ ² (Cu-H65) (Å ²)	0.01±0.003
R(Cu-Al32)	2.96±0.08	σ ² (Cu-Al32) (Å ²)	0.01±0.005
R(Cu-Al17)	2.98±0.08	σ ² (Cu-Al17) (Å ²)	0.01±0.005
R(Cu-C37)	3.03±0.01	σ ² (Cu-C37) (Å ²)	0.01±0.003
R(Cu-C59)	3.06±0.01	σ ² (Cu-C59) (Å ²)	0.01±0.003
R(Cu-C21)	3.06±0.01	σ ² (Cu-C21) (Å ²)	0.01±0.003
R(Cu-H45)	3.14±0.08	σ ² (Cu-H45) (Å ²)	0.01±0.005
R(Cu-H50)	3.17±0.08	σ ² (Cu-H50) (Å ²)	0.01±0.005
R(Cu-O13)	3.40±0.08	σ ² (Cu-O13) (Å ²)	0.01±0.005
R(Cu-O11)	3.40±0.08	σ ² (Cu-O11) (Å ²)	0.01±0.005
R(Cu-O25)	3.80±0.06	σ ² (Cu-O25) (Å ²)	0.009±0.003
R(Cu-O15)	3.82±0.06	σ ² (Cu-O15) (Å ²)	0.009±0.003

3.9. XPS Analysis of DUT-5-CuCl

All the binding energies were corrected with reference to the C1s peak at 284.8 eV. MULTIPAK software was used for peak analysis and de-convolution studies.



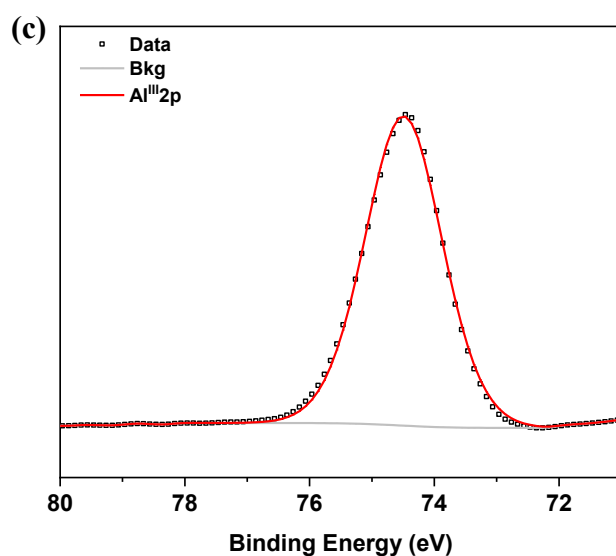


Figure 3.16. (a) Raw XPS data of DUT-5-CuCl. (b) XPS fitting of copper in DUT-5-CuCl. (c) XPS fitting of aluminium in DUT-5-CuCl.

Table 3.7. Comparison of catalytic activity of DUT-5-CuCl with that of other reported heterogeneous catalysts for direct oxidation of styrene to benzaldehyde.

Entry	Reference	Catalyst	Oxidant	T (°C)	Solvent	Time	Conv. (Selectivity)
1	<i>Catal. Sci. Technol.</i> 2014, 4 , 2599–2607	[Cu ₂ (bipy) ₂ (btec)] _∞	H ₂ O ₂	75	DCE	6 h	37% (100%)
2	<i>Chem. Eng. J.</i> 2016, 299 , 135–141	MOF-74(Cu/Co) (Cu-90/Co-10)	O ₂	80	Solvent free	20 h	10.2% (75%)
3	<i>Angew. Chem. Int. Ed.</i> 2017, 56 , 5512–5516	Triple-shelled hollow MOF	TBHP	80	CH ₃ CN	12 h	90% (58%)
4	<i>Adv. Sci.</i> 2019, 6 , 1–7	NH ₂ -MIL-101(Fe) @NTU-COF	TBHP	80	CH ₃ CN	12 h	32% (84%)
5	<i>Inorg. Chem. Commun.</i> 2018, 88 , 47–50	Ag@UiO-66	TBHP	80	CH ₃ CN	24 h	51% (39%)
6	<i>React. Kinet. Mech. Catal.</i> 2016, 119 , 305–318	H ₃ PW ₁₂ O ₄₀ /SBA-15	H ₂ O ₂	70	CH ₃ CN	24 h	22.6% (100%)

7	<i>Microporous Mesoporous Mater.</i> 2012, 162 , 51–59	Ti-Fe-MCM-41	H ₂ O ₂	70	CH ₃ CN	12 h	50% (90%)
8	<i>Advances in Materials Science and Engineering.</i> 2018, 1-7	Zn _{1-x-y} Ag _x Co _y O	H ₂ O ₂	80	CH ₃ CN	24 h	100% (76%)
9	<i>Catal. Sci. Technol.</i> 2018, 8 , 2285-2288	[CuCl ₂ {κ ³ -HC(pz) ₃ }] (pz = pyrazol-1-yl)	H ₂ O ₂	80	CH ₃ CN	15 min	68% (100%)
10	<i>ChemistrySelect.</i> 2022, 7 , e202104279	Cu@MIL-101(Cr)	TBHP	80	CH ₃ CN	8 h	97% (84%)
11	<i>Chinese Journal of Catalysis.</i> 2014, 35 , 1716-1726	Cu-SBA-15	H ₂ O ₂	100	H ₂ O	8 h	84% (84%)
12	<i>Materials Research Express.</i> 2019, 6 , 125101	Cu@Al-MIL-53-P21	TBHP	80	CH ₃ CN	8 h	98% (74%)
13	Our work	DUT-5-CuCl	H₂O₂	80	CH₃CN	7 h	94% (81%)

3.10. Conclusion

In conclusion, we have developed a single-site Cu-catalyst supported by nodes of DUT-5 MOF, which is efficient in oxidizing alkenes to give aldehydes, ketones or vicinal diols selectively using H₂O₂ as the oxidizing agent. The solid MOF catalyst could be reused and recycled several times without decreasing catalytic activity. EXAFS and DFT models were used to explore the coordination environment around the copper centre within the MOF catalyst. The mechanism of oxidation of styrene and the turnover-limiting step in the catalytic cycle were studied by investigating the reaction intermediates, the resting state of the catalyst, and DFT calculations. Our result highlights the significance of MOFs in the development of sustainable and environmentally friendly catalytic methods for the synthesis of fine chemicals.

Chapter 4: Regioselective Oxidative Bromination of Arenes by a Metal-Organic Framework-Confined Mono-Bipyridyl Iron(III) Catalyst

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Abstract: 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.

4.1. Introduction

Halogenation reactions have gained significant importance as organohalides are essential chemicals with significant efficacy in pharmaceutical sciences,²²² material sciences,²²³ imaging techniques,²²⁴ and organic synthesis.^{225–227} Bromoarenes, in particular, are important synthetic precursors for carbon–carbon bond formation reactions through Heck,²²⁸ Stille,²²⁹ and Suzuki²³⁰ transmetallation processes. Furthermore, bromoaromatics serve as potent antibacterial, antifungal, and antiviral agents, as well as industrial intermediates in the production of pharmaceuticals, agrochemicals and other specialty products.^{231–241} Traditionally, bromination reactions are carried out using hazardous, toxic, and corrosive molecular bromine, often in combination with chlorinated solvents.^{242,243} This approach poses significant environmental and health risks due to molecular bromine's toxicity and corrosive nature. Alternative methods involving electrophilic bromination using *N*-bromosuccinimide,^{244,245} an alkyl bromide/sodium hydride/DMSO combinations,²⁴⁶ a bromodimethylsulfonium bromide²⁴⁷ and a hexamethylenetetramine bromine complex²⁴⁸ have been explored.

Oxidative bromination has emerged as an attractive and environmentally benign alternative, as it generates electrophilic bromine using various oxidants.^{249–255} This method offers a more sustainable and economically viable pathway to bromoaromatics compared to classical electrophilic substitutions. In particular, hydrogen peroxide is considered a promising oxidant for oxidative bromination, as the byproduct is only water. Most catalytic systems for oxidative bromination of arenes reported to date require acids,^{256–260} which, while inexpensive and readily available, pose challenges related to product separation and hazardous waste generation.^{261,262} Although oxidative bromination of arenes using bromide salts as halogen sources and oxidants has been explored,^{255,263–266} there remains a pressing need for low-cost, earth-abundant non-toxic catalysts that enable oxidative bromination with high yields and excellent regioselectivity under mild conditions.

Metal-organic frameworks (MOFs) have attracted considerable interest for developing robust single-site heterogeneous earth-abundant catalysts for various applications owing to their high porosity, crystallinity, and molecular tunability, enabling post-synthetic functionalization.^{41,64,190,209,267} In particular, UiO-MOFs are unique due to the exceptional thermal and chemical stability provided by $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ secondary building units (SBUs) and linear dicarboxylate bridging linkers.^{268–271} The post-synthetic modification of

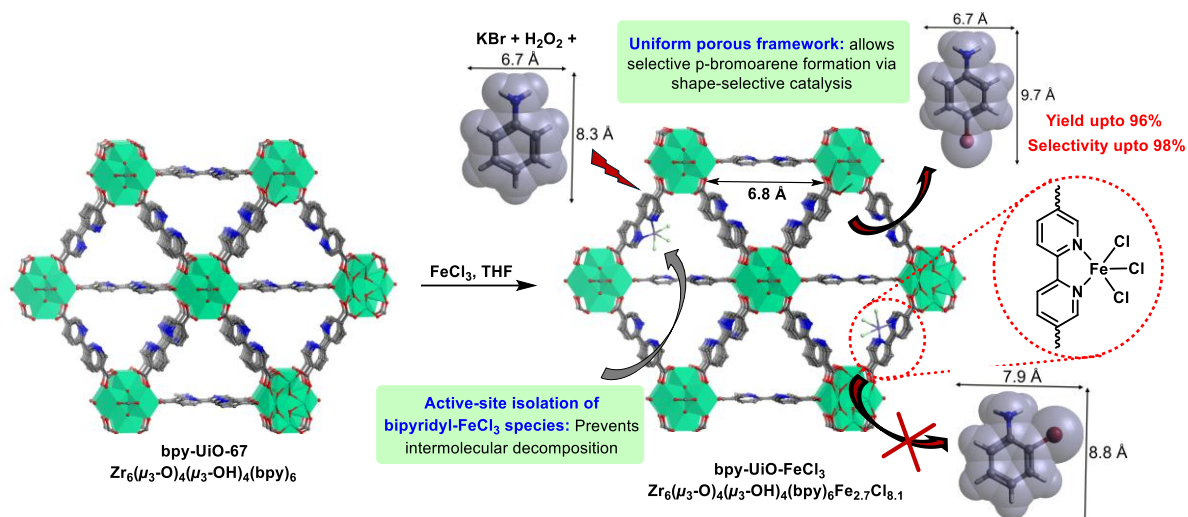


Figure 4.1. Oxidative bromination of aniline using H_2O_2 and KBr with bpy-UiO-FeCl_3 as a shape-selective catalyst.

MOFs enables the functionalization of their organic linkers, facilitating the formation of single-site base-metal catalysts upon metalation. The rigid and porous MOF framework stabilizes coordinatively unsaturated and solution inaccessible base-metal species via active-site isolation by preventing multinuclear deactivation pathways.^{272–274} In addition, MOF-supported single-site catalysts combine the advantages of homogeneous catalysis, including uniform active site distribution, with the stability and recyclability of heterogeneous systems. Moreover, the confinement of active-sites within the robust, well-defined and tunable porous frameworks increases regioselectivity of the reaction via shape-selective catalysis. Herein, we report the development of a highly active, selective and recyclable MOF-supported monomeric 2,2'-bipyridyl-iron(III) chloride catalyst (bpy-UiO-FeCl_3) for oxidative bromination of arenes using H_2O_2 as the oxidant and KBr as the bromine source to afford bromoarenes in high yield and excellent regio-selectivity under mild conditions (Figure 4.1).

4.2. Results and Discussion

4.2.1. Synthesis and Characterization of bpy-UiO-FeCl_3

Bpy-UiO-FeCl_3 was synthesized through the post-synthetic metalation of the freshly prepared bpy-UiO-67 MOF containing bipyridyl-functionalized linkers (Figure 4.1).^{273,275} The synthesis involved a solvothermal reaction between ZrCl_4 and 2,2'-bipyridine-5,5'-dicarboxylic acid in the presence of $\text{CF}_3\text{CO}_2\text{H}$ as a modulator in DMF at 100 °C for 4 days, yielding bpy-UiO-67 MOF with a 63% yield. The resulting pristine bpy-UiO-67 MOFs feature a three-dimensional

porous UiO-topology,²⁶⁸ constructed from $\text{Zr}_6\text{O}_4(\text{OH})_4$ nodes interconnected by 2,2'-bipyridine-5,5'-dicarboxylate (bpy) bridging linkers. By stirring a THF solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with a slurry of bpy-UiO-67, we obtained bpy-UiO- FeCl_3 , which contains bipyridyl-ligated Fe-trichloride species within its linkers. Analysis of digested bpy-UiO- FeCl_3 using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) revealed a Fe-loading of approximately 45% with respect to the bipyridyl linker, which corresponds to the formula of $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{bpy})_6\text{Fe}_{2.7}\text{Cl}_{8.1}$. The Powder X-ray Diffraction (PXRD) pattern of bpy-UiO- FeCl_3 resembles that of the pristine bpy-UiO-67 MOF, indicating that the crystallinity and structure of the bpy-UiO-67 MOFs are retained during post-synthetic modification (Figure 4.2a). Scanning Electron Microscopy-Energy Dispersive X-ray Analysis (SEM-EDX) mapping of bpy-UiO- FeCl_3 demonstrated a uniform distribution of Fe and Zr ions within the MOF particles (Figure 4.2b). Bpy-UiO- FeCl_3 has a Brunauer-Emmett-Teller (BET) surface area of $1235 \text{ m}^2/\text{g}$ and a pore size of 0.68 nm , which is smaller than that of the pristine bpy-UiO-67 MOF. This reduction in surface area and pore size is attributed to the incorporation of the iron moiety within the MOF's pores (Figure 4.2c). Thermogravimetric analysis (TGA) indicates that bpy-UiO- FeCl_3 is thermally stable up to 450°C (Figure 4.6). X-ray Photoelectron Spectroscopy (XPS) analysis of bpy-UiO- FeCl_3 identified the presence of Fe $2p_{3/2}$ and $2p_{1/2}$ binding energy peaks at 711.0 eV and 724.6 eV , respectively, confirming +3 oxidation state of the iron ion (Figure 4.2e). The +4 oxidation state of Zr ions in the bpy-UiO- FeCl_3 was confirmed via XPS, which showed Zr^{4+} binding energies at 182.5 eV and 184.9 eV (Figure 4.16c). In the X-ray Absorption Near Edge Structure (XANES) analysis, the pre-edge energy of Fe in bpy-UiO- FeCl_3 closely matched that of FeCl_3 at 7114 eV , further confirming the presence of Fe^{3+} species (Figure 4.2f). X-band electron paramagnetic resonance (EPR) spectrum reveals a broad signal centered at $g = 2.015$, indicating the presence of a high-spin Fe^{3+} species with low magnetic anisotropy (Figure 4.2d).^{276,277} Analysis of the Fe K-edge Extended X-Ray Absorption Fine Structure (EXAFS) of bpy-UiO- FeCl_3 revealed that the Fe ion is octahedrally coordinated with two nitrogen atoms of bipyridine, three chloride ions, and one CH_3CN molecule (Figure 4.2g). The Fe- $\text{N}_{\text{bipyridine}}$ distance is $1.9 \text{ \AA}$, while the Fe- Cl_a distance is $2.39 \text{ \AA}$, Fe- Cl_b distance is $2.19 \text{ \AA}$ and the Fe- $\text{N}_{\text{CH}_3\text{CN}}$ distance is $2.09 \text{ \AA}$ (Figure 4.2h). The combined EXAFS and EPR data suggest the existence of a high-spin octahedral $(\text{bpy})\text{Fe}^{\text{III}}(\text{Cl})_3(\text{NCCCH}_3)$ species within bpy-UiO- FeCl_3 .

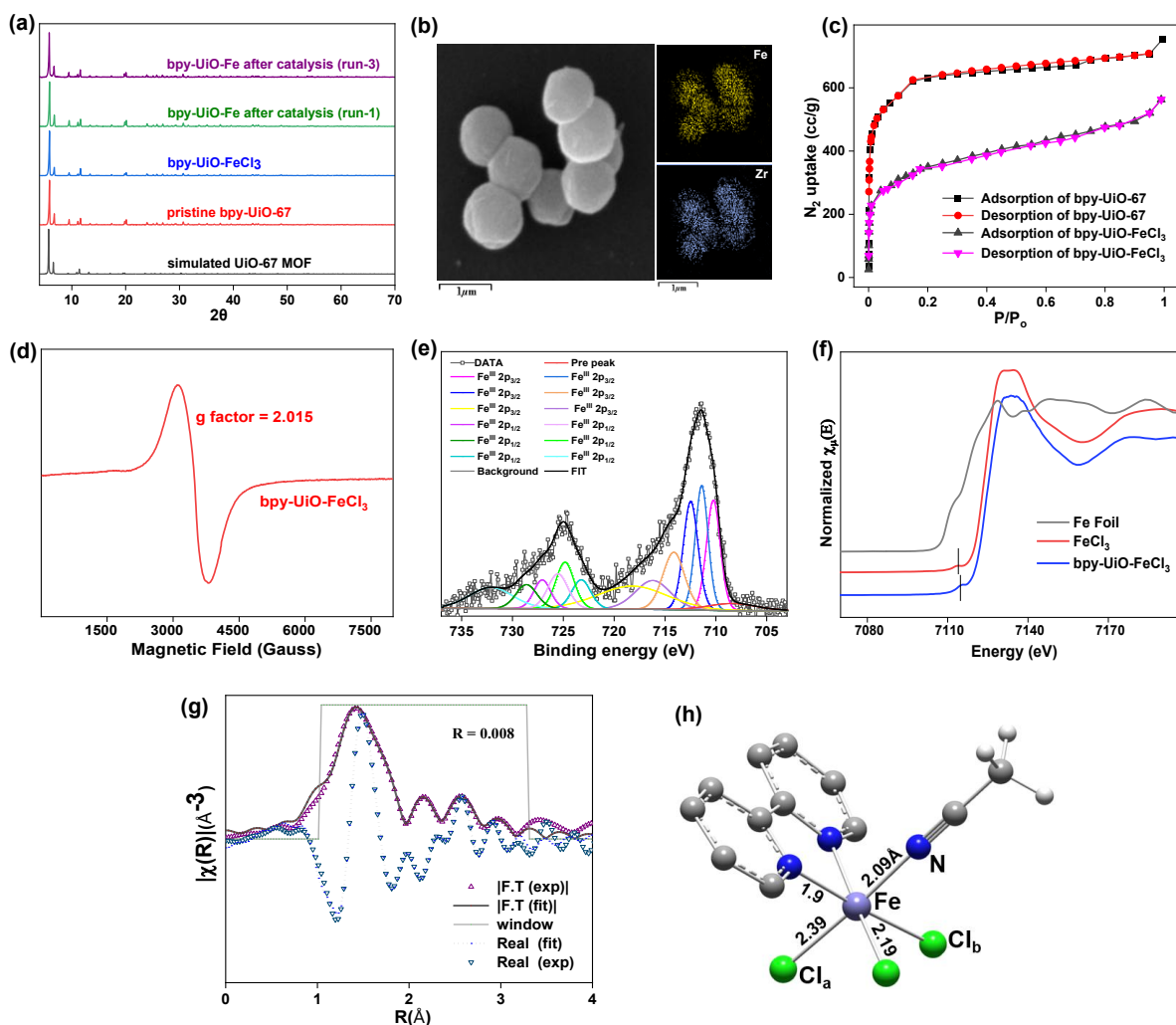


Figure 4.2. (a) PXRD patterns of the simulated UiO-67 MOF (black), pristine bpy-UiO-67 (red), bpy-UiO-FeCl₃ (blue), bpy-UiO-Fe recovered after run-1 of oxidative bromination of aniline (green) and bpy-UiO-Fe recovered after run-3 of catalysis (purple). (b) SEM image of bpy-UiO-FeCl₃ particles along with elemental mapping of Fe and Zr. (c) N₂ sorption isotherms of bpy-UiO-67 (black/red)^[75] and bpy-UiO-FeCl₃ (gray/magenta) measured at 77 K. (d) EPR spectrum of solid bpy-UiO-FeCl₃. (e) Fe 2p XPS spectrum of bpy-UiO-FeCl₃. (f) XANES spectra of metallic Fe(0) foil (gray), FeCl₃ (red) and bpy-UiO-FeCl₃ (blue). (g) EXAFS spectra and fits of bpy-UiO-FeCl₃ in the R space from 1.0-3.3 Å. (h) DFT-optimized structure of bpy-FeCl₃(NCCH₃) moiety within bpy-UiO-FeCl₃ MOFs. The bond distances are given in Å.

4.2.2. Catalytic Oxidative Bromination of Aniline

Bpy-UiO-FeCl₃ is an active heterogeneous catalyst for the oxidative bromination of aniline, utilizing H₂O₂ as the oxidant and KBr as the brominating agent. To optimize the reaction conditions for maximum conversion and yield, we thoroughly investigated the impact of various reaction parameters, including reaction temperature, reaction time, solvents, substrate-to-oxidant ratio, catalyst concentration, and the nature and concentration of the brominating agent. The effect of temperature on the oxidative bromination of aniline was studied over a range of 30-60 °C using 1 mmol of aniline, 4 mg of the catalyst bpy-UiO-FeCl₃ (0.4 mol% of

Fe), 2 mmol of H_2O_2 , 1.1 mmol of KBr, and 5 mL of CH_3CN for a duration of 2 h (Figure 4.3a). The results showed that temperature variation had only a minimal effect on the conversion of aniline; however, regioselectivity decreased at higher temperatures (entries 1-3, Table 4.2). Reaction time plays a critical role in evaluating the catalytic performance of the catalyst. To investigate this, the effect of reaction time on the oxidative bromination of aniline with H_2O_2 was examined over a range of 30-180 min (Figure 4.3b). The results showed a direct correlation between reaction time and the yield of the 4-bromoaniline product. The highest yield of 95% was achieved after 2 h, indicating that longer reaction times enhance substrate interaction and conversion, enabling the catalyst to effectively promote the desired reaction. The study revealed that CH_3CN was the most efficient solvent for the bpy-UiO- FeCl_3 -catalyzed oxidative bromination of aniline using H_2O_2 , achieving a conversion rate of 98% and a selectivity of 97% for the target product (**2a**) within 2 h (Figure 4.3c). This enhanced performance is due to acetonitrile's beneficial solvation properties, which improve the stabilization of reaction intermediates and aid in the transfer of reactants at the catalyst's active sites.

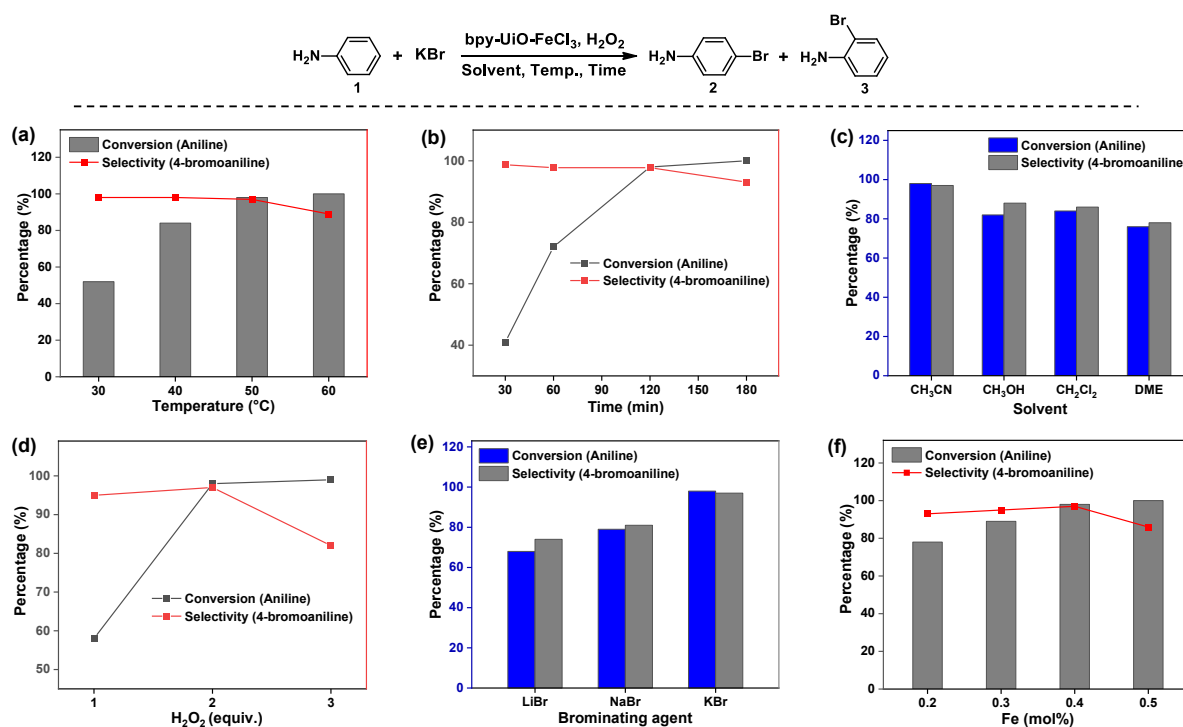


Figure 4.3. (a) Effect of temperature on %conversion and %selectivity of 4-bromoaniline for bpy-UiO- FeCl_3 catalysed oxidative bromination of aniline. Reaction conditions: aniline (1 mmol), H_2O_2 (2 mmol), KBr (1.1 mmol), bpy-UiO- FeCl_3 (4 mg, 0.4 mol% of Fe), CH_3CN (5 mL), 2 h. (b) Effect of time on %conversion and %selectivity of 4-bromoaniline for bpy-UiO- FeCl_3 catalysed oxidative bromination of aniline. Reaction conditions: aniline (1 mmol), H_2O_2 (2 mmol), KBr (1.1 mmol), bpy-UiO- FeCl_3 (4 mg, 0.4 mol% of Fe), CH_3CN (5 mL), 50 °C. (c) Effect of different solvents on %conversion and %selectivity of 4-bromoaniline for bpy-UiO- FeCl_3 catalysed oxidative bromination of aniline. Reaction conditions: aniline (1 mmol), H_2O_2 (2 mmol), KBr

(1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), solvent (5 mL), 50 °C, 2 h. (d) Effect of H₂O₂ amounts on %conversion and %selectivity of 4-bromoaniline for bpy-UiO-FeCl₃ catalysed oxidative bromination of aniline. Reaction conditions: aniline (1 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), CH₃CN (5 mL), 50 °C, 2 h. (e) Effect of brominating agents on %conversion and %selectivity of 4-bromoaniline for bpy-UiO-FeCl₃ catalysed oxidative bromination of aniline. Reaction conditions: aniline (1 mmol), H₂O₂ (2 mmol), brominating agent (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), CH₃CN (5 mL), 50 °C, 2 h. (f) Effect of different Fe-loading on %conversion and %selectivity of 4-bromoaniline for bpy-UiO-FeCl₃ catalysed oxidative bromination of aniline. Reaction conditions: aniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), CH₃CN (5 mL), 50 °C, 2 h.

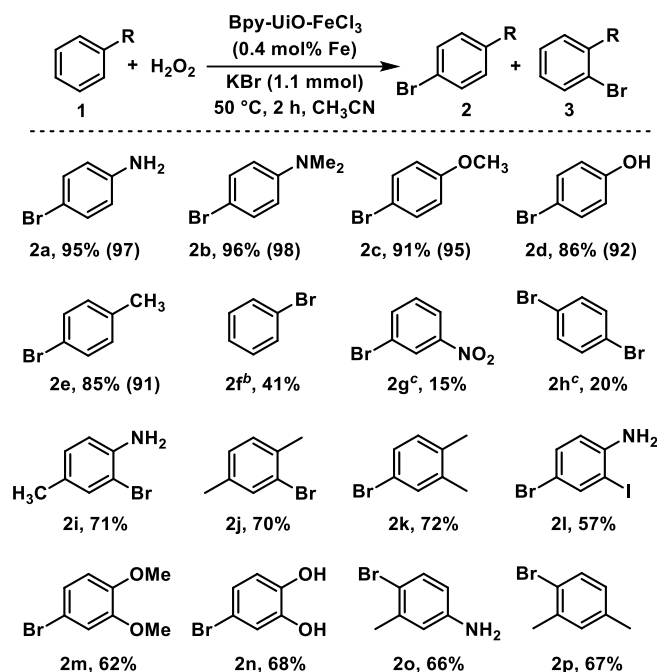
In comparison, other solvents such as CH₃OH, DME and DCM resulted in lower yields of **2a**. A control experiment confirmed the necessity of H₂O₂, as no bromo product was produced in its absence (entry 8, Table 4.2). An investigation of different H₂O₂ concentrations, while keeping other parameters constant, revealed that maximum bromination was achieved at a 1:2 molar ratio (Figure 4.3d). In contrast, a 1:3 molar ratio resulted in decreased yield (84%) and reduced para-selectivity (85%). The effect of different brominating agents on the oxidative bromination of aniline using H₂O₂ as the oxidant was also investigated (Figure 4.3e). Among the brominating agents tested (LiBr, NaBr, KBr), KBr demonstrated the highest efficiency, achieving 98% conversion with excellent regioselectivity for the para-product (97%). In comparison, NaBr and LiBr showed lower activities (entries 11-12, Table 4.2). A KBr concentration of 1.1 mmol yielded the optimal results. The catalyst loading was systematically optimized to achieve maximum efficiency. It was observed that 0.4 mol% of Fe loading in bpy-UiO-FeCl₃ provided the highest conversion rate of 98%. Reducing the Fe-loading in the bpy-UiO-FeCl₃ catalyst from 0.4 mol% to 0.2 mol% resulted in a decline in bromoaniline yield from 95% to 71%, attributed to a reduced availability of active sites. Under the optimized conditions, the reaction achieved the highest yield of 4-bromoaniline (**2a**) at 95%. This was accomplished using a catalyst loading of 0.4 mol% Fe, 1 mmol of aniline, 1.1 mmol of KBr, and 2 mmol of 30% aqueous H₂O₂ in 5 mL of CH₃CN at 50 °C for 2 hours, resulting in a turn-over number (TON) of 238 (entry 2, Table 4.2).

4.2.3. Substrate Scopes for Oxidative Bromination of Arenes

Under the optimized conditions, the oxidative bromination of aromatic substrates, including N,N-dimethylaniline (**1b**), anisole (**1c**), phenol (**1d**), and toluene (**1e**), yielded the corresponding para-bromo products (**2b-2e**) with isolated yields ranging from 85% to 96% and excellent selectivity (91-98%). Benzene (**1f**), due to its lack of activating groups, exhibited significantly lower conversion rates and required extended reaction times to achieve measurable bromination under the same conditions. In contrast, deactivated aromatic rings such

as nitrobenzene (**1g**) and bromobenzene (**1h**) produce the corresponding bromo products with yields of 15-20% after 24 h at 80 °C. 4-substituted aromatics, such as 4-methylaniline (**1i**) and p-xylene (**1j**) were selectively converted to 2-bromo-4-methylaniline (**2i**) and 2-bromo-p-xylene (**2j**) with an isolated yield of 70-71%. In contrast, 2-substituted aromatics such as o-xylene (**1k**), 2-iodoaniline (**1l**), 1,2-dimethoxybenzene (**1m**) and catechol (**1n**) were also selectively converted to the corresponding bromo products (**2k-n**) with an isolated yield of 57-72%. Similarly, 3-substituted aromatics such as 3-methylaniline (**1o**) and m-xylene (**1p**) was selectively converted to 4-bromo-3-methylaniline (**2o**) and 4-bromo-m-xylene (**2p**) respectively, achieving a yield of 66-67% under the same conditions.

Scheme 4.1. Substrate Scope of Oxidative Bromination of Arenes with bpy-UiO-FeCl₃.^a



^a**Conditions:** **1** (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), CH₃CN (5 mL), 50 °C, 2 h. Yields refer to the isolated products. ^bReaction was performed for 10 h. ^cReaction was performed for 24 h at 80 °C.

4.3. Control Experiments

As a heterogeneous catalyst, bpy-UiO-FeCl₃ can be recycled at least three times with consistent activity and no significant structural changes (Figure 4.4a). The percentage of leached Fe and Zr into the supernatant after the first run was 0.02% and 0.6%, respectively, while after the third run it was 0.08% and 1.5%, as analyzed by ICP-OES (Table 4.5). The catalytic activity observed with bpy-UiO-FeCl₃ is over four times greater than that of the homogeneous control, bipyridine-FeCl₃. The latter was synthesized by reacting 5,5'-dimethyl-2,2'-bipyridine with

FeCl₃·6H₂O in a 1:1 molar ratio in THF. The time evolution plot for bpy-UiO-FeCl₃ (0.4 mol% of Fe) catalyzed oxidative bromination of aniline demonstrates a linear increase in the synthesis of 4-bromoaniline, achieving 97% selectivity until 98% conversion of aniline in 2 h (Figure 4.4b). In contrast, under the same reaction conditions and with equivalent Fe-loading, bipyridine-FeCl₃ produced only 26% yield of 4-bromoaniline in 2 hours, with a selectivity of 68% (Figure 4.4b). This enhanced activity of bpy-UiO-FeCl₃ MOF is attributed to the stability of bpy-FeCl₃ species, which are isolated at the linkers, preventing decomposition. In addition, bpy-UiO-FeCl₃ framework features uniform and rigid pores with a size of 0.68 nm, which allow the diffusion of aniline (0.83 x 0.67 nm) and p-bromoaniline (0.97 x 0.67 nm), however, restricts the formation of the larger product, o-bromoaniline (0.88 x 0.79 nm), resulting in a formation of p-bromoaniline with 97% selectivity through shape-selective catalysis. In contrast, the homogeneous bipyridine-FeCl₃ catalyst lacks this structural confinement, leading to only 68% selectivity of p-bromo aniline. Several controlled experiments were conducted to identify the actual catalytic species involved in the bpy-UiO-FeCl₃-catalyzed oxidative bromination of aniline to produce 4-bromoaniline. The results showed that reactions (a) without the bpy-UiO-FeCl₃ catalyst (entry 3, Table 4.3), and (b) with pristine bpy-UiO-67 MOF (entry 2, Table 4.3), all yielded negligible amounts of 4-bromoaniline. The results also showed that reactions (a) with bpy-UiO-FeCl₂ (entry 4, Table 4.2), (d) with FeCl₃·6H₂O (entry 5, Table 4.2) and (e) with Fe nanoparticles (entry 6, Table 4.2), all yielded lower amounts of 4-bromoaniline with less selectivity (Figure 4.4c). This confirms that bpy-UiO-FeCl₃ is the active catalyst for the oxidative bromination of aniline. The oxidative bromination of aniline ceased upon removal of the solid MOF catalyst, indicating that the active species is embedded in the MOF solid.

4.4. Mechanism Exploration of bpy-UiO-FeCl₃ Catalyzed Oxidative Bromination of Aniline

The mechanism of bpy-UiO-FeCl₃-catalyzed oxidative bromination of aniline was investigated by characterizing the catalyst after catalysis and computational studies. The PXRD pattern of the recovered bpy-UiO-Fe MOF after catalysis indicates that both the structure and crystallinity of the MOF remained intact during the reaction (Figure 4.2a). Additionally, the absence of any characteristic peak for metallic iron at higher 2θ angles in the same PXRD pattern suggests that Fe nanoparticles or metallic Fe particulates did not form during the bromination reaction. Again, radical pathway tests utilizing Na₂SO₃ and *tert*-butanol (TBA) as scavengers

demonstrated no impact on the reaction rate, effectively ruling out the possibility of a radical mechanism (Figure 4.11). Based on spectroscopic data and control experiments, we propose

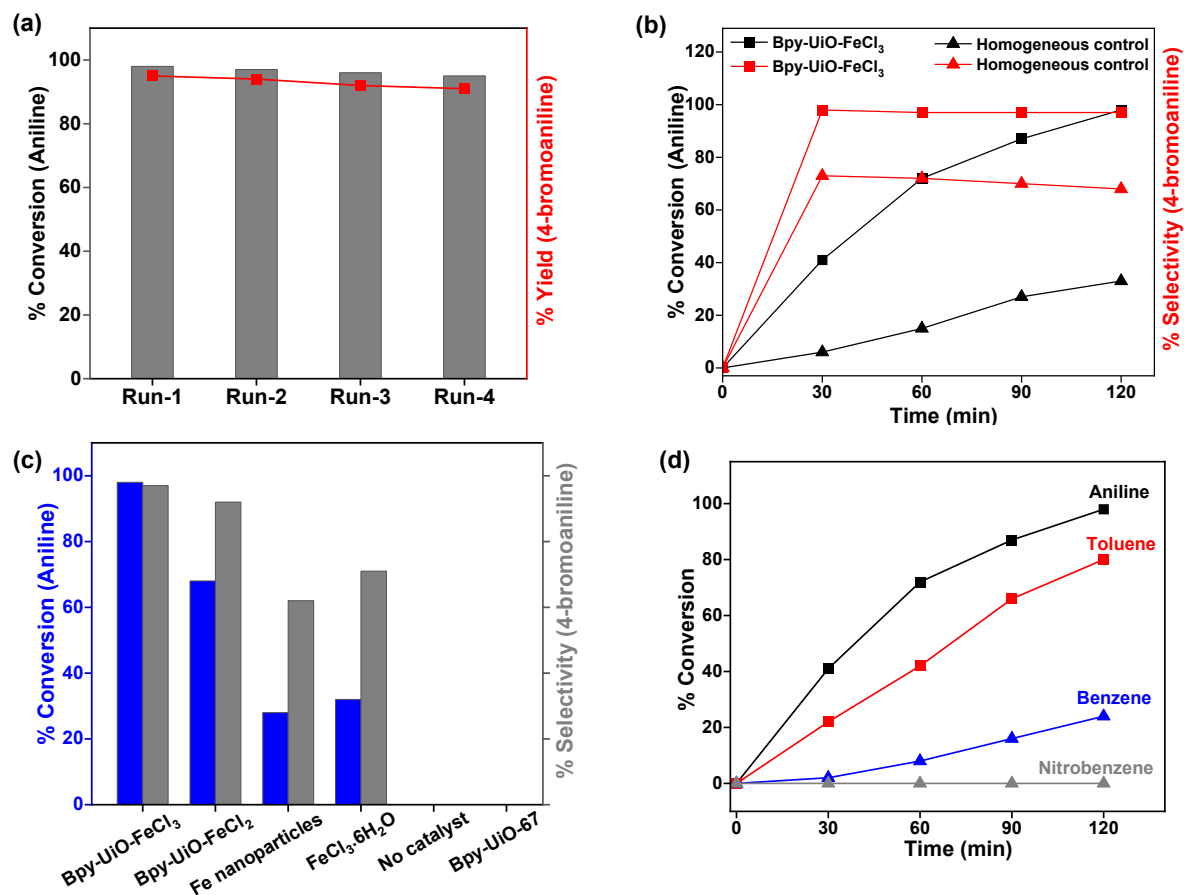


Figure 4.4. (a) Plot for the %conversion of aniline and %yield of 4-bromoaniline at various runs in the recycling of bpy-UiO-FeCl₃ catalyzed oxidative bromination of aniline. (b) Time evaluation studies of oxidative bromination of aniline using bpy-UiO-FeCl₃ and its homogenous control [(bpy)FeCl₃] under identical conditions. Conditions: aniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), catalyst (0.4 mol% of Fe), CH₃CN (5 mL), 50 °C. (c) Comparison of the catalytic activity of bpy-UiO-FeCl₃ with other iron catalysts under identical reaction conditions. Conditions: aniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), catalyst (0.4 mol% of Fe), CH₃CN (5 mL), 50 °C, 2 h. (d) Time evaluation studies of oxidative bromination of aniline, toluene, benzene and nitrobenzene under optimized reaction conditions.

that the reaction of H₂O₂ with bpy-UiO-FeCl₃ initially forms a Fe(III)-hydroperoxy intermediate, [Fe^{III}-OOH] (INT-1). Subsequently, the Br⁻ ion from KBr attacks the oxygen atom coordinated to iron in INT-1, forming the [Fe^{III}-OBr] intermediate (INT-2) and releasing KOH. INT-2 interacts with the aniline substrate to form INT-3, where electrophilic aromatic substitution takes place. The reactive Br⁺ then undergoes an electrophilic attack on the aniline substrate, resulting in the formation of the bromoaniline-bound Fe(III) intermediate (INT-4) via transition state 1 (TS-1). Finally, the desired p-bromoaniline product is released from INT-4, regenerating the initial Fe(III) catalyst, bpy-UiO-Fe and completing the catalytic cycle (Figure 4.5a). Evidence for the electrophilic aromatic substitution mechanism was gathered

through a time-evolution study of reactions involving arenes such as aniline, toluene, benzene, and nitrobenzene under identical conditions (Figure 4.4d). The reaction rates followed the trend aniline > toluene > benzene, consistent with the activating effects of electron-donating groups. In contrast, nitrobenzene did not undergo the reaction due to the deactivating influence of its electron-withdrawing nitro group, rendering the aromatic system unreactive under these conditions.

To gain a deeper understanding of the reaction pathway, we computed the entire catalytic cycle using Density Functional Theory (DFT) with the B3LYP/def2-SVP/SMD (solvent= acetonitrile) level of theory in Gaussian 09 software (Figure 4.5b). The DFT-calculated free energy diagram at 323.15 K for the bpy-UiO-FeCl₃-catalyzed oxidative bromination of aniline indicates that the coordination of H₂O₂ with the bpy-UiO-FeCl₃ MOF is endergonic by 1.9 kcal/mol. Furthermore, nucleophilic substitution of Br⁻ on [Fe^{III}(OOH)] leading to the formation of [Fe^{III}(OBr)] species (INT-2) is endergonic by 30.1 kcal/mol. In the next step, the conversion of INT-2 to INT-3 is endergonic by 0.9 kcal/mol. The subsequent transformation of INT-3 to INT-4 via TS-1 is exergonic by 34.4 kcal/mol, overcoming a barrier of 3.6 kcal/mol. Finally, the release of p-bromoaniline from INT-4 regenerates the bpy-UiO-Fe MOF, which is exergonic by 9.8 kcal/mol. DFT calculation suggests that the nucleophilic substitution of Br⁻ on INT-1 leading to the formation of INT-2 is the turn-over limiting step requiring a free activation energy of 32.0 kcal mol⁻¹ (Figure 4.5b).

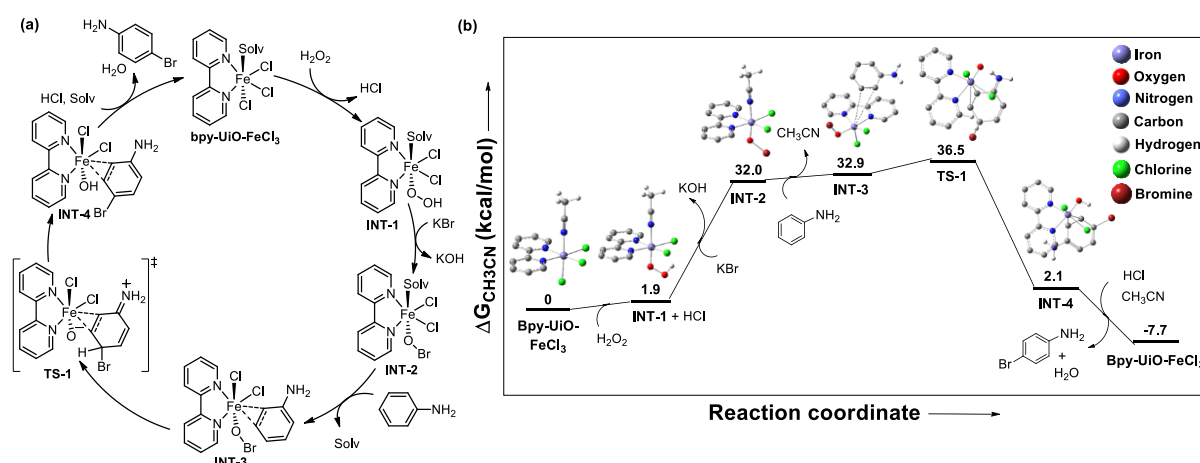


Figure 4.5. (a) Proposed catalytic cycle of bpy-UiO-FeCl₃ catalyzed oxidative bromination of arenes. (b) DFT-calculated free energy profile diagram of bpy-UiO-FeCl₃ catalyzed oxidative bromination of aniline at 323.15 K.

4.5. Experimental Section

4.5.1. Synthesis and Characterization of bpy-UiO-67 and bpy-UiO-FeCl₃

4.5.1.1. Synthesis of 2,2'-bipyridine-5,5'-dicarboxylic acid

2,2'-Bipyridine-5,5'-dicarboxylic acid was synthesized using a modified reported procedure.²⁷⁸ In a round-bottom flask, 5,5'-dimethyl-2,2'-bipyridyl (0.500 g, 2.74 mmol), sodium hydroxide (0.030 g, 0.75 mmol), and 12 mL of deionized water were combined and stirred at 70 °C. Subsequently, sodium hydroxide (1.48 g, 0.037 mol) was slowly added to the mixture until the pH reached 12. Once the mixture became clear, it was allowed to sit for 1 h. Finely powdered potassium permanganate, KMnO₄ (2.140 g, 0.0135 mol) was then added in small portions. The mixture was stirred at 90 °C for 12 h, then cooled to room temperature and filtered. The filtrate was acidified with 12 M hydrochloric acid (HCl), resulting in the formation of a white solid, 2,2'-bipyridine-5,5'-dicarboxylic acid (0.208 g, 0.85 mmol, 31% yield). The product was analyzed by ¹H NMR spectroscopy. ¹H NMR spectrum (500 MHz, DMSO-*d*₆): δ 13.55 (s, 2 H), 9.16 (s, 2 H), 8.54 (d, ³J_{H-H} = 8.8 Hz, 2 H), and 8.45 (d, ³J_{H-H} = 8.4 Hz, 2 H).²⁷⁹

4.5.1.2. Synthesis of bpy-UiO-67 MOF²⁷⁵

To synthesize bpy-UiO-67 MOF, 2,2'-bipyridine-5,5'-dicarboxylic acid (0.026 g, 0.106 mmol) and ZrCl₄ (0.026 g, 0.112 mmol) were dissolved in 13 mL of DMF. The mixture was sonicated for 30 minutes, after which TFA (0.040 mL, 0.523 mmol) was added. The resulting solution was heated in a sealed 15 mL glass vial at 100 °C for 96 h in an oven. After allowing the reaction mixture to cool to room temperature, the white crystalline solid was isolated by centrifugation, yielding bpy-UiO-67 MOF with a 63% yield. The MOF was thoroughly washed with DMF several times, followed by washing with THF, and then stored in THF at room temperature.

4.5.1.3. Synthesis of bpy-UiO-FeCl₃

A solution of FeCl₃·6H₂O (0.09 g, 0.34 mmol) in THF was added to the bpy-UiO-67 MOF. The mixture was left overnight with periodic shaking at room temperature. The solid product was then separated by centrifugation and washed 8-10 times with THF, yielding the bpy-UiO-FeCl₃ MOF. The bpy-UiO-FeCl₃ has 25% solvent weight as analysed by thermogravimetric analysis and 45% iron loading with respect to bpy-moiety of the digested MOF as analyzed by ICP-OES.

Table 4.1. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) data of the digested bpy-UiO-FeCl₃.

Formula	Zr(ppm)	Fe(ppm)
$\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{bpy})_6\text{Fe}_{6x}\text{Cl}_{18x}$	3.24	0.90

Calculation of Fe loading w.r.t bpy-moiety is as follows:

Amount of Zr in digested bpy-UiO-FeCl₃ MOF = 3.24 ppm

Amount of Fe in digested bpy-UiO-FeCl₃ MOF = 0.90 ppm

Mol. weight of Zr = 91.224 g/mol

Mol. weight of Fe = 55.85 g/mol.

Amt. of Zr/ Mol. weight of Zr = $3.24/91.224 = 0.0355$

Amt. of Fe/ Mol. weight of Fe = $0.90/55.85 = 0.0161$

Therefore, 0.0355 of Zr = 0.0161 of Fe

1 Zr = 1 bpy linker = 0.4539 Fe

Hence, % Fe (% x) = $6/6 \times 0.4539 \times 100$

= 45.39% $\approx$ 45%

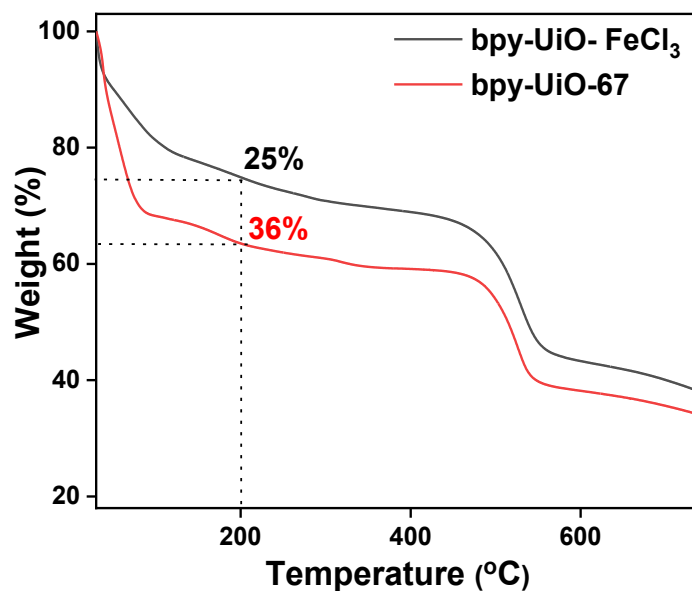


Figure 4.6. TGA curve of freshly prepared bpy-UiO-67 and bpy-UiO-FeCl₃. A solvent weight loss, attributed to THF within the pores, of 36% in bpy-UiO-67 (red) and 25% in bpy-UiO-FeCl₃ (black) was observed from 40 °C to 200 °C. The increased weight of metalated MOF is due to the presence of iron chloride moiety within the MOF.

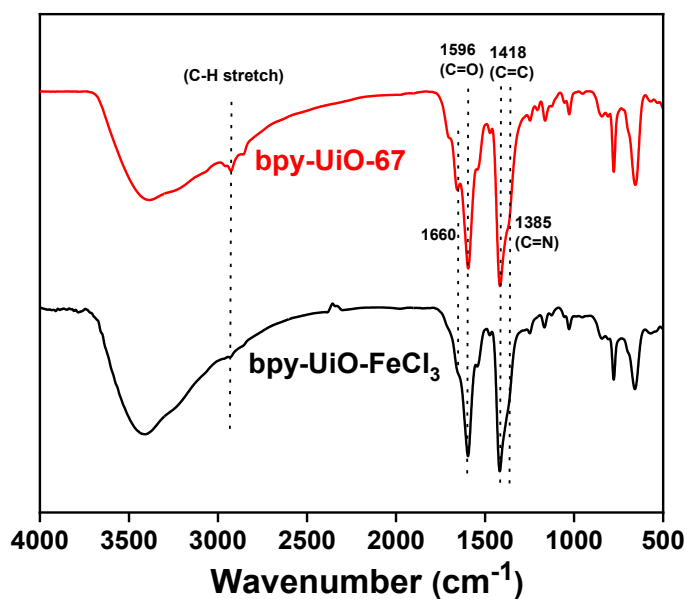


Figure 4.7. FT-IR spectra (KBr) of freshly prepared bpy-UiO-67 (red) and bpy-UiO-FeCl₃ (black). FT-IR spectrum of bpy-UiO-FeCl₃ displays a new characteristic absorption peak at 1660 cm⁻¹, indicating a shift of the C=N bond stretching vibration to a lower wavenumber, which suggests that the C=N bond is involved in coordination.

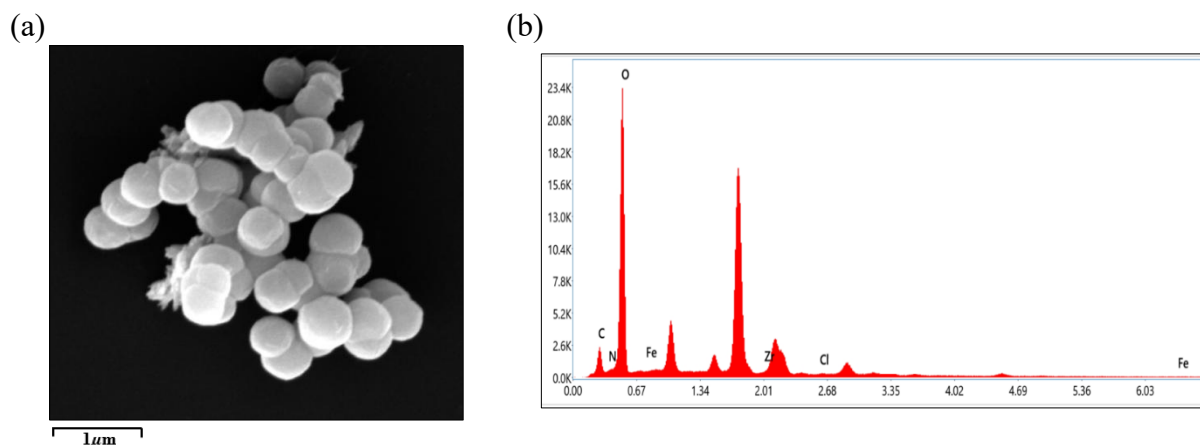


Figure 4.8. a) SEM image and (b) SEM-EDX analysis of bpy-UiO-FeCl₃. SEM image displayed octahedron particles of bpy-UiO-FeCl₃ with an average size of 250 nm.

4.5.2. Catalytic Reactions with bpy-UiO-FeCl₃

4.5.2.1. General procedure for bpy-UiO-FeCl₃ catalyzed oxidative bromination of arenes

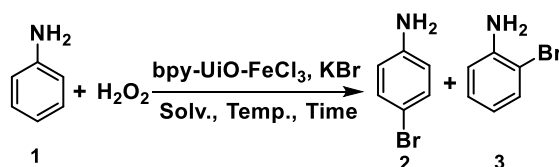
Oxidative bromination of arenes was performed in a 25 mL Schlenk tube. A total of 4 mg of the catalyst bpy-UiO-FeCl₃ (0.4 mol% of Fe) was added to 5 mL of the selected solvent. Next, the arene substrate (1 mmol), potassium bromide, KBr (0.13 g, 1.1 mmol), and 0.2 mL (2 mmol) of 30% aqueous hydrogen peroxide (H₂O₂) were added sequentially, with the H₂O₂

introduced dropwise to minimize immediate degradation. The reaction mixture was stirred at a temperature between 30-60 °C for a duration of 30-180 minutes, depending on the desired conversion and selectivity. Once the reaction was complete, the mixture was allowed to cool to room temperature. The solid catalyst was then filtered and dried. To the filtrate, saturated sodium bicarbonate solution was added, and the organic layer was extracted. Anhydrous sodium sulphate was used to dry the organic layer and solvent was evaporated under reduced pressure. The resulting product was analyzed using gas chromatography coupled with mass spectrometry (GC-MS) for identification and flame ionization detection (GC-FID) for quantification. The products were purified by column chromatography using a mixture of ethyl acetate and petroleum benzene and subsequently analyzed by ^1H and ^{13}C NMR spectroscopy.

4.5.2.2. A typical procedure for bpy-UiO-FeCl₃ catalyzed oxidative bromination of aniline

In a 25 mL Schlenk tube, bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe) was added to 5 mL of acetonitrile (CH₃CN). Sequentially, aniline (1 mmol), potassium bromide, KBr (0.13 g, 1.1 mmol), and 0.2 mL (2 mmol) of 30% aqueous H₂O₂ were added. The hydrogen peroxide solution was introduced dropwise to minimize immediate degradation of the reactants. The reaction mixture was stirred at a temperature around 50 °C for 120 minutes. After completing the reaction, the mixture was allowed to cool to room temperature. The solid catalyst was filtered out and dried. To the remaining liquid, a saturated sodium bicarbonate solution was added, and the organic layer was extracted. Anhydrous sodium sulfate was used to dry the organic layer, and the solvent was evaporated under reduced pressure. The resulting product was analyzed using GC-MS for product identification and GC-FID for quantification. The products were purified by column chromatography using a mixture of ethyl acetate and petroleum benzene and subsequently analyzed by ^1H and ^{13}C NMR spectroscopy.

Table 4.2. Bpy-UiO-FeCl₃ catalyzed oxidative bromination of aniline.^a



Entry No.	H ₂ O ₂ (mmol)	Brominating agent (mmol)	Temp. (°C)	Time (h)	Solvent	% Conv. of 1	%Yield of 2 ^b (2:3)
1	2	KBr (1.1)	40	2	CH ₃ CN	84	82 (98:2)
2	2	KBr (1.1)	50	2	CH ₃ CN	98	95 (97:3)
3	2	KBr (1.1)	60	2	CH ₃ CN	100	89 (89:11)

Table 4.4. Comparison of activities of our MOF catalyst with previously reported catalysts for oxidative bromination.

Entry	Catalyst (loading)	Br source	Substrate	Oxidant	Temp., Time	Conv. (%)	Sel. (%)	Ref.
1.	PS-Fe(III)teta complex (3.66% Fe)	KBr	Aniline	H ₂ O ₂	rt, 2.5 h	96	4-bromo aniline (85)	280
2.	Fe(opbmzl) ₂ -Y (0.45% Fe)	KBr	Aniline	H ₂ O ₂	rt, 3 h	84.4	4-bromo aniline (95.6)	263
3.	MNP@DAPN/Au (300mg)	NBS	Aniline		80 °C, 11 h	95	4-bromo aniline (88)	281
4.	Cu(OAc) ₂	LiBr	Aniline	O ₂	80 °C, 4 h	100	4-bromo aniline (80)	282
5.	NH ₄ VO ₃ (10 mol%)	KBr	Anisole	H ₂ O ₂	rt, 24 h		4-bromo aniline (94*)	283
6.	V ₂ O ₅ (3 mol%)	NaBr	Phenol	H ₂ O ₂	rt, 1h	90	4-bromo phenol (69)	251
7.	4Na ₂ SO ₄ -2H ₂ O ₂ -NaCl adduct	KBr	Aniline	H ₂ O ₂	52 °C, 3 h		4-bromo aniline (90*)	260
8.	Bpy-Uio-FeCl₃ (0.4 mol% Fe)	KBr	Aniline	H₂O₂	50 °C, 2 h	98	4-bromo aniline (97)	This work

*NMR-Yield.

4.5.3. Catalytic Testing of Fe Nanoparticles.

A 3 mL solution of FeCl₃·6H₂O in THF (1.1 mg, 4.01 μmol) was treated with NaEt₃BH (200 μL, 1 M in toluene) for 1 hour. This treatment resulted in the formation of Fe nanoparticles, which settled as a black solid. The nanoparticles were collected by centrifugation and washed thoroughly with THF several times, followed by CH₃CN.

The Fe nanoparticles were then utilized in a reaction setup. In a 25 mL Schlenk tube, the Fe nanoparticles were dispersed in 5 mL of acetonitrile (CH₃CN). Aniline (1 mmol), potassium bromide, KBr (0.13 g, 1.1 mmol), and 30% aqueous hydrogen peroxide (0.2 mL, 2 mmol) were added sequentially. The hydrogen peroxide was introduced dropwise to prevent rapid degradation of the reactants. The reaction mixture was stirred at approximately 50 °C for 120 minutes. After completion of the reaction, the mixture was cooled to room temperature. A saturated sodium bicarbonate solution was added to the mixture, and the organic layer was extracted. The organic phase was dried using anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The resulting product was analyzed by GC-MS for product identification and GC-FID for quantification. The products were purified

using column chromatography with a solvent mixture of ethyl acetate and petroleum benzene. The purified products were further characterized by ^1H NMR spectroscopy.

4.5.4. Test for “Heterogeneity” of bpy-UiO-FeCl₃ for the Oxidative Bromination of Aniline

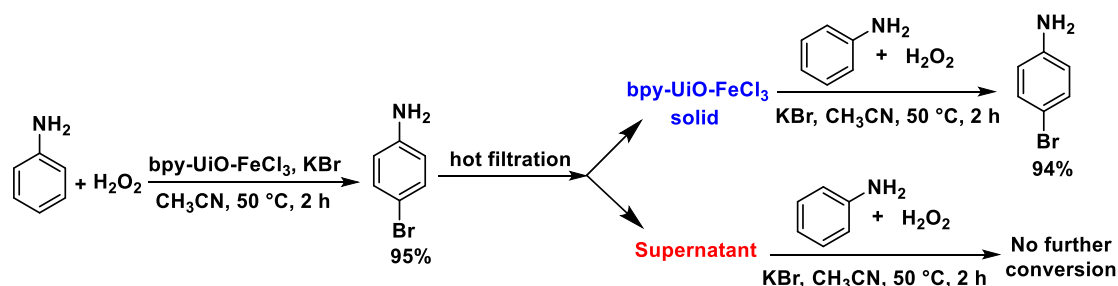


Figure 4.9. Hot filtration test of bpy-UiO-FeCl₃ for the oxidative bromination of aniline.

In a 25 mL Schlenk tube, bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe) was dispersed in 5 mL of CH₃CN as the solvent. To this solution, aniline (1 mmol), potassium bromide, KBr (0.13 g, 1.1 mmol), and 30% aqueous hydrogen peroxide (0.2 mL, 2 mmol) were sequentially added. The reaction mixture was stirred at 50 °C for 120 min. After the reaction, the solid MOF catalyst was separated from the hot suspension by filtration and washed thoroughly with CH₃CN. The filtrate was treated with a saturated sodium bicarbonate solution, and the organic layer was extracted. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. Analysis of the resulting supernatant product revealed a 95% yield of 4-bromoaniline.

Two separate reactions were performed using the recovered solid catalyst and the supernatant from the previous reaction to investigate the catalytic activity further. The extracted solid and supernatant were each transferred into individual Schlenk tubes, with 0.1 mL of aniline (1 mmol), 0.34 mL of 30% aqueous hydrogen peroxide (3 mmol), and 5 mL of CH₃CN added to each. The reaction mixtures were heated in an oil bath at 50 °C for 2 h. Analysis using GC-FID revealed that the reaction with the solid MOF catalyst yielded 94% of 4-bromoaniline, while no further conversion of aniline was observed in the reaction using the supernatant. These results confirm that the solid bpy-UiO-FeCl₃ MOF functions as the true catalyst for the oxidative bromination of aniline, with no significant contribution from leached Fe species.

4.5.5. Recycling of bpy-UiO-FeCl₃ for the Oxidative Bromination of Aniline

The recycle and reuse experiment was conducted to check the stability of bpy-UiO-FeCl₃ catalyst (Table 4.5). The detailed procedure of recycling experiment given below.

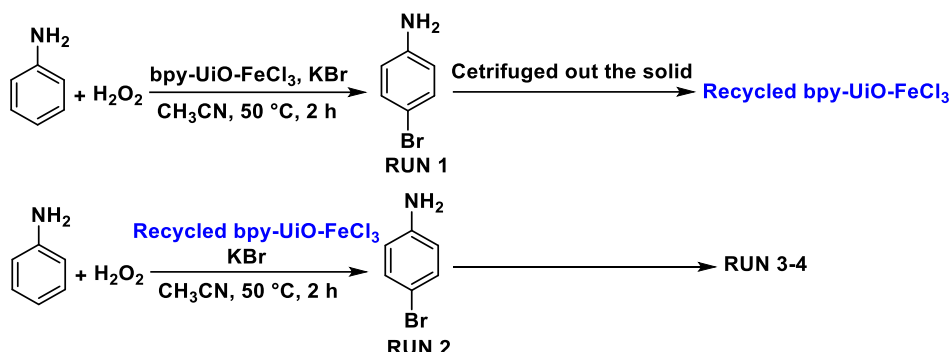


Figure 4.10. Recycle and reuse of bpy-UiO-FeCl₃ for the oxidative bromination of aniline.

In a 25 mL Schlenk tube, bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe) was mixed with 5 mL of acetonitrile (CH₃CN) as the solvent. To this solution, aniline (1 mmol), potassium bromide, KBr (0.13 g, 1.1 mmol), and 30% aqueous hydrogen peroxide (0.2 mL, 2 mmol) were sequentially added. The reaction mixture was stirred at 50 °C for 2 h. After the reaction, the solid MOF catalyst was separated from the suspension by filtration and washed thoroughly with CH₃CN. The filtrate was treated with a saturated sodium bicarbonate solution, and the organic layer was extracted. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. Analysis of the resulting product revealed a 95% yield of 4-bromoaniline. The solid MOF was then recycled.

The recovered MOF-catalyst was again added to the Schlenk tube. Aniline (1 mmol), KBr (0.13 g, 1.1 mmol), and 30% aqueous H₂O₂ (0.2 mL, 2 mmol) in 5 mL CH₃CN were added to the Schlenk tube. The reaction mixture was stirred at 50 °C for 2 h. After the reaction, the solution was analyzed in the same way as mentioned previously in run 1. The recycling and reuse experiments were performed up to 3 times in total.

Table 4.5. %GC-Yield of 4-bromoaniline and the leaching of Fe and Zr at various runs of the recycling of bpy-UiO-FeCl₃ in the oxidative bromination of aniline.

Run	Time	%GC-Yield (4-bromoaniline)	%Leaching (Fe, Zr)
Run-1	2 h	95	0.02, 0.6
Run-2	2 h	94	
Run-3	2 h	92	0.08, 1.5
Run-4	2 h	91	

4.5.6. Radical Scavenging Experiment

To investigate the role of any $\bullet\text{OH}$ in the bpy-UiO- FeCl_3 catalyzed oxidative bromination of aniline, catalysis have been performed in the presence of radical scavengers such as Na_2SO_3 , and *tert*-butyl alcohol (TBA).

4.5.6.1. Radical scavenging experiment using Na_2SO_3 as the radical scavenger

Solid bpy-UiO- FeCl_3 (4 mg, 0.4 mol% of Fe) was dissolved in 5 mL of CH_3CN and transferred into a 25 mL Schlenk tube, which was placed in an oil bath maintained at 50 °C. To this, 5 mmol of Na_2SO_3 was added as a radical scavenger, followed by aniline (1 mmol), KBr (0.13 g, 1.1 mmol), and 30% aqueous H_2O_2 (0.2 mL, 2 mmol). After 2 h, the solid MOF catalyst was separated from the reaction mixture by filtration and thoroughly washed with CH_3CN . The filtrate was treated with a saturated NaHCO_3 solution, and the organic layer was extracted. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The resulting product was analyzed using GC-FID.

4.5.6.2. Radical scavenging experiment using *tert*-butyl alcohol (TBA) as the radical scavenger

Solid bpy-UiO- FeCl_3 (4 mg, 0.4 mol% of Fe) was dissolved in 5 mL of CH_3CN and transferred into a 25 mL Schlenk tube, which was placed in an oil bath maintained at 50 °C. To this, 5 mmol of *tert*-butyl alcohol (TBA) was added as a radical scavenger, followed by aniline (1 mmol), KBr (0.13 g, 1.1 mmol), and 30% aqueous H_2O_2 (0.2 mL, 2 mmol). After 2 hours, the MOF catalyst was filtered and washed with CH_3CN . The filtrate was neutralized with saturated NaHCO_3 , extracted, and the organic phase was dried over Na_2SO_4 . After solvent removal under reduced pressure, the product was analyzed by GC-FID.

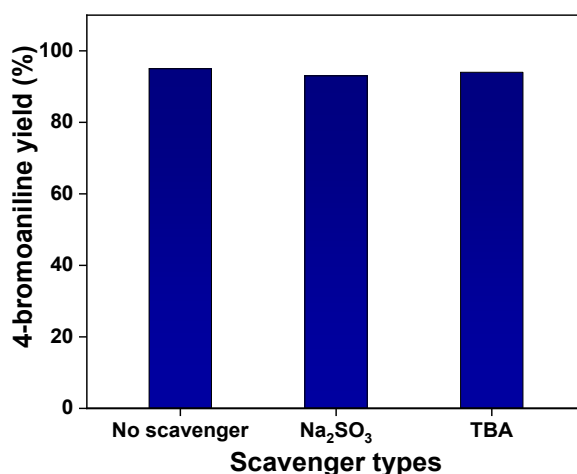


Figure 4.11. Radical scavenger tests. Reaction conditions: bpy-UiO- FeCl_3 (0.4 mol% of Fe), aniline (1 mmol), KBr (1.1 mmol), H_2O_2 (30%) (2 eq.), 5 mL CH_3CN , 50 °C, 2h, trapping agent (5 mmol).

4.6. Characterization of the Products

4-bromoaniline (2a).²⁶⁰ 4-bromoaniline was synthesized with 95% yield according to the general procedure for the oxidative bromination of arenes using aniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield 4-bromoaniline product. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.22 (d, J = 6.7 Hz, 2H), 6.55 (d, J = 6.7 Hz, 2H), 3.46 (s, 2H). ¹³C NMR (126 MHz, CDCl₃, ppm): δ 145.40, 131.99, 116.71, 110.17.

4-bromo-N,N-dimethylaniline (2b).²⁸⁴ 4-bromo-N,N-dimethylaniline was synthesized with 96% yield according to the general procedure for the oxidative bromination of arenes using N,N-dimethylaniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield 4-bromo-N,N-dimethylaniline product. ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.30 (d, J = 9.0 Hz, 2 H), 6.59 (d, J = 9.0 Hz, 2 H), 2.93 (s, 6 H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 149.51, 131.68, 114.11, 108.51, 40.57.

4-bromoanisole (2c).²⁸⁵ 4-bromoanisole was synthesized with 91% yield according to the general procedure for the oxidative bromination of arenes using anisole (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield the product. ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.37 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H). ¹³C NMR (50 MHz, CDCl₃, ppm): δ 158.6, 132.1, 115.6, 112.7, 55.3.

4-bromophenol (2d).²⁸⁶ 4-bromophenol was synthesized with 86% yield according to the general procedure for the oxidative bromination of arenes using phenol (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield 4-bromophenol product. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.37-7.28 (m, 2H), 6.76-6.66 (m, 2H), 5.25 (s, 1H). ¹³C NMR (101 MHz, CDCl₃, ppm): δ 154.6, 132.4, 117.2, 112.8.

4-bromotoluene (2e).²⁸¹ 4-bromotoluene was synthesized with 85% yield according to the general procedure for the oxidative bromination of arenes using toluene (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield the product. ¹H NMR (500 MHz, CDCl₃, ppm): δ 7.42 (d, J = 8.50 Hz, 2H), 7.10 (d, J = 8 Hz, 2H), 2.36 (s, 3H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 136, 131, 130, 119, 20.9.

Bromobenzene (2f).²⁸¹ Bromobenzene was synthesized with 41% yield according to the general procedure for the oxidative bromination of arenes using benzene (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 10 h. After 10 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield bromobenzene product. ¹H NMR (500 MHz, CDCl₃, ppm): δ 7.56-7.54 (d, J = 7.5 Hz, 2H), 7.35-7.26(m, 3H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 132, 130.5, 127.3, 123.

2-bromo-4-methylaniline (2i).²⁸⁷ 2-bromo-4-methylaniline was synthesized with 71% yield according to the general procedure for the oxidative bromination of arenes using 4-methylaniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield the product. ¹H NMR (500 MHz, CDCl₃, ppm): δ 7.24 (s, 1H), 6.92 (d, J = 8.05 Hz, 1H), 6.68 (d, J = 8.05 Hz, 1H), 3.93 (br, 2H), 2.23 (s, 3H).

2-bromo-1,4-dimethylbenzene (2j).²⁴³ 2-bromo-1,4-dimethylbenzene was synthesized with 70% yield according to the general procedure for the oxidative bromination of arenes using 1,4-dimethylbenzene (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield 2-bromo-1,4-dimethylbenzene product. ¹H NMR (90 MHz, CDCl₃, ppm): δ 82.0(s,3H), 2.1(s,3H), 6.45(d, H), 7.05(d, H), 6.65(s, H).

4-bromo-1,2-dimethylbenzene (2k).²⁴³ 4-bromo-1,2-dimethylbenzene was synthesized with 72% yield according to the general procedure for the oxidative bromination of arenes using 1,2-dimethylbenzene (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4

mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield 4-bromo-1,2-dimethylbenzene product. ¹H NMR (90 MHz, CDCl₃, ppm): δ 82.1(s, 3H), 2.4(s, 3H), 7.1-7.45(m, 3H).

4-bromo-2-iodoaniline (2l).²⁸⁸ 4-bromo-2-iodoaniline was synthesized with 57% yield according to the general procedure for the oxidative bromination of arenes using 2-iodoaniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield 4-bromo-2-iodoaniline product. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.73 (d, J = 2.4 Hz, 1H), 7.22 (dd, J₁ = 8.4 Hz, J₂ = 2.0 Hz, 1H), 6.92 (d, S7 J = 8.8 Hz, 1H), 4.10 (s, 2H). ¹³C NMR (400 MHz, CDCl₃, ppm): δ 146.1, 140.5, 132.2, 115.7, 110.0, 84.2.

4-bromo-1,2-dimethoxybenzene (2m). 4-bromo-1,2-dimethoxybenzene was synthesized with 62% yield according to the general procedure for the oxidative bromination of arenes using 1,2-dimethoxybenzene (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield 4-bromo-1,2-dimethoxybenzene product. ¹H NMR (400 MHz, DMSO, ppm): δ 7.09 (d, J = 2.0 Hz, 1 H), 7.05 (dd, J = 8.6, 2.0 Hz, 1 H), 6.9 (d, J = 8.6 Hz, 1 H), 3.76 (s, 3 H), 3.73 (s, 3 H). ¹³C NMR (100 MHz, DMSO, ppm): δ 150.3, 148.8, 123.5, 115.3, 113.8, 112.3, 56.2, 56.0.

4-bromo catechol (2n).²⁸⁹ 4-bromo catechol was synthesized with 68% yield according to the general procedure for the oxidative bromination of arenes using catechol (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield 4-bromo catechol product. ¹H NMR (400 MHz, CD₃OD, ppm): δ 6.66 (1 H, d, J=8.5 Hz), 6.77 (1 H, dd, J=8.4, 2.3 Hz), 6.89 (1 H, d, J=2.3 Hz). ¹³C NMR (100 MHz, CD₃OD, ppm): δ 112.0, 117.8, 119.5, 123.6, 146.1, and 147.8.

4-bromo-3-methylaniline (2o).²⁹⁰ 4-bromo-3-methylaniline was synthesized with 66% yield according to the general procedure for the oxidative bromination of arenes using 3-

methylaniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo, followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield 4-bromo-3-methylaniline product. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.28 (d, J = 8.4 Hz, 1H), 6.59 (d, J = 2.4 Hz, 1H), 6.42 (dd, J = 2.4 Hz, J = 8.4 Hz, 1H), 3.60 (br s, 2H), 2.32 (s, 3H). ¹³C NMR (126 MHz, CDCl₃, ppm): δ 145.6, 138.4, 132.7, 117.5, 114.3, 113.0, 22.8.

1-bromo-2,4-dimethylbenzene (2p).²⁹¹ 1-bromo-2,4-dimethylbenzene was synthesized with 67% yield according to the general procedure for the oxidative bromination of arenes using 1,3-dimethylbenzene (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), acetonitrile (5 mL), 50 °C, 2 h. After 2 h, the combined organic extracts were concentrated in vacuo followed by column chromatography using a mixture of ethyl acetate and petroleum benzene (5:1) as an eluent to yield 1-bromo-2,4-dimethylbenzene product. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.39 (d, J = 8.1 Hz, 1H), 7.05 (s, 1H), 6.86 (d, J = 8.1 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H). ¹³C NMR (126 MHz, CDCl₃, ppm): δ 137.4, 137.0, 132.0, 131.7, 128.1, 121.5, 22.8, 20.8.

4.7. DFT Calculations

All quantum chemical calculations were done using the density functional theory (DFT) with B3LYP²⁹²/def2-SVP²⁹³ level of theory as implemented in the Gaussian 09 software suite.^{215,217,219,294,295} Electronic structure complexes were optimized at the unrestricted level. All calculations were performed in the solvated state and at 323.15 K. The solvent effect was incorporated using a continuum solvation model, SMD²⁹⁶ taking acetonitrile as the solvent. Each structure was first optimized, and then frequency calculation was performed to confirm its geometry and to obtain the thermochemical data. Internal energies were compared directly after accounting for the difference in the number of coordinated CH₃CN molecules. To reduce the computational costs, a simplified bipyridyl ligand was used in these calculations. All the 3D structures were viewed using Gauss View 5.0 software.

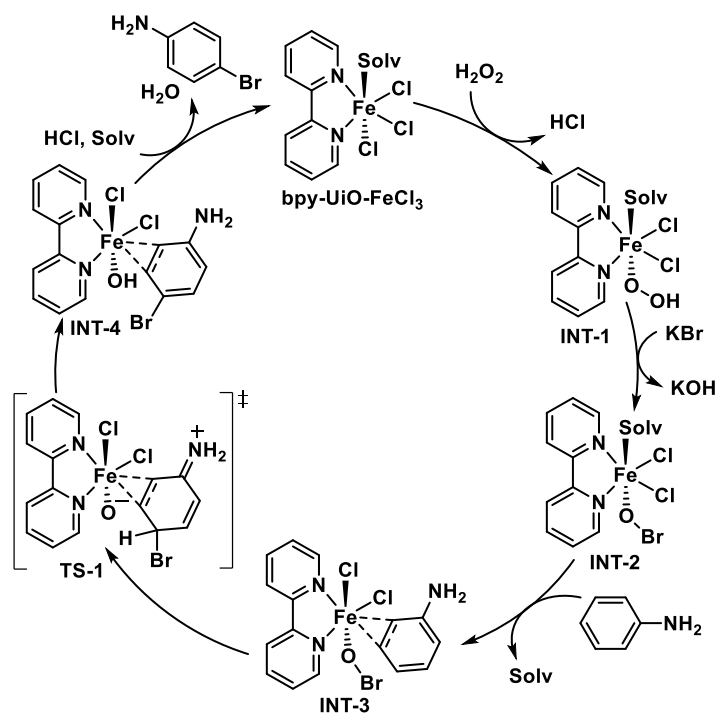
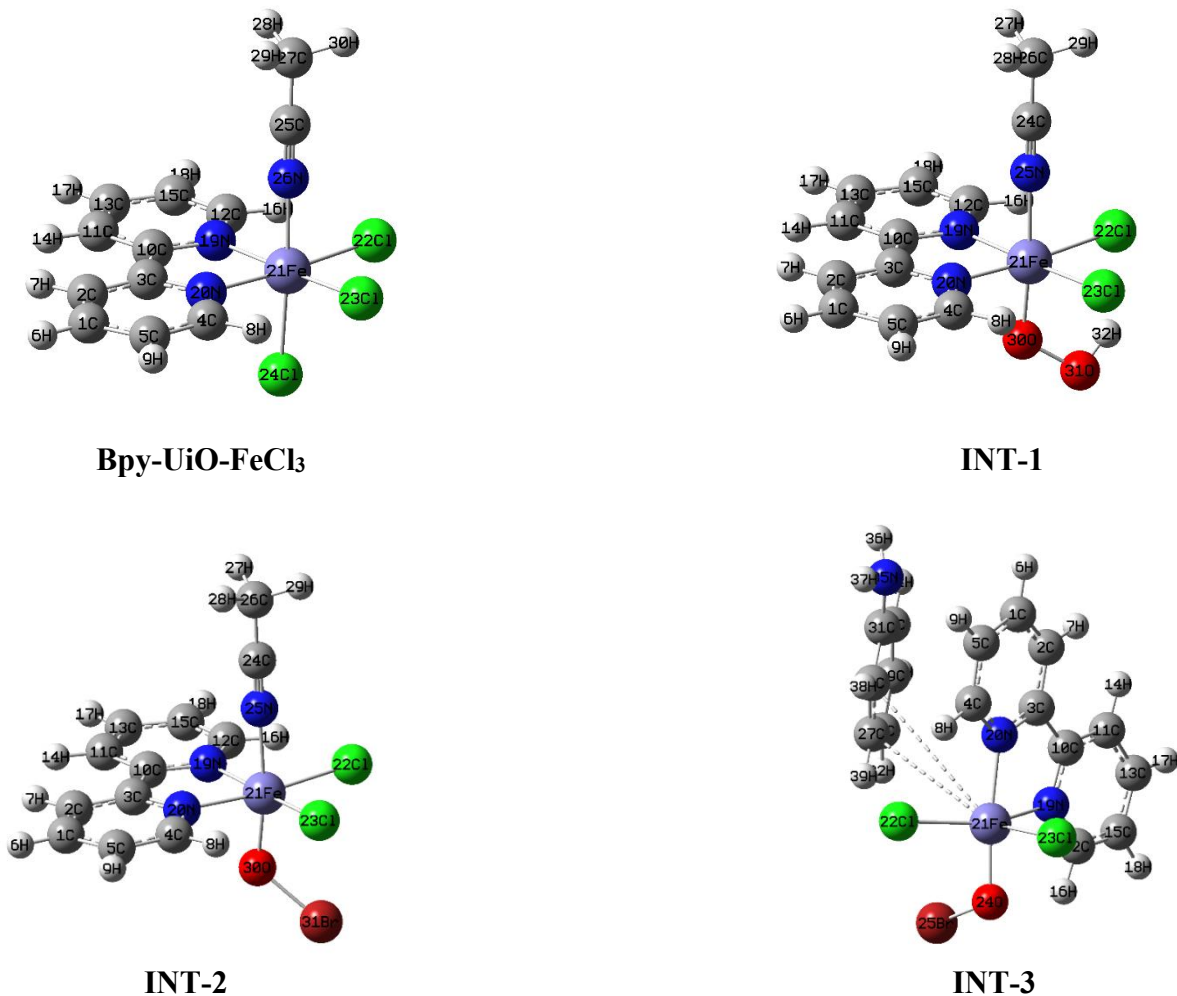


Figure 4.12. Proposed catalytic cycle of bpy-UiO-FeCl_3 -catalyzed oxidative bromination of aniline.



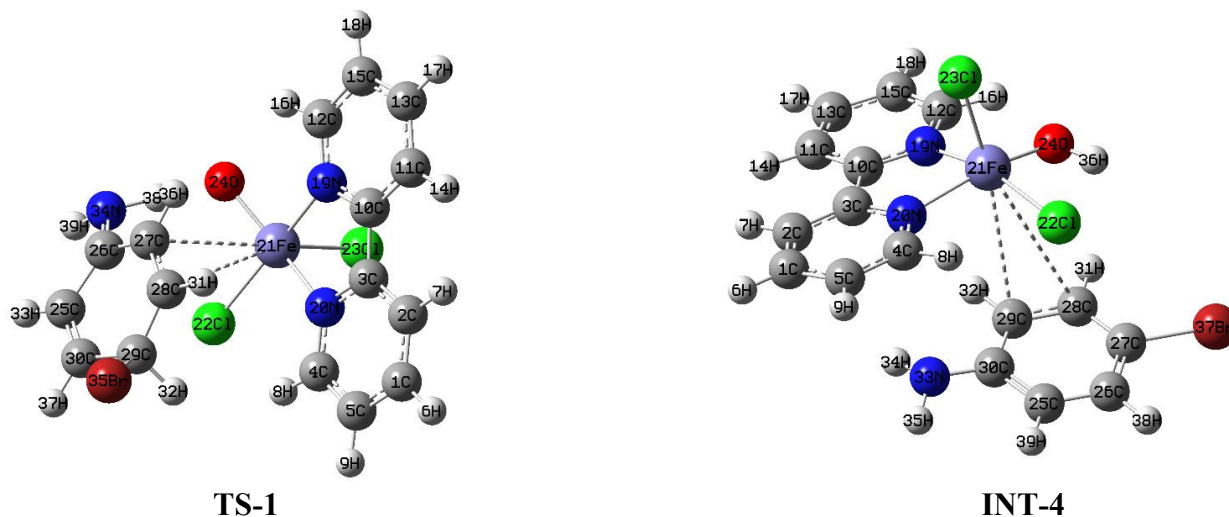


Figure 4.13. DFT-optimized structures of intermediates and transition states of the catalytic cycle in bpy-UiO-FeCl₃ catalyzed oxidative bromination of aniline.

4.7.1. Cartesian Coordinates of the DFT-Optimized Structures

Cartesian coordinates of bpy-UiO-FeCl₃

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-4.205349	-1.182255	0.003445
2	C	-2.815683	-1.285711	-0.035503
3	C	-2.044039	-0.119301	-0.013116
4	C	-3.959023	1.205444	0.085933
5	C	-4.786556	0.084006	0.067247
6	H	-4.823619	-2.082534	-0.011017
7	H	-2.336002	-2.263499	-0.075235
8	H	-4.353862	2.221463	0.135692
9	H	-5.869441	0.215008	0.103369
10	C	-0.571587	-0.102819	-0.028464
11	C	0.227908	-1.248039	-0.103028
12	C	1.313480	1.267847	0.045264
13	C	1.615112	-1.110309	-0.097737
14	H	-0.228432	-2.235633	-0.165145
15	C	2.167509	0.168170	-0.020660
16	H	1.683545	2.292807	0.105793
17	H	2.254429	-1.994154	-0.152961
18	H	3.247534	0.324887	-0.012055
19	N	-0.019171	1.130509	0.040433
20	N	-2.624230	1.102612	0.042663
21	Fe	-1.336679	2.668822	0.146406
22	Cl	0.285240	4.282793	0.208874
23	Cl	-2.993355	4.246447	0.119296
24	Cl	-1.379339	2.419958	2.426015
25	C	-1.247146	2.870808	-2.984625
26	N	-1.284453	2.772708	-1.836255
27	C	-1.173177	2.986212	-4.428721
28	H	-0.257778	2.496363	-4.794262
29	H	-2.050081	2.502313	-4.885113
30	H	-1.155759	4.048916	-4.714841

Cartesian coordinates of INT-1

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-4.212601	-1.186338	0.014907
2	C	-2.823021	-1.292673	-0.028436
3	C	-2.049170	-0.127356	-0.004569
4	C	-3.961455	1.200904	0.101724
5	C	-4.791899	0.081067	0.082202
6	H	-4.832386	-2.085019	-0.001054
7	H	-2.348267	-2.271960	-0.075579
8	H	-4.349608	2.219941	0.153893
9	H	-5.874209	0.212424	0.120941
10	C	-0.576247	-0.109456	-0.027777
11	C	0.227464	-1.252024	-0.103218
12	C	1.304498	1.269670	0.031741
13	C	1.614444	-1.107957	-0.106337
14	H	-0.222281	-2.242511	-0.159210
15	C	2.162934	0.173061	-0.034770
16	H	1.665530	2.298760	0.086782
17	H	2.256695	-1.989040	-0.163415
18	H	3.242126	0.332491	-0.032094
19	N	-0.026944	1.125229	0.033882
20	N	-2.627415	1.094621	0.055870
21	Fe	-1.340141	2.656614	0.152469
22	Cl	0.264846	4.311023	0.222145
23	Cl	-2.999599	4.248398	0.077209
24	C	-1.204984	2.862690	-2.981602
25	N	-1.246420	2.764352	-1.838704
26	C	-1.152995	2.993306	-4.426586
27	H	-0.240542	2.513344	-4.810060
28	H	-2.032424	2.508015	-4.875074
29	H	-1.146155	4.057985	-4.703076
30	O	-1.387962	2.470316	1.962277
31	O	-1.405328	3.662961	2.527693
32	H	-1.428148	3.564700	3.482378

Cartesian coordinates of INT-2

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-4.212601	-1.186338	0.014907
2	C	-2.823021	-1.292673	-0.028436
3	C	-2.049170	-0.127356	-0.004569
4	C	-3.961455	1.200904	0.101724
5	C	-4.791899	0.081067	0.082202
6	H	-4.832386	-2.085019	-0.001054
7	H	-2.348267	-2.271960	-0.075579
8	H	-4.349608	2.219941	0.153893
9	H	-5.874209	0.212424	0.120941
10	C	-0.576247	-0.109456	-0.027777
11	C	0.227464	-1.252024	-0.103218
12	C	1.304498	1.269670	0.031741
13	C	1.614444	-1.107957	-0.106337
14	H	-0.222281	-2.242511	-0.159210
15	C	2.162934	0.173061	-0.034770
16	H	1.665530	2.298760	0.086782
17	H	2.256695	-1.989040	-0.163415
18	H	3.242126	0.332491	-0.032094
19	N	-0.026944	1.125229	0.033882
20	N	-2.627415	1.094621	0.055870
21	Fe	-1.340141	2.656614	0.152469
22	Cl	0.264846	4.311023	0.222145
23	Cl	-2.999599	4.248398	0.077209
24	C	-1.204984	2.862690	-2.981602
25	N	-1.246420	2.764352	-1.838704
26	C	-1.152995	2.993306	-4.426586
27	H	-0.240542	2.513344	-4.810060
28	H	-2.032424	2.508015	-4.875074
29	H	-1.146155	4.057985	-4.703076
30	O	-1.387962	2.470316	1.962277
31	Br	-1.411642	4.096651	2.733299

Cartesian coordinates of INT-3

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-4.092771	-1.027771	-0.479746
2	C	-2.706024	-1.168526	-0.434362
3	C	-1.904110	-0.022917	-0.403971
4	C	-3.780329	1.351858	-0.473819
5	C	-4.639323	0.253482	-0.496201
6	H	-4.735185	-1.910781	-0.503167
7	H	-2.255007	-2.159729	-0.423497
8	H	-4.151322	2.377394	-0.493818
9	H	-5.718097	0.415270	-0.528151
10	C	-0.431562	-0.052879	-0.347341
11	C	0.333956	-1.223289	-0.344684
12	C	1.498246	1.256916	-0.304602
13	C	1.724931	-1.129941	-0.320907
14	H	-0.148911	-2.199220	-0.368409
15	C	2.318457	0.131261	-0.304571
16	H	1.922585	2.259938	-0.301707
17	H	2.335232	-2.035687	-0.324112
18	H	3.402406	0.255605	-0.299019
19	N	0.160827	1.166742	-0.306008
20	N	-2.448560	1.219546	-0.425028
21	Fe	-1.067793	2.740736	-0.509978
22	Cl	-2.693909	4.363466	-0.443083
23	Cl	-1.059581	2.608395	-2.780634
24	O	0.171396	4.072526	-0.727514
25	Br	1.444316	4.736417	0.449685
26	C	-2.430735	2.871710	2.672465
27	C	-1.038863	2.915501	2.678791
28	C	-0.312545	1.881516	3.299707
29	C	-1.003668	0.836056	3.919874
30	C	-2.403919	0.808750	3.929924
31	C	-3.138316	1.822660	3.291294

32	H	0.779593	1.898352	3.296859
33	H	-0.450448	0.036621	4.420400
34	H	-2.934859	-0.006238	4.430420
35	N	-4.536232	1.781252	3.197342
36	H	-4.959727	1.140424	3.854534
37	H	-4.977243	2.686494	3.296310
38	H	-2.973439	3.655355	2.143080
39	H	-0.482124	3.731674	2.204863

Cartesian coordinates of TS-1

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-3.627480	-1.670802	-0.785646
2	C	-2.269695	-1.362330	-0.869853
3	C	-1.866009	-0.031067	-0.723973
4	C	-4.068119	0.658646	-0.415944
5	C	-4.544055	-0.644333	-0.557244
6	H	-3.961947	-2.704434	-0.899235
7	H	-1.536117	-2.148218	-1.047526
8	H	-4.737046	1.500959	-0.229529
9	H	-5.615435	-0.839900	-0.486774
10	C	-0.460708	0.416399	-0.805803
11	C	0.627238	-0.433991	-1.032616
12	C	0.958435	2.268227	-0.686892
13	C	1.912672	0.104223	-1.084575
14	H	0.472047	-1.503865	-1.168520
15	C	2.084014	1.477783	-0.906182
16	H	1.024571	3.348174	-0.542555
17	H	2.771630	-0.546081	-1.263862
18	H	3.071755	1.940644	-0.935851
19	N	-0.273211	1.745334	-0.640400
20	N	-2.764705	0.954670	-0.496612
21	Fe	-1.911752	2.907846	-0.410328
22	Cl	-3.913854	3.831213	0.274011
23	Cl	-2.151189	3.170136	-2.595936
24	O	-1.039966	4.124861	0.107422
25	C	-2.329311	2.664689	5.558337
26	C	-1.555374	1.686706	6.151192
27	C	-0.853102	0.742778	5.362502
28	C	-0.967590	0.809525	3.950731
29	C	-1.741414	1.777280	3.345296
30	C	-2.448012	2.734064	4.138343
31	H	-0.352783	-0.102961	5.831427
32	H	-0.438492	0.077537	3.335780
33	H	-1.826632	1.829703	2.257712
34	H	-2.873940	3.396284	6.160435
35	H	-1.505845	1.627409	7.241440
36	N	-3.215474	3.673355	3.559066
37	H	-3.326680	3.729953	2.543082
38	H	-3.698045	4.361863	4.128759
39	Br	1.807180	1.726822	5.782764

Cartesian coordinates of INT-4

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-4.207565	-1.130812	0.016839
2	C	-2.817468	-1.240457	-0.001980
3	C	-2.042319	-0.075265	0.030158
4	C	-3.953634	1.255389	0.098067
5	C	-4.786794	0.137549	0.067557
6	H	-4.828512	-2.029272	-0.004219
7	H	-2.342628	-2.220842	-0.033414
8	H	-4.339293	2.276630	0.141402
9	H	-5.869920	0.270979	0.086476
10	C	-0.566361	-0.062200	0.027305
11	C	0.228836	-1.211663	-0.046490
12	C	1.321868	1.298602	0.133647
13	C	1.616853	-1.079092	-0.023222
14	H	-0.229430	-2.197406	-0.122156

15	C	2.174113	0.196404	0.072536
16	H	1.690021	2.324826	0.203547
17	H	2.253168	-1.965292	-0.077855
18	H	3.254753	0.347835	0.097474
19	N	-0.009617	1.167705	0.108721
20	N	-2.620187	1.146445	0.078873
21	Fe	-1.328799	2.714937	0.229448
22	Cl	-2.984155	4.323775	0.153190
23	Cl	-1.286307	2.779404	-2.078261
24	O	-0.056362	3.988070	0.235408
25	C	-2.724118	4.750475	2.507883
26	C	-1.389065	5.150227	2.442292
27	C	-0.389839	4.207823	2.200126
28	C	-0.725376	2.864758	2.024601
29	C	-2.060085	2.465103	2.090662
30	C	-3.059590	3.408072	2.331929
31	H	0.062656	2.121878	1.833732
32	H	-2.324849	1.406684	1.952378
33	N	-4.466169	2.986609	2.401233
34	H	-4.700524	2.470638	1.577308
35	H	-4.601775	2.408915	3.206144
36	H	0.565106	4.042167	0.965100
37	Be	1.437809	4.755127	2.109223
38	H	-1.131719	6.179942	2.577790
39	H	-3.490656	5.473658	2.693160

4.8. X-ray Absorption Spectroscopic Analysis (XAS)

X-ray Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) measurements have been carried out at the Energy-Scanning EXAFS beamline (BL-9) at the Indus-2 Synchrotron Source at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.²²⁰ All the measurements were performed at room temperature. This beamline operates in the energy range of 4 keV to 25 keV. The beamline optics consist of a Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si (111) based double crystal monochromator (DCM). The second crystal of the DCM is a sagittal cylindrical crystal which is used for horizontal focusing of the beam while another Rh/Pt coated bendable post mirror facing downward is used for vertical focusing of the beam at the sample position. Two ionization chambers (300 mm length each) have been used for data collection in the transmission mode; one ionization chamber for measuring incident flux, the second one for measuring transmitted flux. For energy calibration, standard metal foils were used. Appropriate gas pressure and gas mixture have been chosen to achieve 10-20% absorption in the first ionization chamber and 70-90% absorption in the second ionization chamber to obtain a better signal-to-noise ratio. Pellets were made from powder samples for recording absorption spectra. Sample powder was mixed homogeneously with cellulose powder in appropriate proportion and pressed (2 Ton) into a 15 mm diameter disc. The amount of the sample was estimated such that to get a reasonable edge jump at a particular absorption edge of the element to be probed. Spectra were collected at the iron K-edge in transmission mode and were calibrated against the reference spectrum of metallic iron (7112 eV). Data were processed using Demeter software.²²¹ A metallic iron foil standard was used as a reference for energy calibration and was measured simultaneously with experimental samples.

4.8.1. XANES Analysis

The oxidation state of Fe within bpy-UiO-FeCl₃ were determined by comparison of its pre-edge position with that of FeCl₃. The position of the pre-edge of bpy-UiO-FeCl₃ (7114.4 eV) aligned well with that of FeCl₃ (7114 eV). We, therefore, concluded that Fe ion in bpy-UiO-FeCl₃ has +3 oxidation state. Furthermore, a smaller intensity of pre-edge indicates the presence of octahedral geometry.

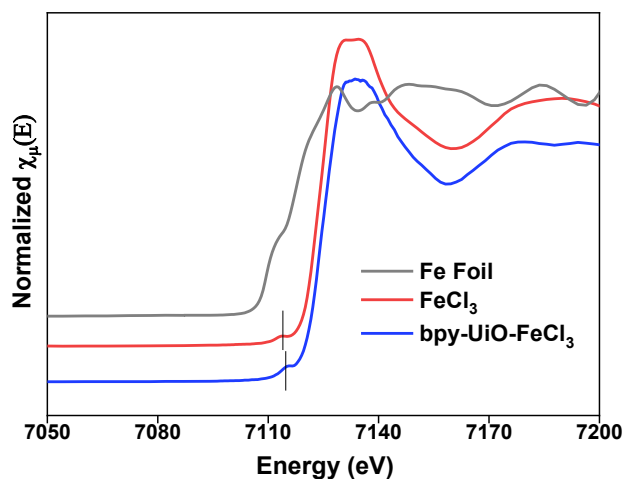


Figure 4.14. $\mu(E)$ XAS spectra of metallic Fe(0) foil (gray), FeCl_3 (red) and bpy-UiO-FeCl_3 (blue).

4.8.2. EXAFS Fitting using DFT Optimized Structures

The spectra were calibrated against the reference spectra and aligned to the first peak in the smoothed first derivative of the absorption spectrum, the background noise was removed, and the spectra were processed to obtain a normalized unit edge step. The fitting parameters of bpy-UiO-FeCl_3 are summarized in Table 4.6.

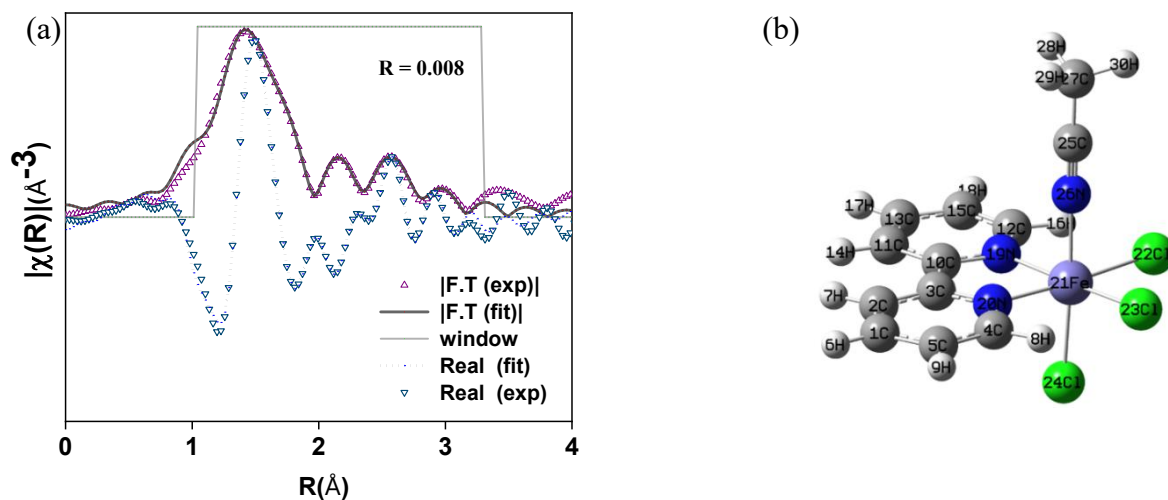


Figure 4.15. (a) EXAFS spectra and fits of $\text{bpy-UiO-FeCl}_3(\text{NCCH}_3)$ in the R space from 1 to 3.3 Å. (b) DFT optimized structure of $\text{bpy-FeCl}_3(\text{NCCH}_3)$.

Table 4.6. Summary of EXAFS parameters of $\text{bpy-UiO-FeCl}_3(\text{NCCH}_3)$.

Sample	$\text{bpy-UiO-FeCl}_3(\text{NCCH}_3)$	Fitting range	k 2-12.2 Å ⁻¹ R 1.0-3.3 Å
Independent points	15	R-factor	0.008
Variables	12	S_o^2	0.67
Reduced chi-square	18.39	$\Delta E_0(\text{eV})$	-6.24
$R(\text{Fe-N20})$ (Å)	1.90 ± 0.007	$\sigma^2(\text{Fe-N20})$ (Å ²)	0.003 ± 0.001

R(Fe-N19) (Å)	1.90±0.0007	σ^2 (Fe-N19) (Å ²)	0.003±0.001
R(Fe-N26) (Å)	2.09±0.006	σ^2 (Fe-N26) (Å ²)	0.003±0.002
R(Fe-Cl22) (Å)	2.19±0.07	σ^2 (Fe-Cl22) (Å ²)	0.002±0.001
R(Fe-Cl23) (Å)	2.19±0.07	σ^2 (Fe-Cl23) (Å ²)	0.003±0.002
R(Fe-Cl24) (Å)	2.39±0.006	σ^2 (Fe-Cl24) (Å ²)	0.004±0.003
R(Fe-C20) (Å)	2.77±0.09	σ^2 (Fe-C20) (Å ²)	0.005±0.003
R(Fe-C19) (Å)	2.80±0.09	σ^2 (Fe-C19) (Å ²)	0.005±0.003
R(Fe-C25) (Å)	2.92±0.07	σ^2 (Fe-C25) (Å ²)	0.01±0.005
R(Fe-C12) (Å)	3.06±0.07	σ^2 (Fe-C12) (Å ²)	0.01±0.005

4.9. XPS Analysis of bpy-UiO-FeCl₃

All the binding energies were corrected with reference to the C1s peak at 284.8 eV. MULTIPAK software was used for peak analysis and de-convolution studies.

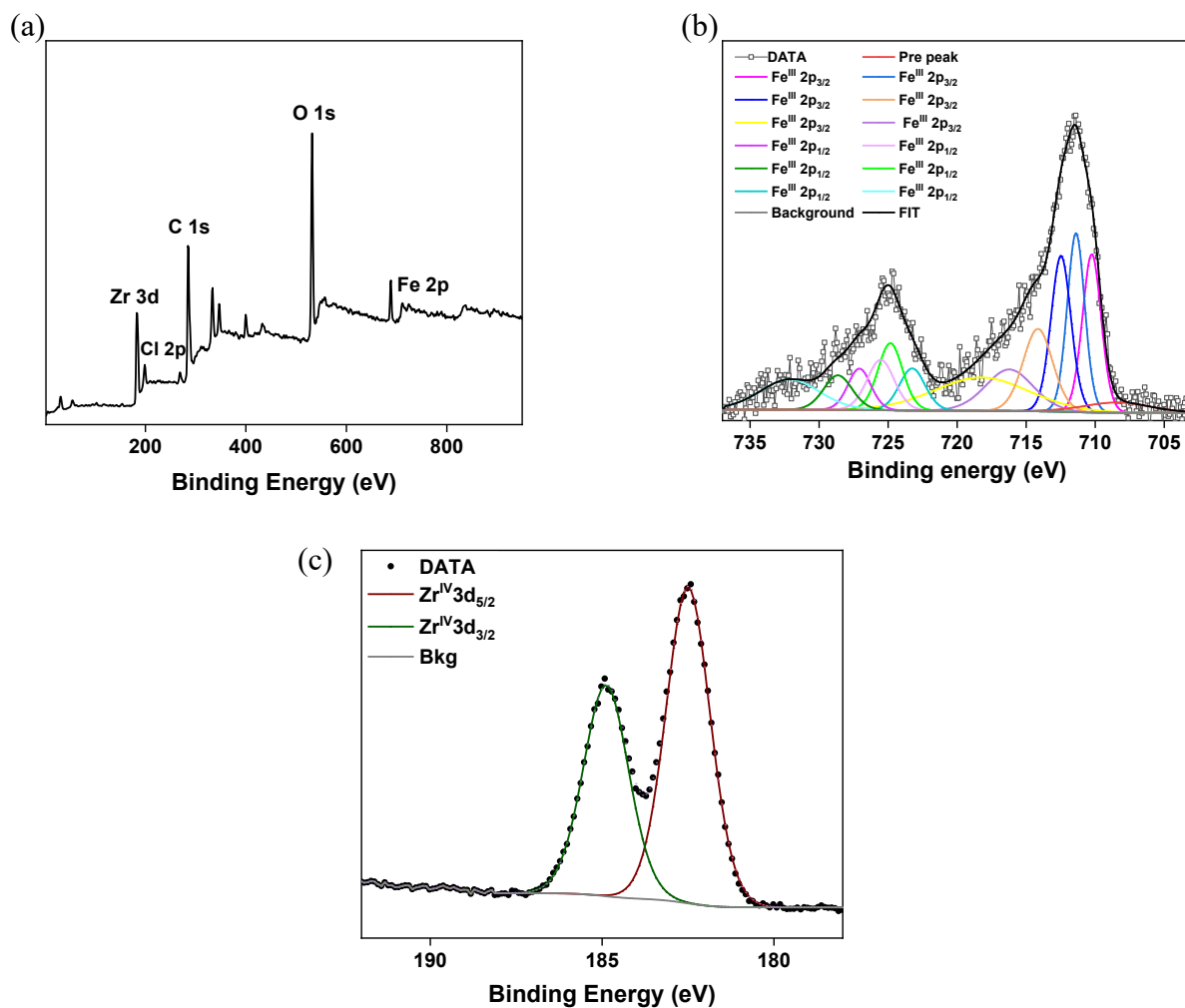


Figure 4.16. (a) Raw XPS data of bpy-UiO-FeCl₃. (b) XPS fitting of iron in bpy-UiO-FeCl₃. (c) XPS fitting of zirconium in bpy-UiO-FeCl₃.

Table 4.7. XPS fitting parameters for Fe(III) in bpy-UiO-FeCl₃ MOF.

Component	Position (eV)	FWHM (eV)	Area%	Line shape
Fe(III) 2p	710.25	1.5	11.76	GL(30)
Fe(III) 2p	711.39	1.4	12.37	GL(30)
Fe(III) 2p	712.48	1.6	12.32	GL(30)
Fe(III) 2p	714.16	1.7	9.64	GL(30)
Fe(III) 2p	716.23	4.3	7.80	GL(30)
Fe(III) 2p	719.01	5.1	12.47	GL(30)
Fe(III) 2p	723.26	1.9	4.27	GL(30)
Fe(III) 2p	724.84	1.9	6.54	GL(30)
Fe(III) 2p	725.55	2.1	5.42	GL(30)
Fe(III) 2p	727.09	1.9	3.76	GL(30)
Fe(III) 2p	728.65	2.3	3.89	GL(30)
Fe(III) 2p	732.15	4.3	7.07	GL(30)
Fe(III) 2p	708.46	3.7	2.67	GL(30)

4.10. Conclusion

In summary, we have successfully synthesized a porous and highly robust zirconium-based metal-organic framework (MOF)-supported mono bipyridyl-iron(III) chloride catalyst through active-site isolation. Bpy-UiO-FeCl₃ demonstrates high selectivity and recyclability for the oxidative bromination of various substituted arenes using hydrogen peroxide (H₂O₂) as the oxidant and potassium bromide (KBr) as the bromine source. Mono-substituted arenes were converted to para-bromoarenes with excellent selectivities ranging from 90% to 98%. The uniform and regular porous structure of the MOF facilitates shape-selective catalysis preventing the formation of larger ortho-bromoarene products, ensuring the exclusive formation of para-bromoarenes, unlike homogeneous catalysts that typically exhibit lower selectivity. Bpy-UiO-FeCl₃ is also effective for a wide range of 1,2-, 1,3-, and 1,4-substituted arenes, converting them into the desired bromo products with moderate to good yields under mild reaction conditions. Through spectroscopic and computational studies, we investigated the mechanism and identified the turnover-limiting step in the catalytic cycle. Our findings highlight the importance of MOFs in creating sustainable, earth-abundant metal catalysts for the direct oxidative bromination of arenes, enabling the eco-friendly synthesis of haloarenes.

Chapter 5: Selective Monoborylation of Methane by Metal-Organic Framework Confined Mononuclear Pyridylimine-Iridium(I) Hydride

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Abstract: 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]IrH, 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.

5.1 Introduction

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.^{297–299} However, the methane C–H bond activation under mild conditions is highly challenging owing to the intrinsic inertness stemming from considerable C–H bond dissociation energy (104 kcal/mol) with a large HOMO–LUMO gap, low acidity and polarization difficulty.^{300–303} In addition, methane borylation reactions typically suffer from poor selectivity originating from the over-borylation of methane C–H bonds, competitive solvent C–H borylation, and boron-byproduct formation. Furthermore, the mono-functionalized product is more reactive than methane itself, making the selective monoborylation of methane extremely challenging.

Early reports of developing homogeneous catalysts for methane borylation using bis(pinacolato)diboron (B₂pin₂) as the borylating agent were based on 1,10-phenanthroline- and diphosphine-ligated Ir, Rh and Ru complexes, which gave a mixture of monoborylated (CH₃Bpin) and diborylated methane [CH₂(Bpin)₂] at 150 °C with selectivity spanning 2:1 to 31:1.^{304,305} Farha and co-workers elegantly employed a metal–organic framework (MOF) as the porous solid support with appropriate pore sizes,^{17,35,195,211,306–311} in which an embedded iridium(III) catalyst enables selective mono C–H borylation over multiborylation of methane within the confined reaction space via shape-selective catalysis, leading to the formation of CH₃Bpin in 19.5% yield with a turnover number (TON) of 67.⁵⁶ Subsequently, a mono(phosphine) MOF-supported-Ir catalyst outperformed other Ir-catalysts based on chelating phenanthroline, bipyridine, and diphosphine ligands to give CH₃Bpin with a TON of 127.³¹² Despite significant progress in developing catalysts for selective monoborylation of methane, these catalytic systems also generate a considerable amount of boron-byproducts such as HOBpin, pinBOBpin and Sol-Bpin during the borylation reactions.^{313–315} Herein, we report a MOF-confined mononuclear pyridylimine-ligated iridium(I)-hydride, which is a highly robust and active heterogeneous catalyst for chemoselective monoborylation of methane to afford CH₃Bpin in a near-quantitative yield.

5.2. Results and Discussion

5.2.1. Synthesis and Characterization of UiO-68 MOF Supported Pyridylimine-Iridium Hydride [PyrIm-UiO-IrH]

Pyrim-UiO-IrH MOF has a UiO-68 topology,^{308,316} built from $\text{Zr}_6\text{O}_4(\text{OH})_4$ nodes and linear 2'-amino-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate bridging linkers bearing pyridylimine-ligated iridium(I)-hydride species. Pyrim-UiO-IrH was synthesized by metalation of a pyridylimine-

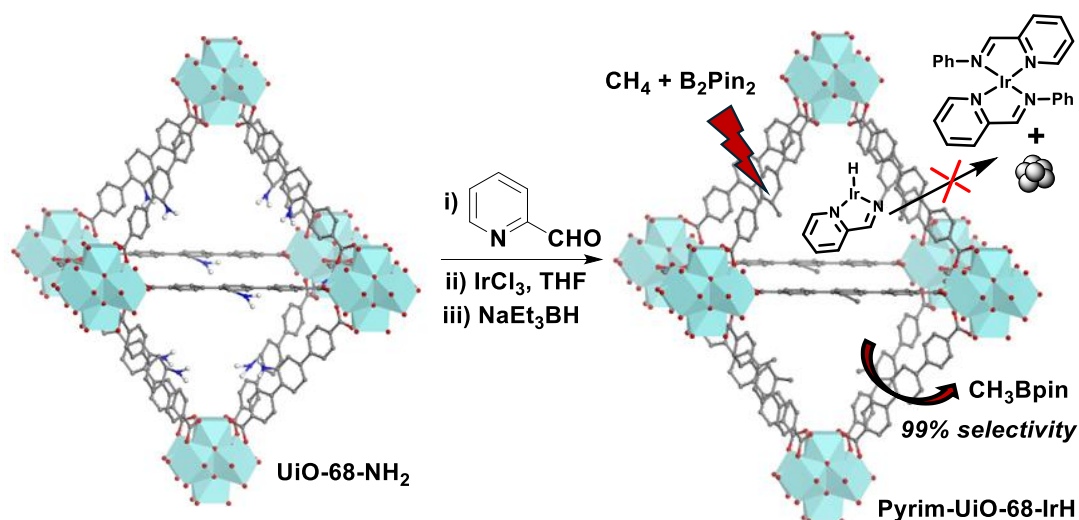


Figure 5.1. Synthesis of pyrim-UiO-IrH MOF via post-synthetic modification of pristine amino-functionalized UiO-68-MOF for methane monoborylation.

functionalized zirconium UiO-68-MOF (pyrim-UiO) with $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ followed by treatment of NaEt_3BH .³¹⁷ The reaction of pyrim-UiO MOF and $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ in THF formed pyrim-UiO- IrCl_3 MOF bearing pyridylimine-ligated IrCl_3 species at its linkers. The extended X-ray absorption fine structure (EXAFS) of pyrim-UiO- IrCl_3 at the Ir L₃-edge fitted well with the DFT-optimized structure of (pyrim) $\text{IrCl}_3(\text{THF})$, indicating the presence of an octahedral Ir^{III} -species, in which Ir^{+3} ion is coordinated two nitrogen atoms of pyridylimine, three chlorine atoms and a THF molecule (Figure 5.2b). The treatment of pyrim-UiO- IrCl_3 with NaEt_3BH in THF at room temperature furnished pyrim-UiO-IrH. PXRD patterns of pyrim-UiO-IrH, simulated UiO-68 MOF, and pristine UiO-68-NH₂ are comparable indicating that pyrim-UiO-IrH has a UiO-68 topology and that pristine MOF's structure and crystallinity were not altered during post-synthetic modifications (Figure 5.2a).

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis of the digested pyrim-UiO-IrH revealed a Ir-loading of ~32% with respect to the pyridylimine moiety, corresponding to the formula of $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_4\text{Ir}_{0.32}\text{H}_{0.32})_6$. Pyrim-UiO-IrH has a BET surface area of 1245 m²/g, and a pore size of 0.8 nm, which is lower than that of pristine pyrim-UiO MOF, due to the incorporation of iridium-moiety within the MOF's pores (Figure 5.2d). Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) mapping of pyrim-UiO-IrH displayed uniform distributions of Ir and Zr ions through the MOF particle (Figure 5.2e). The IR spectrum (KBr) of pyrim-UiO-IrH showed a characteristic $\nu_{\text{Ir-H}}$

stretching frequency at 2140 cm^{-1} (Figure 5.2f). X-ray absorption near edge structure (XANES) showed the Ir L_3 -edge energy of pyrim-UiO-IrH at 11.216 KeV, which is 3 eV lower than that of pyrim-UiO-IrCl₃ and 1.0 eV higher than Ir(0) foil, suggesting a formal +1 oxidation state for Ir ion in pyrim-UiO-IrH (Figure 5.21). The existence of Ir^I-species in pyrim-UiO-IrH was further confirmed by X-ray photoelectron spectroscopy (XPS), which displayed Ir 4f_{7/2} and 4f_{5/2} binding energy peaks at 60.3 eV and 63.1 eV, respectively, and ~2.1-2.3 eV lower than those of pyrim-UiO-IrCl₃ and IrCl₃ (Figure 5.2g). The EXAFS analysis of pyrim-UiO-IrH at the Ir L_3 -edge suggests the existence of mono pyridylimine-ligated iridium(I)-hydride moiety within the MOF (Figure 5.2h).

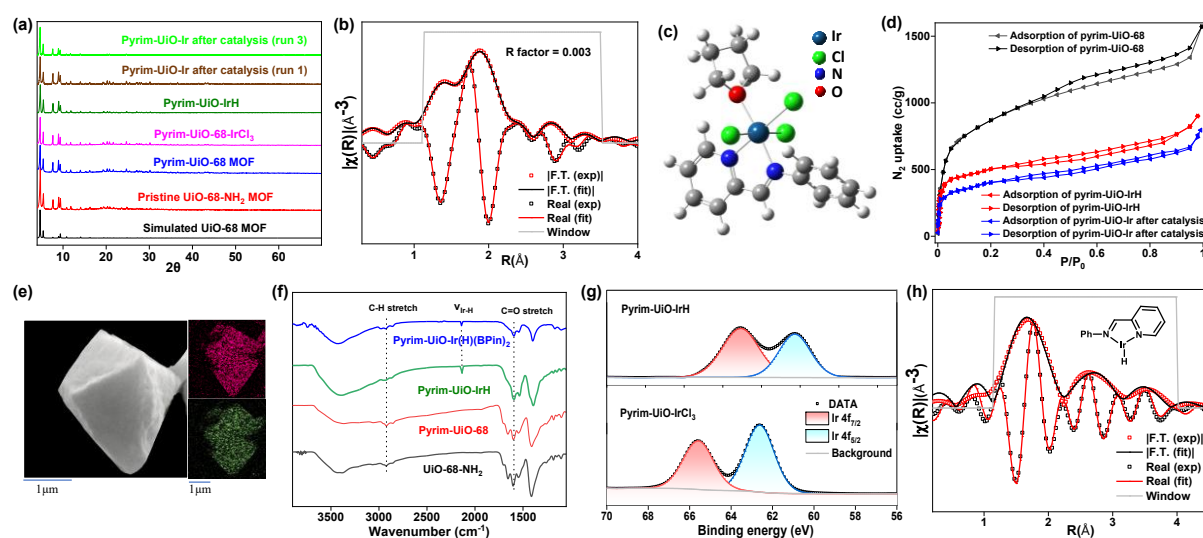


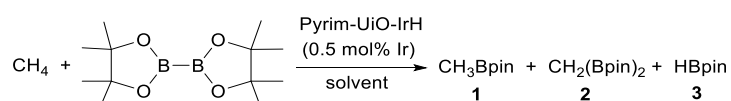
Figure 5.2. a) PXRD patterns of simulated UiO-68 MOF (black), pristine UiO-68-NH₂ MOF (red), pyrim-UiO-68 MOF (blue), pyrim-UiO-IrCl₃ (magenta), pyrim-UiO-IrH (olive), pyrim-UiO-Ir after run 1 (brown) and pyrim-UiO-Ir after run 3 (green). b) EXAFS spectra (red and black hollow squares) and fits (red and black solid lines) of pyrim-UiO-IrCl₃ in the R space from 1.15 - 3.5 Å. c) DFT optimised structure of (pyrim)IrCl₃(THF) molecule. d) BET nitrogen sorption isotherms of pyrim-UiO-68 (black), pyrim-UiO-IrH (red) and pyrim-UiO-Ir after catalysis (blue) measured at 77 K. e) SEM image of a pyrim-UiO-IrH particle along with elemental mapping of Zr and Ir. f) IR (KBr) spectrum of UiO-68-NH₂ (black), pyrim-UiO-68 MOF (red), pyrim-UiO-IrH (green) and pyrim-UiO-IrH(BPin)₂ (blue). g) Ir 4f XPS spectra of pyrim-UiO-IrCl₃ and pyrim-UiO-IrH. h) EXAFS spectra (red and black hollow squares) and fits (red and black solid lines) of pyrim-UiO-IrH in the R space from 1.15 - 4.0 Å.

5.2.2. Catalytic Direct Borylation of Methane

Pyrim-UiO-IrH catalyzed methane borylation reactions were conducted in a high-pressure batch reactor using B₂pin₂ as the borylating agent and the limiting reagent in a suitable solvent under a desired methane pressure. Initial trials using 0.2 mmol of B₂pin₂ and pyrim-UiO-IrH (0.5 mol% Ir) in several different solvents at 130 °C under 40 bar of CH₄ for 24 h revealed that cyclohexane gave the highest yield of CH₃Bpin (98%) with complete conversion of B₂pin₂ (entries 1-4, Table 5.1). CH₄ borylation in other solvents such as THF, toluene, heptane and

DMF gave lesser yields of CH₃Bpin, due to the formation of various byproducts such as borylated solvents, CH₂(Bpin)₂, pinBOBpin, and HOBpin.⁵⁶ Further screening of reaction temperature, CH₄ pressure, catalyst loading, and reaction time showed that 0.5 mol% Ir-loading, 130 °C, 40 bar of CH₄, and 24 h of reaction are optimal for selective mono-borylation of methane ([entry 1, Table 5.1](#)). The borylation reaction did not occur below 100 °C, however, the formation of a significant amount of HOBpin, pinBOBpin and C₆H₁₁Bpin was observed at 150 °C ([entries 6-7, Table 5.1](#)). The borylation reactions under 20 bar and 30 bar of CH₄ afforded CH₃Bpin in only 26% and 47% yields, respectively ([entries 8-9, Table 1](#)), presumably due to the lower solubility of CH₄ at lower pressure. Pyrim-UiO-IrH catalyzed CH₄ borylation under optimal reaction conditions afford CH₃Bpin in 98% yield, giving rise to the highest TON of 196 ([entry 1, Table 5.1](#)). Gas chromatography (GC) analysis of the crude reaction mixture showed the exclusive formation of CH₃Bpin with no detectable diborylated product CH₂(Bpin)₂.

Table 5.1. Optimization of pyrim-UiO-IrH catalyzed mono C–H borylation of methane.^a



Entry	Solvent	T (°C)	P (bar)	Time (h)	Conv. of B ₂ pin ₂	%Yield of 1 ^b (Selectivity) ^c	TON
1	C ₆ H ₁₂	130	40	24	100	98 (98)	196
2	THF	130	40	24	89	29 (33)	58
3	Toluene	130	40	24	80	35 (44)	70
4	Heptane	130	40	24	84	72 (86)	144
5	C ₆ H ₁₂	130	40	18	87	85 (98)	170
6	C ₆ H ₁₂	110	40	24	20	19 (95)	38
7	C ₆ H ₁₂	150	40	24	100	78 (78)	156
8	C ₆ H ₁₂	130	20	24	27	26 (96)	52
9	C ₆ H ₁₂	130	30	24	48	47 (98)	94
10	C ₆ H ₁₂	130	40	48	100	82 (82)	164

^aReaction conditions: 1.9 mg of pyrim-UiO-IrH (1.02 μmol of Ir), 51 mg B₂pin₂ (0.2 mmol), 2 mL solvents. ^bYield was determined by GC as GC peak area (CH₃Bpin)/peak area (total boron species) × 100. ^cSelectivity was calculated as GC peak area (CH₃Bpin)/peak area (total products) × 100.

Importantly, pyrim-UiO-IrH was at least 24 times more active than its homogeneous control ([Ph(pyrim)(PhCO₂Me)₂]IrH, which produced only 4% CH₃Bpin under the identical reaction conditions and Ir-loading (0.5 mol%) ([Figure 5.3a](#)). The much higher catalytic activity of pyrim-UiO-IrH than its homogeneous Ir analogue is likely due to the greater stability of the

pyrim-IrH species via active-site isolation at the linkers that prevent intermolecular decomposition. As a heterogeneous catalyst, pyrim-UiO-Ir 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 (Figure 5.3b). No borylated product was detected when the methane borylation was carried out in the absence of MOF catalyst or with the pristine pyrim-UiO-68 or with $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (entries 15-17, Table 5.1). The production of CH_3Bpin ceased upon removing the solid MOF pyrim-UiO-IrH from the reaction mixture, suggesting that the catalytic moiety is embedded within the MOF (Figure 5.10). A catalytic reaction with 40 bar N_2 instead of CH_4 and 0.2 mmol B_2pin_2 was conducted at 130 °C in cyclohexane for 24 h. In this reaction, no CH_3Bpin product was formed, signifying CH_4 as the only carbon source for CH_3Bpin formation (Section 5.4.3). Importantly, pyrim-UiO-68-IrH was almost four times more active and significantly chemoselective than pyrim-UiO-66-IrH MOF, having similar UiO-topology but smaller pore sizes in methane borylation due to the facile diffusion of the substrates and formation of smaller monoborylated products within the pores of UiO-68 MOFs via shape-selective catalysis (Figure 5.14 and section 5.4.6).

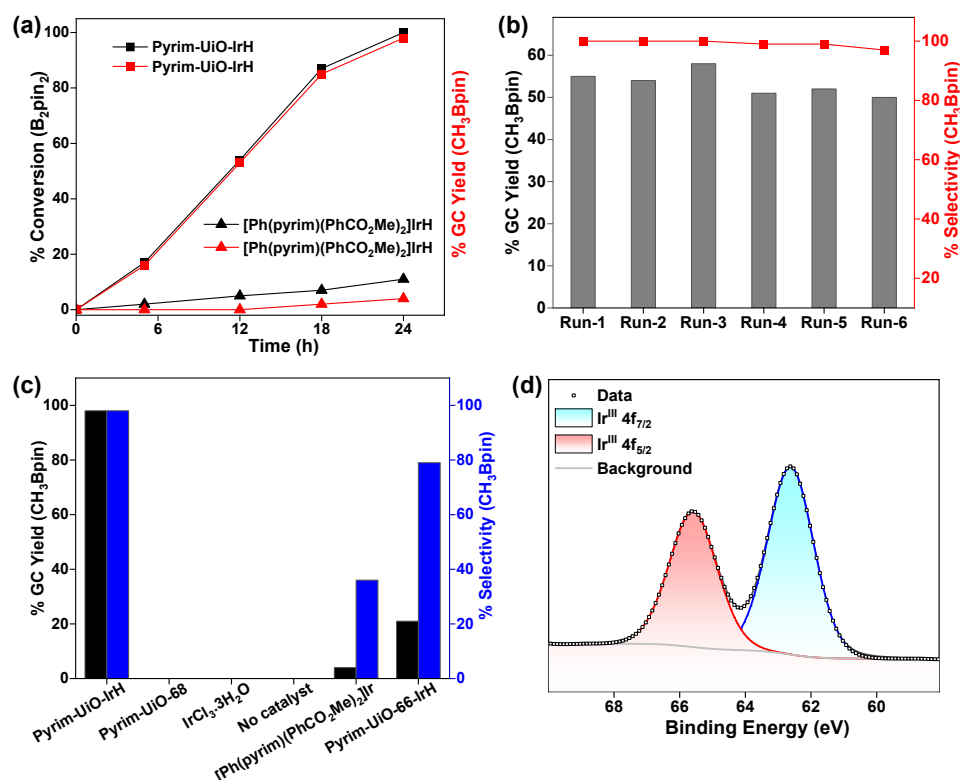


Figure 5.3. a) Plot of %GC conversion and %GC yield of CH_3Bpin vs time for CH_4 borylation using pyrim-UiO-IrH (0.5 mol% Ir) and $[\text{Ph}(\text{pyrim})(\text{PhCO}_2\text{Me})_2]\text{IrH}$ (0.5 mol% Ir) under identical conditions. b) Plot for the %GC yield and %selectivity of CH_3Bpin at various runs in the recycling of pyrim-UiO-IrH (0.5 mol% Ir). c) Comparison of the catalytic activity for the conversion of CH_4 to CH_3Bpin over pyrim-UiO-IrH with other catalysts under identical reaction conditions. Conditions: 1.9 mg of pyrim-UiO-IrH (1.02 μmol of Ir) or equivalent Ir-loading for other catalysts, 2 mL C_6H_{12} , 130 °C, 40 bar CH_4 and 24 h. d) Ir 4f XPS spectrum of pyrim-UiO-IrH(Bpin)₂.

5.3. Mechanism Exploration of Pyrim-UiO-IrH Catalyzed Methane Borylation

The reaction between pyrim-UiO-Ir^IH and B₂Pin₂ at 130 °C for 30 min forms pyrim-UiO-Ir^{III}(Bpin)₂(H), which was characterized by XPS and IR spectroscopy (Figure 5.3d and 5.2f). Pyrim-UiO-Ir^{III}(Bpin)₂(H) showed similar catalytic activity to pyrim-UiO-68-Ir^IH, suggesting Ir^{III}(Bpin)₂(H) species as the potential catalytic intermediate. We propose that pyrim-UiO-Ir catalyzed methane borylation proceeds via a Ir^{III}-Ir^V-Ir^{III} catalytic cycle,^{20,22} in which the oxidative addition of methane to pyrim-UiO-Ir^{III}(Bpin)₂(H) (INT-1) first form seven coordinated pyrim-UiO-Ir^V(CH₃)(H)₂(Bpin)₂ (INT-2) followed by reductive elimination of CH₃Bpin to generate pyrim-UiO-Ir^{III}(Bpin)(H)₂ (Figure 5.4). Further oxidative addition of B₂pin₂ followed by reductive elimination of HBpin regenerates pyrim-UiO-Ir^{III}(Bpin)₂(H). DFT calculation suggests that the boron-assisted oxidative addition of methane is the turn-over limiting step requiring a free activation energy of 34.9 kcal/mol, similar to the reported 1,10-phenanthroline- and diphosphine-ligated Ir catalysts.^{20,22} However, the higher catalytic activity of pyrim-UiO-Ir in methane borylation is attributed to the facile oxidative addition of methane to the Ir^{III}(H)Bpin)₂ species as opposed to the sterically encumbered Ir^{III}(Bpin)₃ species in other systems.

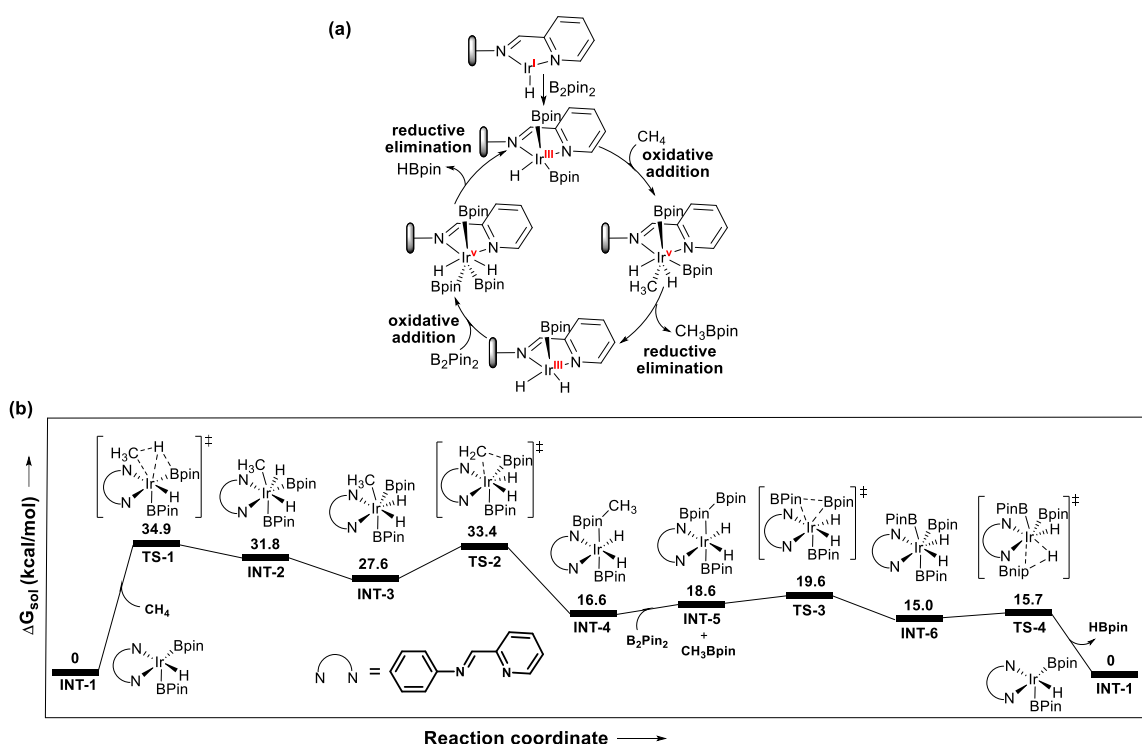
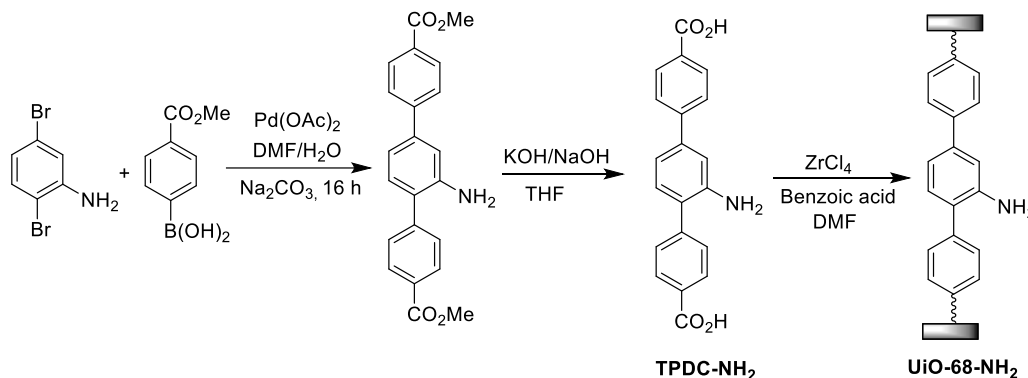


Figure 5.4. a) Proposed catalytic cycle of pyrim-UiO-IrH catalyzed methane borylation. b) DFT-calculated free energy profile at 403 K for pyrim-UiO-IrH catalyzed methane borylation reaction.

5.4. Experimental Section

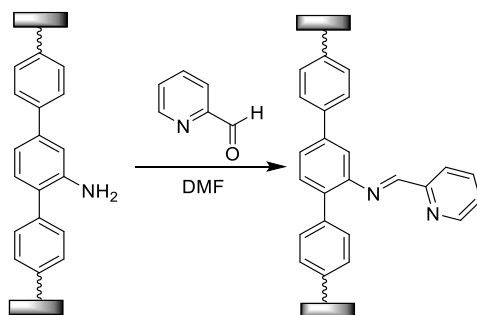
5.4.1. Synthesis and Characterization of Pyridylimine-Functionalized UiO-68 MOFs

5.4.1.1. Synthesis of UiO-68-NH₂ MOF³¹⁸



In a 10 mL glass vial, TPDC-NH₂ (2'-amino-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid) ligand (0.010 g, 0.03 mmol), which was synthesized with the help modified procedure^{207,319}, and benzoic acid (0.073 g, 0.6 mmol) were dissolved in a DMF solution (1.22 mL) followed by the addition of ZrCl₄ (0.007 g, 0.03 mmol). The resulting mixture was sonicated for few minutes and then kept it in a preheated oven at 70 °C for 3 d. After cooling to room temperature, the crystalline solid was isolated by centrifugation and washed it by DMF several times to afford UiO-68-NH₂ MOFs in 41% yield.

5.4.1.2. Synthesis of pyrim-UiO MOFs via post-synthetic modification of UiO-68-NH₂ MOFs³¹⁷



In a centrifuge tube inside the glovebox, UiO-68-NH₂ MOF (0.017 g, 0.006 mmol) was added in 1 mL DMF followed by the addition of 2-pyridinecarboxaldehyde (4 μ L, 0.04 mmol). It was then left overnight with periodic shaking. The resultant solid was washed multiple times with DMF to obtain pyrim-UiO-68 MOF as a light brown solid.

5.4.1.3. Analysis of digested pyrim-UiO MOFs by ^1H NMR

Sample of pyrim-UiO MOF was charged in a vial containing 0.5 mL of $\text{DMSO-}d_6$, and then 0.5 mL saturated solution of K_3PO_4 in D_2O was added to it and mixed well. The top organic layer was taken and analyzed by ^1H NMR.

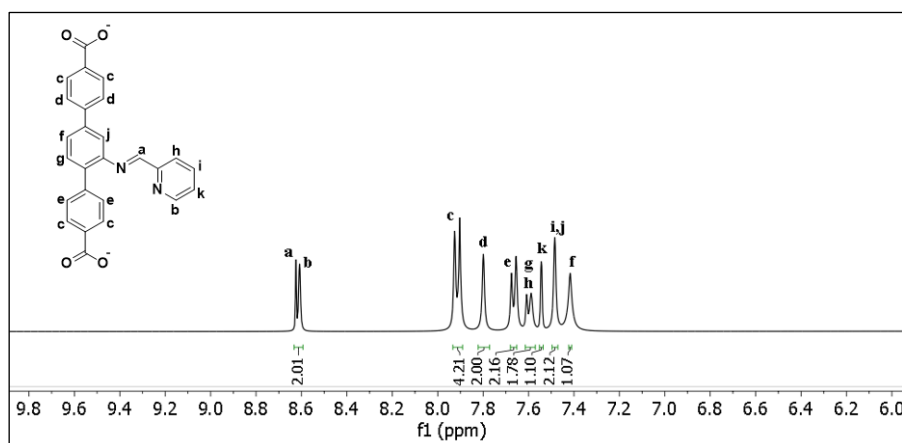


Figure 5.5. ^1H NMR spectrum (500 MHz, $\text{DMSO-}d_6$) of pyrim-UiO MOF digested in $\text{K}_3\text{PO}_4/\text{D}_2\text{O}/\text{DMSO-}d_6$.

5.4.1.4. Synthesis of pyrim-UiO- IrCl_3

Pyrim-UiO MOF (0.030 g, 0.009 mmol) in THF was charged into a vial to which a 1 mL THF solution of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.019 g, 0.054 mmol) was added. The mixture was stirred slowly overnight at room temperature. The resultant solid was centrifuged out of suspension and washed with THF 4-5 times. Pyrim-UiO- IrCl_3 has 28% solvent weight based on TGA analysis and 32% Ir-loading based on ICP-OES analysis.

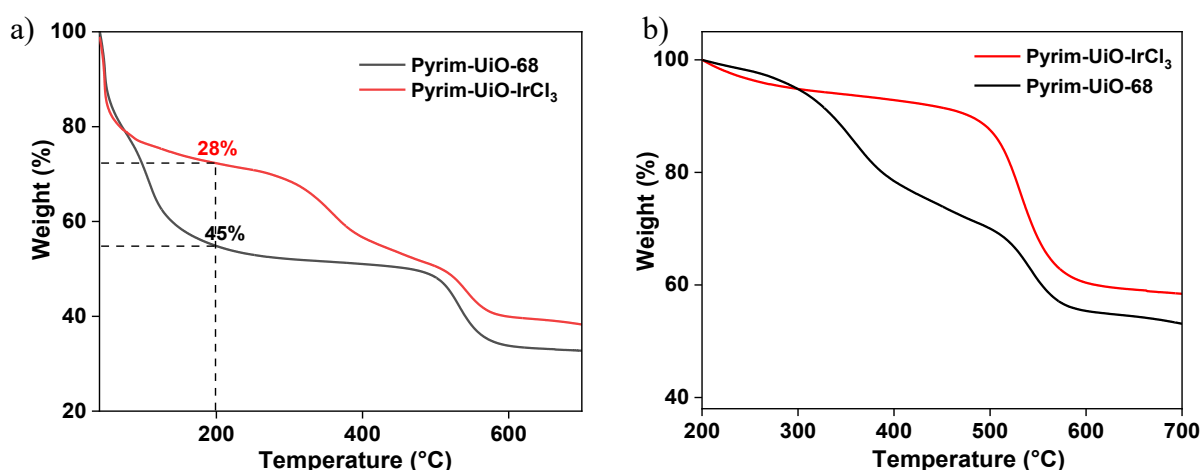


Figure 5.6. (a) TGA curve of freshly prepared pyrim-UiO-68 and pyrim-UiO- IrCl_3 . A solvent weight loss of 45% was observed in pyrim-UiO-68 and 28% in pyrim-UiO- IrCl_3 at the range of temperature from 40 °C to 200 °C. (b) TGA curve of freshly prepared pyrim-UiO-68 (black) and pyrim-UiO- IrCl_3 (red).

pyrim-UiO-IrCl₃ (red) from 200-700 °C. The increased weight of metalated MOF is due to the presence of iridium within the MOF.

5.4.1.5. Synthesis of pyrim-UiO-IrH

Pyrim-UiO-IrCl₃ (0.016 g, 0.0038 mmol) was charged into a vial containing 3 mL of THF. NaEt₃BH (15 µL, 1 M in toluene) was added dropwise to the vial, and the mixture was stirred gently for 1 h at room temperature to give pyrim-UiO-IrH as black colored solid. The resultant MOF catalyst was separated via centrifugation and then washed with THF several times. Pyrim-UiO-IrH was then used directly for the catalysis.

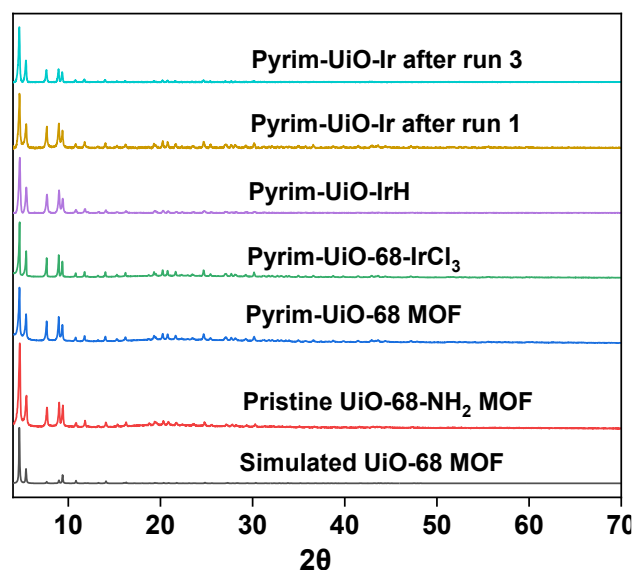


Figure 5.7. PXRD patterns of simulated UiO-68 MOF (black), pristine UiO-68-NH₂ MOF (red), pyrim-UiO-68 MOF (blue), pyrim-UiO-IrCl₃ (green), pyrim-UiO-IrH (violet), pyrim-UiO-Ir after run 1 (mustard brown) and pyrim-UiO-Ir after run 3 (light blue).

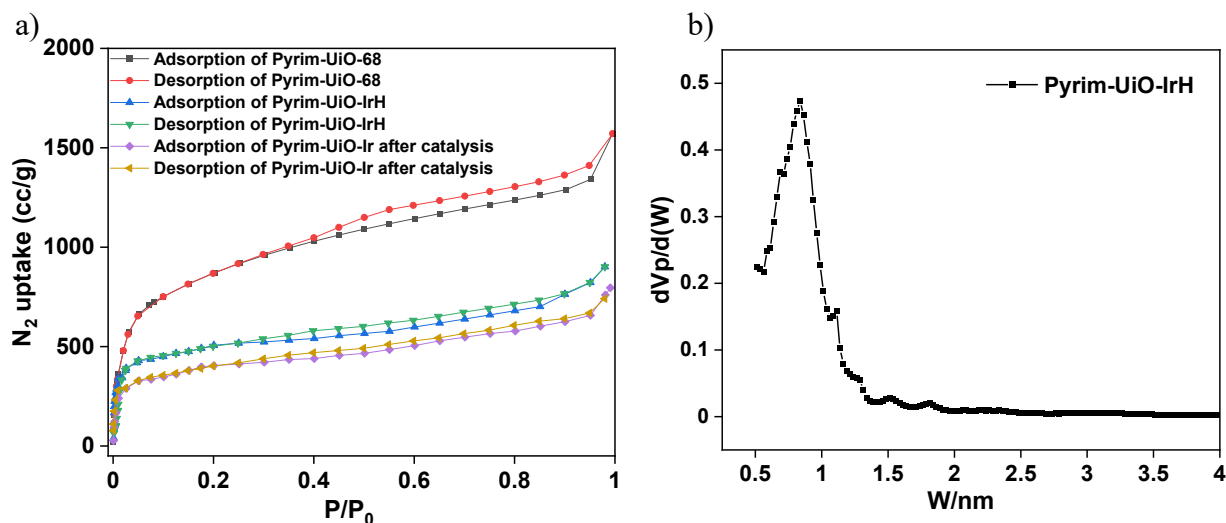


Figure 5.8. a) Brunauer–Emmett–Teller (BET) nitrogen sorption isotherms of pyrim-UiO-68, pyrim-UiO-IrH and pyrim-UiO-Ir after catalysis measured at 77 K. Pyrim-UiO-68 and pyrim-UiO-IrH have a BET surface area

of 2342 m²/g and 1245 m²/g respectively. b) HK pore distribution plot of pyrim-UiO-IrH. Pore size for pyrim-UiO-IrH was determined to be 0.8 nm.

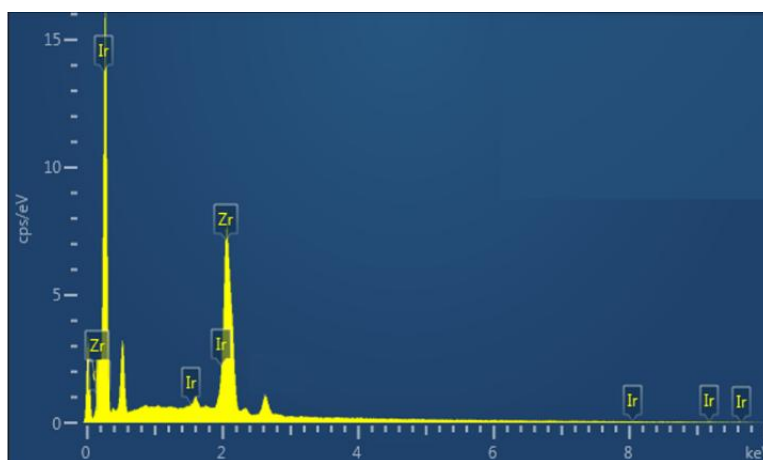
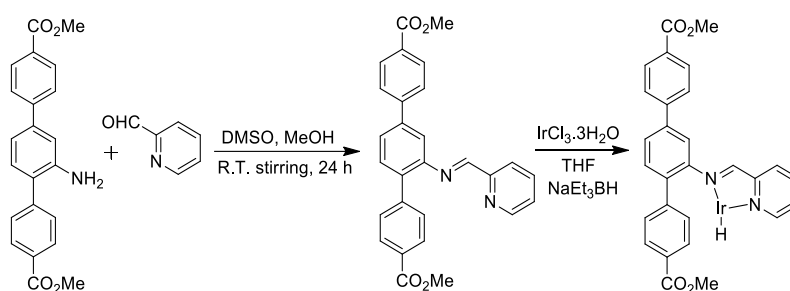


Figure 5.9. SEM-EDX analysis of pyrim-UiO-IrH.

5.4.1.6. Synthesis of homogeneous pyridylimine-iridium complex



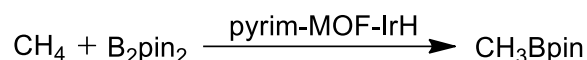
Under inert condition, dimethyl 2'-amino-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (0.200 g, 0.553 mmol) was dissolved in 30 mL of DMSO in a 50 mL Schlenk flask. To the reaction mixture, 1 mL of methanol was added followed by the addition of 2-pyridine carboxaldehyde (0.073 mL, 0.774 mmol). The resulting clear light-yellow colour solution was stirred for 24 h at room temperature. A light-yellow precipitate was formed, which was isolated through centrifugation followed by washing with methanol for three times and then dried under vacuum to afford the pyridylimine ligand as a yellow solid (0.180 g, 0.399 mmol, 72%). ¹H NMR (500 MHz, CDCl₃): δ 8.71 (s, 2 H), 8.14 (d, ³J_{H-H} = 8.2 Hz, 2 H), 8.09 (s, 2 H), 8.02 (d, ³J_{H-H} = 7.9 Hz, 1 H), 7.77 (dd, ³J_{H-H} = 14.0, 8.2 Hz, 3 H), 7.66 – 7.58 (m, 4 H), 7.44 (s, 1 H), 7.40 – 7.36 (m, 1 H), 3.95 (d, ³J_{H-H} = 6.8 Hz, 6 H). m/z (ESI) Anal calcd. for C₂₈H₂₃N₂O₄[M+H]⁺: 451.1658; Found: 451.1641 (err. -3.7 ppm).

In a vial, the pyridylimine ligand, dimethyl 2'-((pyridin-2-ylmethylene)amino)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (0.036 g, 0.080 mmol), was added to a solution of

IrCl₃·3H₂O (0.028 g, 0.080 mmol) in THF (until saturated). It was then left overnight, the pyridylimine-iridium complex was obtained. NaEt₃BH (15 μL, 1 M in toluene) was added dropwise to the vial containing complex, and the mixture was stirred gently for 1 h at room temperature to give pyridylimine-iridium hydride complex.

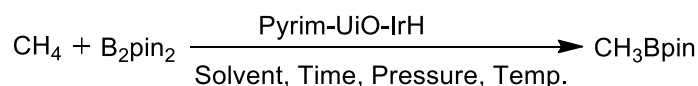
5.4.2. Catalytic Reactions with Pyrim-UiO-IrH

5.4.2.1. General procedure for pyrim-UiO-IrH catalysed borylation of methane



In the glovebox, pyrim-UiO-IrH (0.5 mol% of Ir) in 2 mL solvent was transferred into a glass liner. B₂pin₂ was subsequently added to the liner, which was then securely fitted into a high-pressure reactor and sealed. The sealed Parr reactor was then removed from the glovebox and purged with CH₄ two to three times. Subsequently, the Parr reactor was pressurized to 20-40 bar with CH₄ and heated to a temperature range of 110-150 °C, where it was maintained for a duration of 10 to 48 hours. The reactor was subsequently cooled, and the pressure was released. The MOF was separated from the reaction mixture through centrifugation, and the resulting supernatant was analyzed using GC-MS and GC-FID to determine the conversion and yield for CH₃Bpin.

Table 5.2. Optimization reaction conditions for borylation of methane.^a



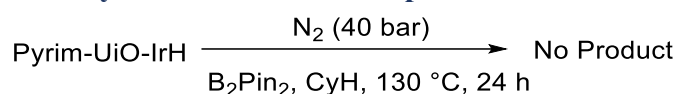
Entry	Catalyst	Borylating agent	Temperature (°C)	Pressure (bar)	Time (h)	Solvent	%GC-Yield (Selectivity)
1	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	130	40	12 h	CyH	54 (98)
2	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	130	40	18 h	CyH	85 (98)
3	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	130	40	24 h	CyH	98 (98)
4	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	130	40	30 h	CyH	90 (90)
5	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	130	40	48 h	CyH	82 (82)
6	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	110	40	24 h	CyH	19 (95)

7 ^b	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	150	40	24 h	CyH	78 (78)
8	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	130	20	24 h	CyH	26 (96)
9	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	130	30	24 h	CyH	47 (98)
10	Pyrim-UiO-IrH (0.3 mol%)	B ₂ pin ₂ (0.2 mmol)	130	40	24 h	CyH	30 (98)
11	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	130	40	24 h	THF	29 (33)
12	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	130	40	24 h	Toluene	35 (44)
13	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	130	40	24 h	Heptane	72 (86)
14	Pyrim-UiO-IrH (0.5 mol%)	B ₂ pin ₂ (0.2 mmol)	130	40	24 h	DMF	21 (24)
15	No catalyst	B ₂ pin ₂ (0.2 mmol)	130	40	24 h	CyH	0
16	Pyrim-UiO-68	B ₂ pin ₂ (0.2 mmol)	130	40	24 h	CyH	0
17	IrCl ₃ ·3H ₂ O (0.5 mol%)	B ₂ pin ₂ (0.5 mmol)	130	40	24 h	CyH	0
18 ^c	Pyrim-UiO-IrH (0.5 mol%)	HBpin (0.2 mmol)	130	40	24 h	CyH	0

^aReaction conditions: 1.9 mg of pyrim-UiO-IrH (1.02 μmol of Ir), 51 mg B₂pin₂ (0.2 mmol), 2 mL solvents.

^bLower yield was due to the generation of sol-Bpin and oxygenated byproducts such as HOBpin and pinBOBpin, stemming from the interaction of B₂pin₂ with OH groups residing on the Zr₆ nodes of the MOF.^{320,321} ^cHBpin was used as the borylating agent.

5.4.3. Blank Reaction of Pyrim-UiO-IrH with B₂pin₂ Under N₂ without Methane.



In the glovebox, pyrim-UiO-IrH (1.9 mg, 0.5 mol% of Ir) in 2 mL cyclohexane was transferred into a glass liner. B₂pin₂ (51 mg, 0.2 mmol) was subsequently added to the liner, which was then securely fitted into a high-pressure reactor and sealed. The sealed Parr reactor was then removed from the glovebox and purged with N₂ two to three times. The reactor was pressurized with 40 bar nitrogen and then heated at 130 °C for 24 h without any mechanical stirring. The reactor was subsequently cooled, and the pressure was released. The MOF was separated from the reaction mixture through centrifugation, and the resulting supernatant was analyzed using GC-MS and GC-FID to determine the conversion and yield for CH₃Bpin. In

this reaction, no trace of products was formed, suggesting CH₄ as the sole carbon source for CH₃Bpin in the pyrim-UiO-IrH catalyzed methane borylation.

5.4.4. Test for “Heterogeneity” of Pyrim-UiO-IrH in Borylation of CH₄

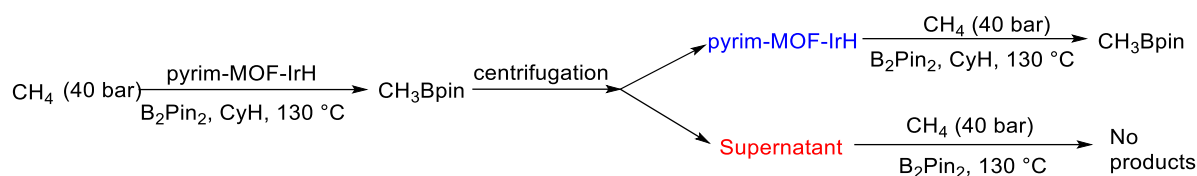


Figure 5.10. Heterogeneity test of pyrim-UiO-IrH for the borylation of methane.

In the glovebox, pyrim-UiO-IrH (1.9 mg, 0.5 mol% of Ir) in 2 mL cyclohexane was transferred into a glass liner. B₂pin₂ (51 mg, 0.2 mmol) was subsequently added to the liner, which was then securely fitted into a high-pressure reactor and sealed. The sealed Parr reactor was then removed from the glovebox and purged with CH₄ two to three times. The reactor was pressurized with 40 bar methane and then heated at 130 °C for 24 h without any mechanical stirring. The system was subsequently cooled, and the pressure was released. The solid MOF was removed from suspension to separate the solid and the supernatant, inside the glove box and washed with cyclohexane multiple times.

Two reactions were set up separately in two different Parr reactors, one with the solid and the other one with the supernatant recovered from the previous reaction. The extracted solid and supernatant were added into two separate liners, and B₂pin₂ (51 mg, 0.2 mmol) was added to each liner. 2 mL cyclohexane was added to the liner containing the solid MOF. Then both the liners were fitted into two separate Parr reactors and sealed. The sealed Parr reactors were taken out from the glovebox and purged with CH₄ gas two times. The Parr reactors were pressurized to 40 bar of CH₄ and stirred at 130 °C for 24 h. After the completion of the reaction, the pressure of the reactors was released. The reactions were analysed with the GC-MS and GC-FID, which showed that the reaction with the solid MOF gave 98% yield, while the reaction with supernatant gave 0% conversion. This experiment excludes the potential of any leached Ir-species responsible for catalysis and confirms that solid pyrim-UiO-IrH was the actual catalyst for the borylation of methane.

5.4.5. Recycling of Pyrim-UiO-IrH for the Borylation of Methane

The recycle and reuse experiment was conducted at ~50-60% conversion to check the stability of the pyrim-UiO-IrH MOF-catalyst (Table 5.3). The detailed procedure of recycling experiment given below.

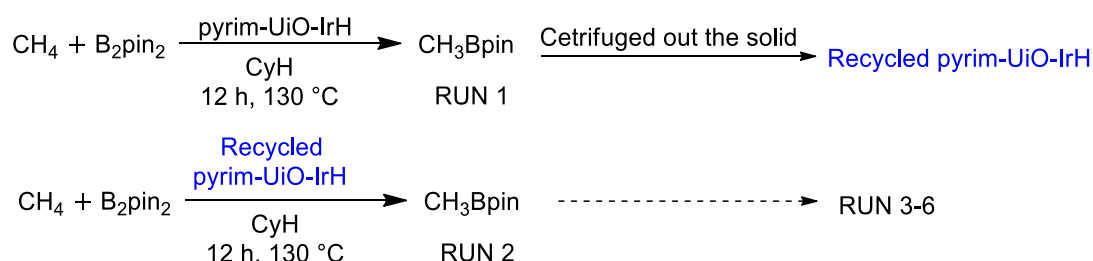


Figure 5.11. Recycle and reuse of pyrim-UiO-IrH in borylation of methane.

In the glovebox, pyrim-UiO-IrH (1.9 mg, 0.5 mol% of Ir) in 2 mL cyclohexane was transferred into a glass liner. B₂pin₂ (51 mg, 0.2 mmol) was subsequently added to the liner, which was then securely fitted into a high-pressure reactor and sealed. The sealed Parr reactor was then removed from the glovebox and purged with CH₄ two to three times. The reactor was pressurized with 40 bar methane and then heated at 130 °C for 12 h without any mechanical stirring. The system was subsequently cooled, and the pressure was released. The solid MOF was removed from suspension to separate the solid and the supernatant, inside the glove box and washed with cyclohexane multiple times. The yield of CH₃Bpin was determined by GC-MS and GC-FID analysis. The solid MOF was then recycled.

Inside the glovebox, the recovered MOF-catalyst was again added to the glass liner. 2 mL cyclohexane and B₂pin₂ (51 mg, 0.2 mmol) were added to the glass liner and sealed it in a Parr reactor. The Parr reactor was taken out from the glove box and was purged with the CH₄ gas and then pressurized it to 40 bar of CH₄. The reactor was heated at 130 °C for 12 h. After the reaction, the solution was analyzed in the same way as mentioned previously in run 1. The recycling and reuse experiments were performed up to 5 times in total.

Table 5.3. %Conversion of B₂pin₂, %GC-Yield of CH₃Bpin and the leaching of Ir and Zr at various runs of the recycling of pyrim-UiO-IrH in the borylation of methane.

Run	Time	%Conv. (B ₂ pin ₂)	%GC-Yield	%Leaching (Ir, Zr)
Run-1	12 h	56	55	0.013, 0.03
Run-2	12 h	55	54	
Run-3	12 h	59	58	0.04, 0.06
Run-4	12 h	53	51	

Run-5	12 h	54	52	0.06, 0.08
Run-6	12 h	53	50	

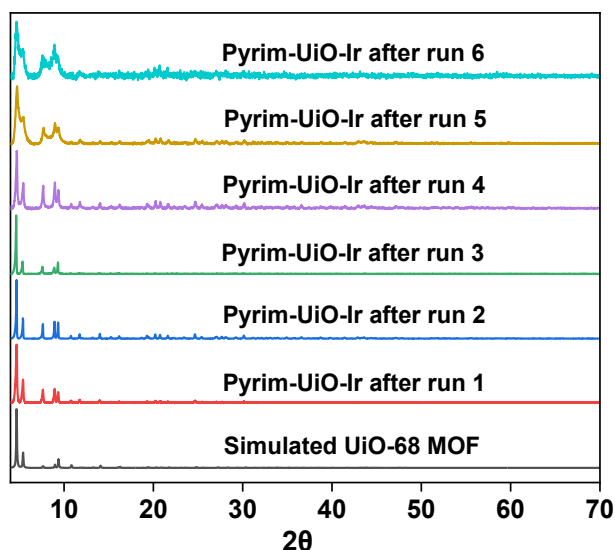


Figure 5.12. PXRD patterns of simulated UiO-68 MOF (black), pyrim-UiO-Ir after run 1 (red), pyrim-UiO-Ir after run 2 (blue), pyrim-UiO-Ir after run 3 (green), pyrim-UiO-Ir after run 4 (violet), pyrim-UiO-Ir after run 5 (mustard brown) and pyrim-UiO-Ir after run 6 (light blue).

5.4.6. Investigation of the Effect of Pore Sizes on the Rate of Catalysis

The effect of pore sizes on the rate of catalytic reaction was investigated by comparing the rate of borylation reactions of methane catalyzed by pyrim-UiO-IrH with that of pyrim-UiO-66-IrH under identical reaction conditions. Pyrim-UiO-66-IrH has the same topology but smaller pore sizes compared to pyrim-UiO-IrH.

5.4.6.1 Synthesis and characterizations of pyrim-UiO-66-IrH

The synthesis was performed following a modified procedure.³²² In a vial, 2-aminoterephthalic acid (0.032 g, 0.176 mmol) was dissolved in a DMF solution (4.5 mL) followed by the addition of ZrCl_4 (0.044 g, 0.188 mmol). The mixture was sonicated for 20 minutes and then placed in a teflon sealed hydrobomb and heated at 120 °C for 24 h. After cooling to room temperature, the crystalline solids were isolated by centrifugation and washed by DMF several times to afford UiO-66-NH₂ MOF. UiO-66-NH₂-MOF was functionalized with pyridylimine moiety. In a 1.5 mL centrifuge tube, UiO-66-NH₂ MOF (0.017 g, 0.016 mmol) was added in 1 mL DMF followed by addition of 2-pyridinecarboxaldehyde (6 μL , 0.056 mmol). It was then left overnight with periodic shaking. The solid was washed various times with DMF to obtain pyrim-UiO-66 as light brown solid. Pyrim-UiO-66 MOF (0.020 g, 0.009 mmol) in THF was charged into a vial, and then 1 mL THF solution of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.019 g, 0.054 mmol) was

added to it. The mixture was stirred slowly overnight at room temperature. The resultant solid was centrifuged out of suspension and washed with THF 4-5 times. Pyrim-UiO-66-IrCl₃ has 28% Ir-loading based on ICP-OES analysis. Treatment of NaEt₃BH (15 μ L, 1 M in toluene) to pyrim-UiO-66-IrCl₃ (0.012 g, 0.00369 mmol) gave pyrim-UiO-66-IrH as black colored solid.

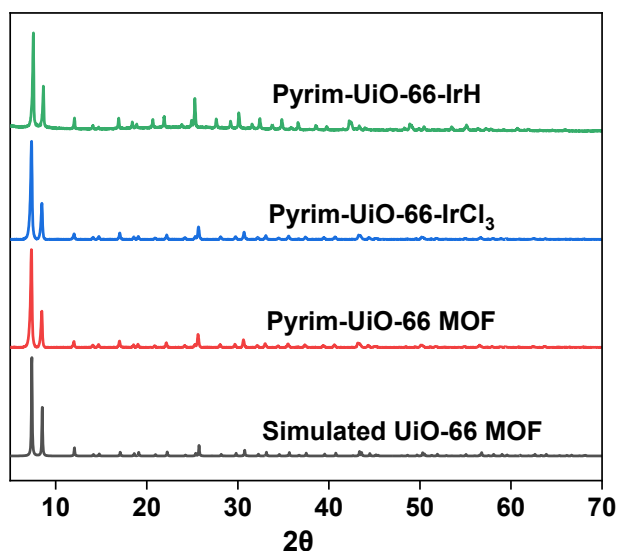


Figure 5.13. PXRD patterns of simulated UiO-66 MOF (black), pyrim-UiO-66 MOF (red), pyrim-UiO-66-IrCl₃ (blue) and pyrim-UiO-66-IrH (green).

5.4.6.2 Comparison of the catalytic activities of pyrim-UiO-IrH with that of pyrim-UiO-66-IrH in the borylation of methane under identical conditions

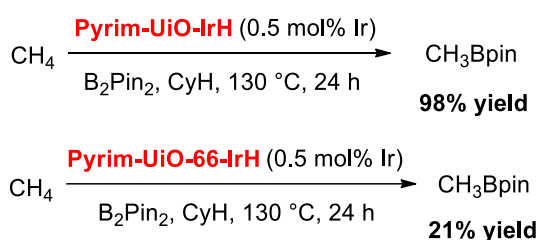


Figure 5.14. The borylation of methane catalyzed by pyrim-UiO-IrH with that of pyrim-UiO-66-IrH under identical reaction conditions.

In a glovebox, two separate 5 mL vials were charged with pre-activated pyrim-UiO-IrH (1.9 mg, 0.5 mol% of Ir) and pyrim-UiO-66-IrH (1.6 mg, 0.5 mol% of Ir) each and washed with THF multiple times. Each MOF slurry in 2 mL cyclohexane were transferred to two different glass liners containing B₂pin₂ (51 mg, 0.2 mmol). The liners were fitted into the Parr reactors and sealed properly. The sealed Parr reactors were taken out from the glove box. The reactors were purged twice with the CH₄, then charged with 40 bar CH₄ each and stirred at 130 °C for 24 h. After the completion of the reaction, the pressure from the reactors were released. The

solid MOF was then removed from suspension inside the glove box and the supernatant were analysed by GC-MS. The yield of CH₃Bpin were 98% and 21% with pyrim-UiO-IrH and pyrim-UiO-66-IrH respectively. This experiment indicates that the larger pore size MOF (pyrim-UiO-IrH) have comparatively higher efficiency than the smaller pore size pyrim-UiO-66-IrH MOF due to the facile diffusion of substrates into the larger pores of pyrim-UiO-IrH.

5.4.7. C–H Borylation of Methane Using Pyrim-MOF-IrH and Its Homogeneous Control [Ph(pyrim)(PhCO₂Me)₂]IrH as Catalysts Under Identical Conditions to Compare Their Catalytic Activities

Out of the two Parr reactors, one was charged with B₂pin₂ (51 mg, 0.2 mmol), [Ph(pyrim)(PhCO₂Me)₂]IrH (0.0007 g, 0.0011 mmol) and cyclohexane (2 mL) and another reactor was charged with B₂pin₂ (51 mg, 0.2 mmol), pyrim-UiO-IrH (1.9 mg, 0.5 mol% Ir) and cyclohexane (2 mL) in a glovebox. Both the reactors were purged twice with CH₄, then charged with 40 bar CH₄ each and stirred at 130 °C for 24 h. After the completion of the reaction, the pressure from the reactors were released. The yield (%) of the products were monitored by GC-MS and GC-FID (Figure 5.15).

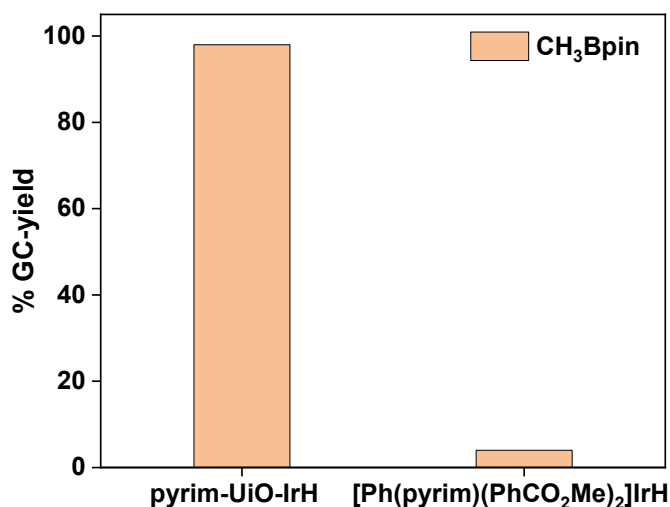


Figure 5.15. C–H borylation of methane using pyrim-UiO-IrH and its homogeneous control [Ph(pyrim)(PhCO₂Me)₂]IrH as catalysts under identical conditions.

Table 5.4. %Conversion of B₂pin₂, %GC-Yield of CH₃Bpin and the leaching of Ir and Zr at various runs of the recycling of pyrim-UiO-IrH in the borylation of methane.

Catalyst	Ir (μmol)	Conv. of B ₂ Pin ₂ (%)	CH ₃ Bpin (%)	CH ₂ (Bpin) ₂ (%)	HBpin (%)	HOBpin (%)	solvBpin (%)	TON
Pyrim-UiO-IrH	1.02	100	98	0	0	1	1	196
[Ph(pyrim)(PhCO ₂ Me) ₂]IrH	1.1	11	4	1	0	5	1	8

Reaction conditions: 2 mL of C₆H₁₂, 51 mg B₂pin₂ (0.2 mmol), 130 °C, 40 bar CH₄ and 24 h.

5.5. Analysis and quantification of CH₃Bpin by GC-MS and GC-FID

A) The conversions and yields of the reactions were determined by Agilent 7890B gas chromatograph equipped with a flame ionisation detector (FID) and a mass detector (Agilent 5977B GC/MSD) and a HP-5MS Ultra Inert 30m-250µm-0.25µm column. GC conditions: Inj: 220 °C; Det: 250 °C; Column temp: 40 °C followed by a ramp of 5 °C/min to 240 °C; Column flow: 1.0 mL/min.

The conversion and yield of CH₃Bpin were determined for each reaction run by measuring the relative amount of boron species through the corrected integration of GC-MS peaks as follows.³²¹

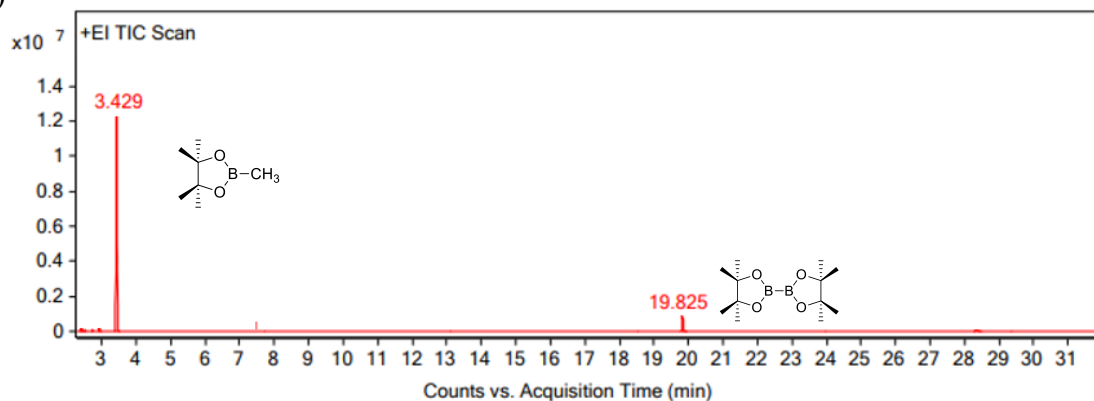
$$\text{Conversion\%} = \left[1 - \frac{\text{B}_2\text{Pin}_2 \text{ remaining}}{(\text{B}_2\text{Pin}_2 + \text{CH}_3\text{Bpin} + \text{HOBpin} + \text{SolBpin} + \text{etc})} \right] \times 100\%$$

$$\text{Yield of CH}_3\text{Bpin\%} = \left[\frac{\text{CH}_3\text{Bpin}}{(\text{B}_2\text{Pin}_2 + \text{CH}_3\text{Bpin} + \text{HOBpin} + \text{SolBpin} + \text{etc})} \right] \times 100\%$$

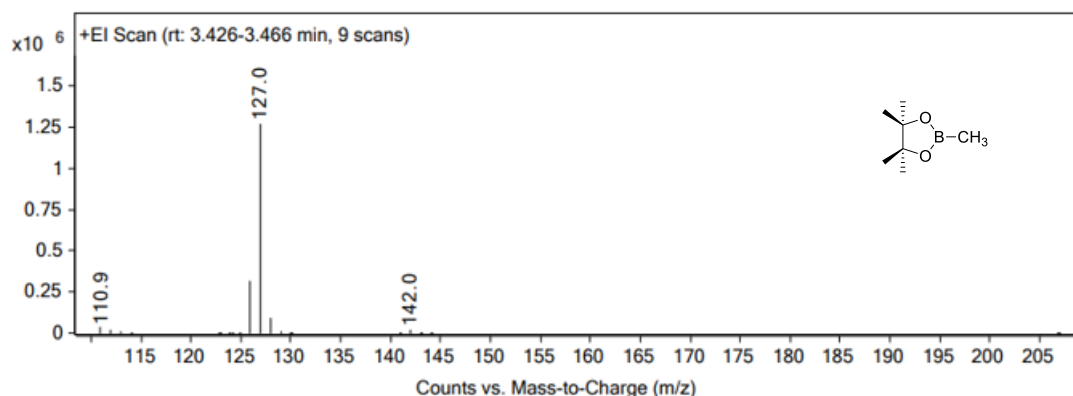
$$\text{Selectivity of CH}_3\text{Bpin\%} = \left[\frac{\text{CH}_3\text{Bpin}}{\text{Overall product formed}} \right] \times 100\%$$

$$\text{TON of CH}_3\text{Bpin} = \frac{\% \text{ Yield of CH}_3\text{Bpin}}{\% \text{ Ir Loading}}$$

a)



b)



c)

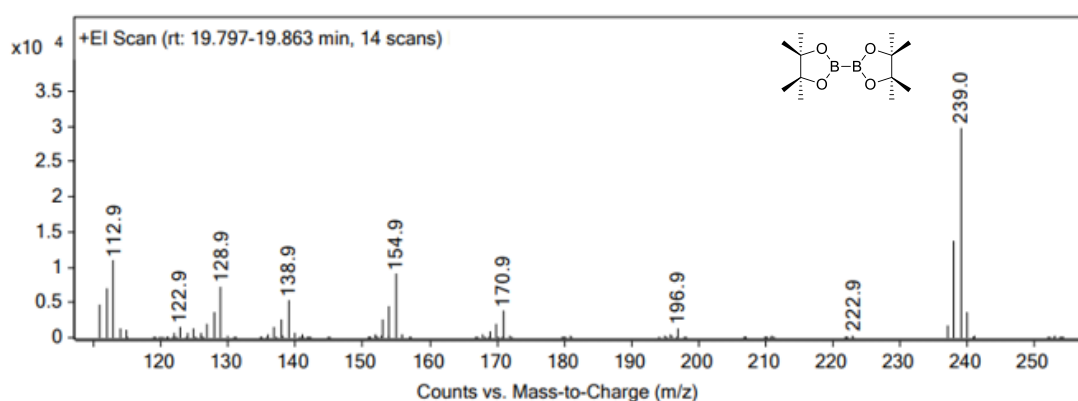
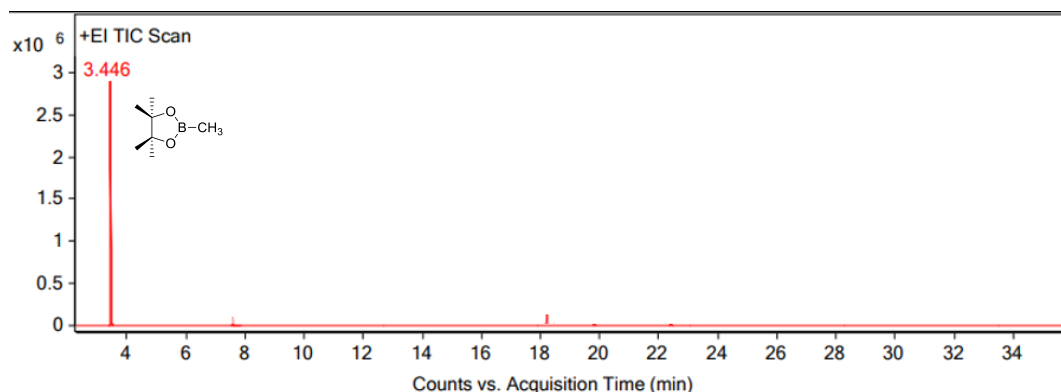


Figure 5.16. The GC-MS spectra of the crude reaction mixture after 18 h of catalysis (87% B₂pin₂ conversion) using pyrim-UiO-IrH. Reaction conditions: 1.9 mg of pyrim-UiO-IrH (1.02 μ mol of Ir), 2 mL of C₆H₁₂, 51 mg B₂pin₂ (0.2 mmol), 130 $^{\circ}$ C, 40 bar CH₄ and 18 h.

a)



b)

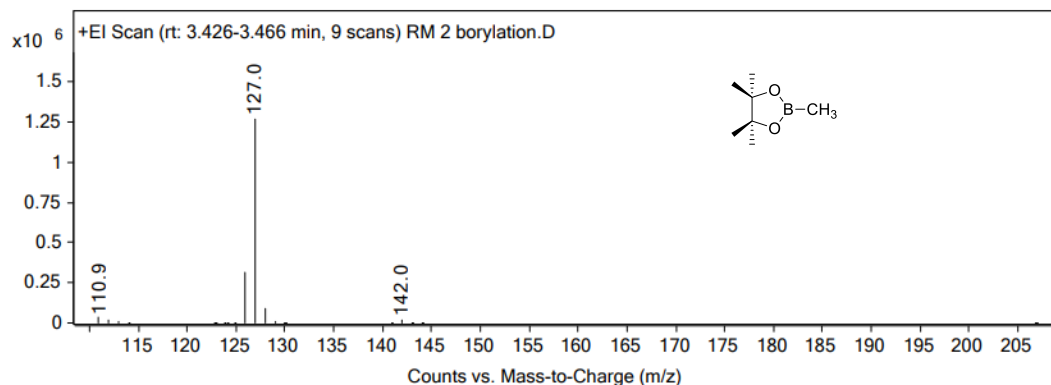


Figure 5.17. The GC-MS spectra of the crude reaction mixture after 24 h of catalysis (100% B₂pin₂ conversion) using pyrim-UiO-IrH. Reaction conditions: 1.9 mg of pyrim-UiO-IrH (1.02 μ mol of Ir), 2 mL of C₆H₁₂, 51 mg B₂pin₂ (0.2 mmol), 130 $^{\circ}$ C, 40 bar CH₄ and 24 h.

B) The yield of CH₃Bpin under optimized conditions [1.02 μ mol of Ir, B₂pin₂ (0.2 mmol), 2 mL C₆H₁₂, 130 $^{\circ}$ C, 40 bar CH₄ and 24 h] was also determined by GC analysis using mesitylene as an

internal standard. First, we made a GC-calibration curve using known quantities of MeBpin with mesitylene as an internal standard (I.S.) as shown below.

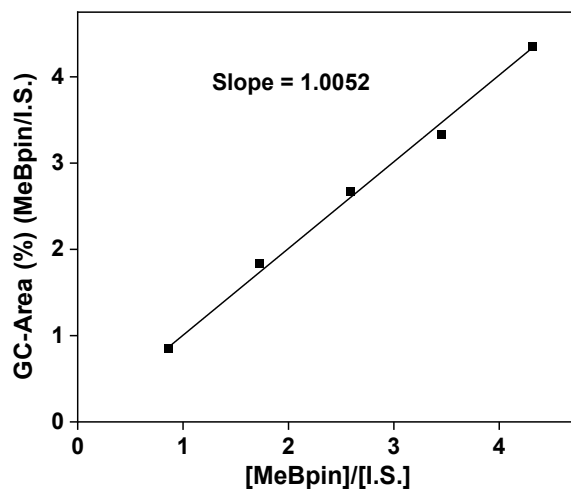


Figure 5.18. GC calibration plot employing various concentrations of MeBpin with mesitylene as an internal standard.

From the above calibration plot, slope = 1.0052

Analysis: [Mesitylene] = 0.07188618 M

%GC-Area of MeBpin peak = 57.68%

%GC-Area of Mesitylene peak = 42.32%

[MeBpin] = ?

Now,

$$\%GC\text{-Area of MeBpin} / \%GC\text{-Area of I.S.} = \text{Slope} \times [\text{MeBpin}] / [\text{I.S.}]$$

$$\Rightarrow 57.68 / 42.32 = 1.0052 \times [\text{MeBpin}] / 0.07188618$$

$$\Rightarrow [\text{MeBpin}] = 0.0975 \text{ M}$$

$$M = n / V$$

$$n \text{ (mmol)} = M \times V \text{ (mL)}$$

$$\text{mmol of MeBpin produced} = 0.0975 \times 2 = 0.195 \text{ mmol [Since 2 mL of solvent was used]}$$

$$\% \text{ Yield (MeBpin)} = \text{mmol of product (MeBpin)} / \text{mmol of reactant taken} \times 100 \%$$

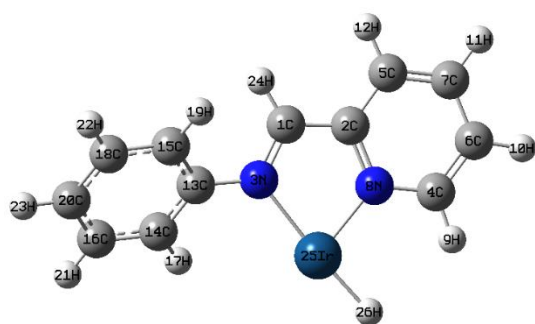
$$= (0.195/0.2) \times 100 = 97.5\%$$

(The absence of a peak corresponding to B₂pin₂ in the GC spectrum indicates complete consumption of the reactant, signifying a full conversion rate)

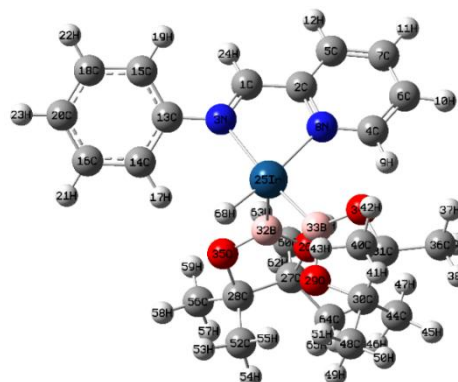
The yields of MeBpin obtained using the GC-calibration curve is close to the value afforded from the alternative method described in above section 5A (SI), thereby confirming the reliability of our experimental protocol.

5.6. DFT Calculations

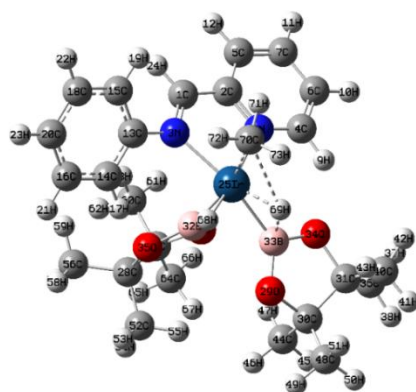
All quantum chemical calculations were done using the density functional theory (DFT) functional B3LYP/genecp along with sdd basis set method for Ir and 6-31G basis set for C, N, H, O and B atoms as implemented in the Gaussian 16 software suite.^{215–219} Electronic structure complexes were optimized at the unrestricted level. All calculations were performed in the solvated state and at 403.15 K. We used the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) as the default SCRF method by using THF as the solvent for pyrim-UiO-IrCl₃(THF) at room temperature (298.15K) and cyclohexane as the solvent for all other molecules in this DFT calculation at 403.15 K. Each structure was first optimized, and then frequency calculation was performed to confirm its geometry and to obtain the thermochemical data.



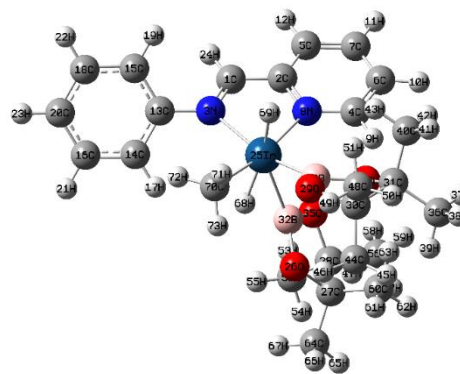
Pyrim-UiO-IrH



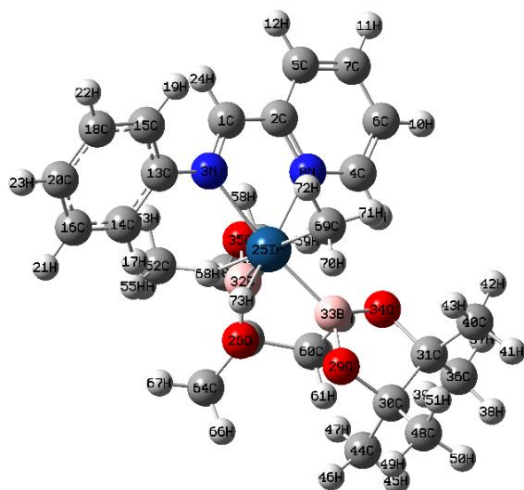
INT-1



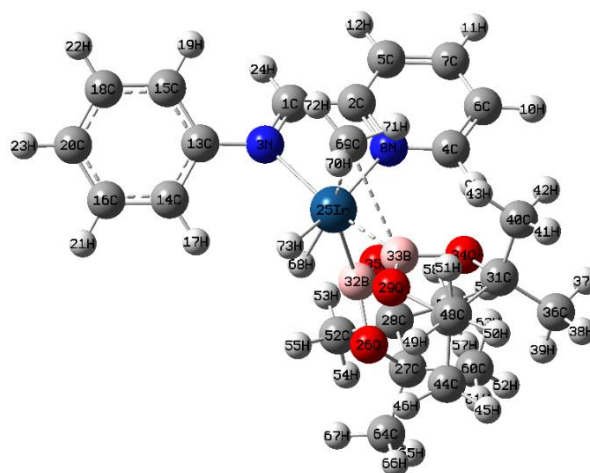
TS-1



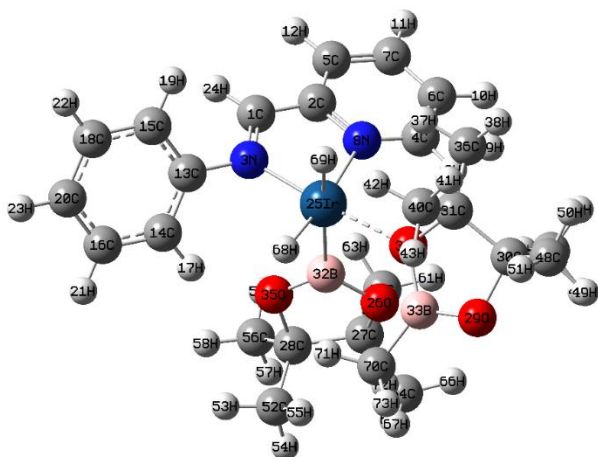
INT-2



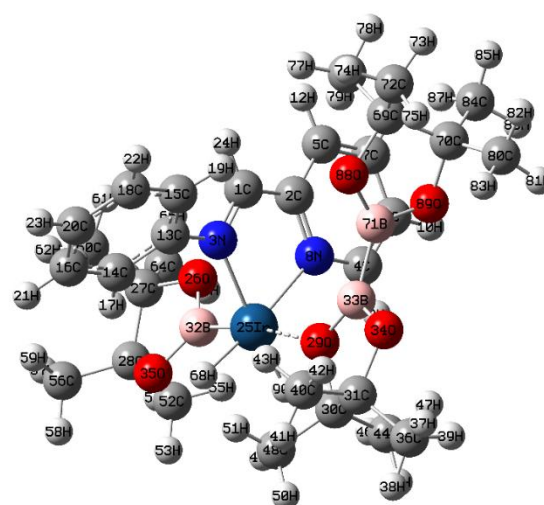
INT-3



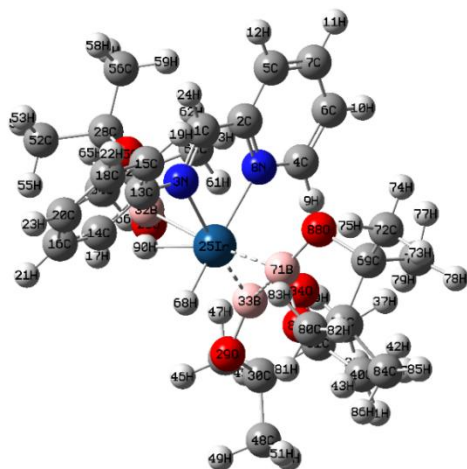
TS-2



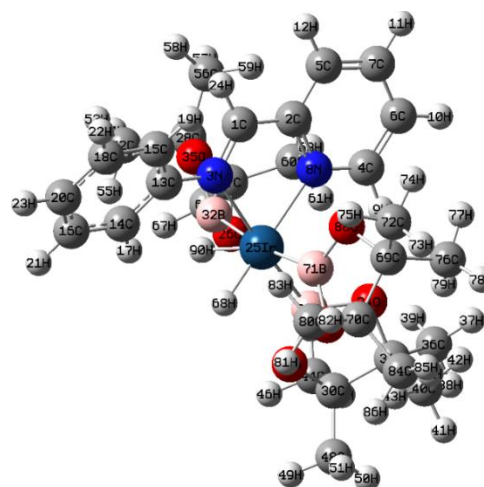
INT-4



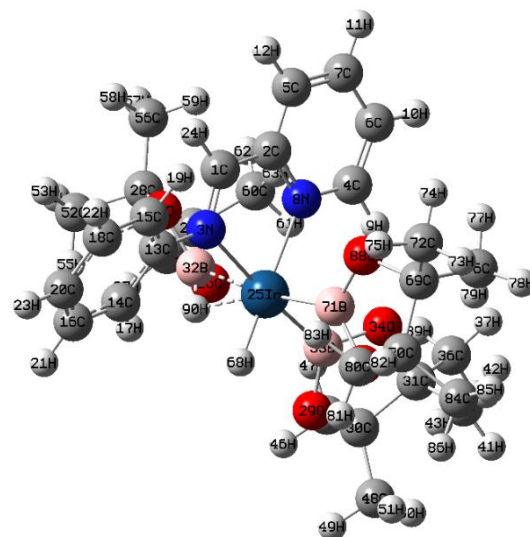
INT-5



TS-3



INT-6



TS-4

Figure 5.19. DFT-optimized structures of intermediates and transition states of the catalytic cycle in pyrim-UiO-IrH catalysed methane borylation using B₂pin₂.

5.6.1. Cartesian coordinates of the DFT-optimized structures.

Cartesian coordinates of Pyrim-UiO-IrH

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-14.186325	-5.662331	-12.600542
2	C	-13.696708	-4.661369	-11.705306
3	N	-14.333675	-5.282408	-13.858102
4	C	-12.955394	-2.410745	-11.535603
5	C	-13.480725	-4.847629	-10.331602
6	C	-12.732818	-2.568860	-10.174692
7	C	-12.997000	-3.802325	-9.552443
8	N	-13.435550	-3.430502	-12.316832
9	H	-12.765836	-1.481978	-12.050312
10	H	-12.355178	-1.728139	-9.605455
11	H	-12.827447	-3.934828	-8.490954
12	H	-13.698262	-5.817356	-9.898437
13	C	-14.758960	-6.206432	-14.862166
14	C	-15.608466	-5.740958	-15.880226
15	C	-14.322602	-7.543773	-14.871096
16	C	-16.032715	-6.610653	-16.888433
17	H	-15.940581	-4.707588	-15.856861
18	C	-14.745689	-8.404998	-15.887911
19	H	-13.634676	-7.895579	-14.109833
20	C	-15.602640	-7.944369	-16.896365
21	H	-16.696151	-6.247364	-17.666089
22	H	-14.397810	-9.432588	-15.897680
23	H	-15.925215	-8.615935	-17.684823
24	H	-14.434135	-6.660362	-12.254966
25	Ir	-13.784312	-3.294161	-14.232310
26	H	-13.286125	-1.725904	-14.413264

Cartesian coordinates of INT-1

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-13.876811	-5.699012	-12.934968
2	C	-13.062349	-4.846612	-12.083608

3	N	-14.209485	-5.306337	-14.130494
4	C	-11.902242	-2.816219	-11.888750
5	C	-12.744079	-5.197099	-10.765923
6	C	-11.558690	-3.112052	-10.563518
7	C	-11.981147	-4.316503	-9.993501
8	N	-12.640894	-3.666922	-12.638150
9	H	-11.594864	-1.906946	-12.393919
10	H	-10.966725	-2.403644	-9.996265
11	H	-11.724638	-4.565721	-8.970076
12	H	-13.094687	-6.139040	-10.358910
13	C	-15.000907	-6.175041	-14.953397
14	C	-16.098188	-5.633963	-15.641170
15	C	-14.692169	-7.541861	-15.066029
16	C	-16.902449	-6.477626	-16.412592
17	H	-16.306389	-4.574304	-15.539318
18	C	-15.491858	-8.369878	-15.860043
19	H	-13.815083	-7.942651	-14.567863
20	C	-16.603460	-7.842637	-16.527805
21	H	-17.762030	-6.065834	-16.931431
22	H	-15.241799	-9.421003	-15.961142
23	H	-17.225335	-8.486919	-17.140834
24	H	-14.224532	-6.650760	-12.533004
25	Ir	-13.285015	-3.339631	-14.783555
26	O	-14.832899	-0.725751	-14.297569
27	C	-16.197391	-0.269809	-13.892823
28	C	-17.116161	-1.394715	-14.506358
29	O	-11.951421	-0.996241	-16.412322
30	C	-11.269160	0.312018	-16.188780
31	C	-10.545731	0.070442	-14.811240
32	B	-14.847362	-2.125970	-14.538091
33	B	-12.190573	-1.648481	-15.169758
34	O	-11.435215	-0.944031	-14.172203
35	O	-16.200161	-2.579081	-14.490704
36	C	-10.474592	1.287124	-13.890054
37	H	-9.987051	1.009377	-12.949474
38	H	-9.888332	2.091575	-14.350573
39	H	-11.471126	1.667165	-13.657462
40	C	-9.165260	-0.588137	-14.952217
41	H	-8.426445	0.107866	-15.364732

42	H	-8.821157	-0.907870	-13.963395
43	H	-9.214906	-1.469558	-15.598493
44	C	-12.380138	1.369731	-16.119575
45	H	-11.970481	2.376970	-15.982518
46	H	-12.941161	1.348649	-17.058936
47	H	-13.078361	1.145885	-15.308951
48	C	-10.339933	0.576127	-17.372433
49	H	-10.935012	0.688271	-18.284254
50	H	-9.770841	1.501811	-17.222287
51	H	-9.638232	-0.246485	-17.526073
52	C	-17.483657	-1.147543	-15.975516
53	H	-17.988735	-2.036287	-16.366923
54	H	-18.162728	-0.293916	-16.079341
55	H	-16.589296	-0.979634	-16.580536
56	C	-18.354557	-1.743896	-13.683776
57	H	-19.031598	-0.883598	-13.616881
58	H	-18.894978	-2.563584	-14.167774
59	H	-18.091073	-2.062280	-12.672882
60	C	-16.207784	-0.241773	-12.357918
61	H	-15.398536	0.408633	-12.012465
62	H	-17.155310	0.147053	-11.968672
63	H	-16.042851	-1.241297	-11.944083
64	C	-16.415794	1.130057	-14.462201
65	H	-17.434459	1.480397	-14.256024
66	H	-15.714832	1.829003	-13.994687
67	H	-16.246900	1.150162	-15.540468
68	H	-13.608677	-3.338509	-16.309609

Cartesian coordinates of TS-1

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-13.831763	-5.735345	-12.948223
2	C	-13.017301	-4.882945	-12.096864
3	N	-14.164436	-5.342670	-14.143750
4	C	-11.857193	-2.852553	-11.902006
5	C	-12.699030	-5.233432	-10.779179
6	C	-11.513641	-3.148385	-10.576774
7	C	-11.936098	-4.352836	-10.006756
8	N	-12.595845	-3.703255	-12.651405
9	H	-11.549815	-1.943279	-12.407175
10	H	-10.921676	-2.439977	-10.009520
11	H	-11.679589	-4.602054	-8.983331
12	H	-13.049638	-6.175373	-10.372165
13	C	-14.955859	-6.211374	-14.966652
14	C	-16.053139	-5.670296	-15.654425
15	C	-14.647120	-7.578195	-15.079285
16	C	-16.857401	-6.513959	-16.425847
17	H	-16.261340	-4.610637	-15.552573
18	C	-15.446810	-8.406211	-15.873298
19	H	-13.770035	-7.978984	-14.581118
20	C	-16.558411	-7.878970	-16.541060
21	H	-17.716982	-6.102167	-16.944686
22	H	-15.196750	-9.457336	-15.974397
23	H	-17.180286	-8.523252	-17.154089
24	H	-14.179483	-6.687093	-12.546259
25	Ir	-13.239966	-3.375964	-14.796810
26	O	-14.787851	-0.762084	-14.310824
27	C	-16.152342	-0.306142	-13.906078
28	C	-17.071112	-1.431048	-14.519613
29	O	-11.906373	-1.032574	-16.425577
30	C	-11.224111	0.275685	-16.202036
31	C	-10.500682	0.034109	-14.824496
32	B	-14.802314	-2.162303	-14.551346
33	B	-12.145524	-1.684814	-15.183014
34	O	-11.390167	-0.980364	-14.185459
35	O	-16.155113	-2.615415	-14.503959
36	C	-10.429543	1.250791	-13.903310
37	H	-9.942002	0.973044	-12.962729
38	H	-9.843283	2.055242	-14.363828
39	H	-11.426078	1.630832	-13.670718
40	C	-9.120211	-0.624470	-14.965472
41	H	-8.381396	0.071533	-15.377987
42	H	-8.776108	-0.944203	-13.976650

43	H	-9.169857	-1.505892	-15.611748
44	C	-12.335090	1.333398	-16.132830
45	H	-11.925432	2.340637	-15.995774
46	H	-12.896113	1.312316	-17.072191
47	H	-13.033312	1.109552	-15.322206
48	C	-10.294884	0.539794	-17.385688
49	H	-10.889963	0.651938	-18.297509
50	H	-9.725792	1.465478	-17.235542
51	H	-9.593183	-0.282818	-17.539329
52	C	-17.438608	-1.183876	-15.988771
53	H	-17.943686	-2.072620	-16.380178
54	H	-18.117679	-0.330249	-16.092597
55	H	-16.544247	-1.015967	-16.593791
56	C	-18.309508	-1.780229	-13.697032
57	H	-18.986550	-0.919931	-13.630136
58	H	-18.849930	-2.599917	-14.181029
59	H	-18.046024	-2.098613	-12.686137
60	C	-16.162736	-0.278106	-12.371173
61	H	-15.353487	0.372300	-12.025720
62	H	-17.110262	0.110720	-11.981927
63	H	-15.997802	-1.277630	-11.957339
64	C	-16.370745	1.093724	-14.475457
65	H	-17.389410	1.444064	-14.269279
66	H	-15.669783	1.792670	-14.007942
67	H	-16.201851	1.113829	-15.553723
68	H	-13.842928	-3.061514	-16.200790
69	H	-11.795354	-3.881995	-15.097857
70	C	-13.273335	-4.877812	-16.162182
71	H	-12.964560	-5.790262	-15.696356
72	H	-14.266464	-4.990619	-16.544110
73	H	-12.606569	-4.644169	-16.965757

Cartesian coordinates of INT-2

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-13.831763	-5.735345	-12.948223
2	C	-13.017301	-4.882945	-12.096864
3	N	-14.164436	-5.342670	-14.143750
4	C	-11.857193	-2.852553	-11.902006
5	C	-12.699030	-5.233432	-10.779179
6	C	-11.513641	-3.148385	-10.576774
7	C	-11.936098	-4.352836	-10.006756
8	N	-12.595845	-3.703255	-12.651405
9	H	-11.549815	-1.943279	-12.407175
10	H	-10.921676	-2.439977	-10.009520
11	H	-11.679589	-4.602054	-8.983331
12	H	-13.049638	-6.175373	-10.372165
13	C	-14.955859	-6.211374	-14.966652
14	C	-16.053139	-5.670296	-15.654425
15	C	-14.647120	-7.578195	-15.079285
16	C	-16.857401	-6.513959	-16.425847
17	H	-16.261340	-4.610637	-15.552573
18	C	-15.446810	-8.406211	-15.873298
19	H	-13.770035	-7.978984	-14.581118
20	C	-16.558411	-7.878970	-16.541060
21	H	-17.716982	-6.102167	-16.944686
22	H	-15.196750	-9.457336	-15.974397
23	H	-17.180286	-8.523252	-17.154089
24	H	-14.179483	-6.687093	-12.546259
25	Ir	-13.239966	-3.375964	-14.796810
26	O	-14.787851	-0.762084	-14.310824
27	C	-16.152342	-0.306142	-13.906078
28	C	-17.071112	-1.431048	-14.519613
29	O	-11.906373	-1.032574	-16.425577
30	C	-11.224111	0.275685	-16.202036
31	C	-10.500682	0.034109	-14.824496
32	B	-14.802314	-2.162303	-14.551346
33	B	-12.145524	-1.684814	-15.183014
34	O	-11.390167	-0.980364	-14.185459
35	O	-16.155113	-2.615415	-14.503959
36	C	-10.429543	1.250791	-13.903310
37	H	-9.942002	0.973044	-12.962729
38	H	-9.843283	2.055242	-14.363828

39	H	-11.426078	1.630832	-13.670718
40	C	-9.120211	-0.624470	-14.965472
41	H	-8.381396	0.071533	-15.377987
42	H	-8.776108	-0.944203	-13.976650
43	H	-9.169857	-1.505892	-15.611748
44	C	-12.335090	1.333398	-16.132830
45	H	-11.925432	2.340637	-15.995774
46	H	-12.896113	1.312316	-17.072191
47	H	-13.033312	1.109552	-15.322206
48	C	-10.294884	0.539794	-17.385688
49	H	-10.889963	0.651938	-18.297509
50	H	-9.725792	1.465478	-17.235542
51	H	-9.593183	-0.282818	-17.539329
52	C	-17.438608	-1.183876	-15.988771
53	H	-17.943686	-2.072620	-16.380178
54	H	-18.117679	-0.330249	-16.092597
55	H	-16.544247	-1.015967	-16.593791
56	C	-18.309508	-1.780229	-13.697032
57	H	-18.986550	-0.919931	-13.630136
58	H	-18.849930	-2.599917	-14.181029
59	H	-18.046024	-2.098613	-12.686137
60	C	-16.162736	-0.278106	-12.371173
61	H	-15.353487	0.372300	-12.025720
62	H	-17.110262	0.110720	-11.981927
63	H	-15.997802	-1.277630	-11.957339
64	C	-16.370745	1.093724	-14.475457
65	H	-17.389410	1.444064	-14.269279
66	H	-15.669783	1.792670	-14.007942
67	H	-16.201851	1.113829	-15.553723
68	H	-13.842928	-3.061514	-16.200790
69	H	-11.795354	-3.881995	-15.097857
70	C	-13.273335	-4.877812	-16.162182
71	H	-12.964560	-5.790262	-15.696356
72	H	-14.266464	-4.990619	-16.544110
73	H	-12.606569	-4.644169	-16.965757

Cartesian coordinates of INT-3

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-13.831763	-5.735345	-12.948223
2	C	-13.017301	-4.882945	-12.096864
3	N	-14.164436	-5.342670	-14.143750
4	C	-11.857193	-2.852553	-11.902006
5	C	-12.699030	-5.233432	-10.779179
6	C	-11.513641	-3.148385	-10.576774
7	C	-11.936098	-4.352836	-10.006756
8	N	-12.595845	-3.703255	-12.651405
9	H	-11.549815	-1.943279	-12.407175
10	H	-10.921676	-2.439977	-10.009520
11	H	-11.679589	-4.602054	-8.983331
12	H	-13.049638	-6.175373	-10.372165
13	C	-14.955859	-6.211374	-14.966652
14	C	-16.053139	-5.670296	-15.654425
15	C	-14.647120	-7.578195	-15.079285
16	C	-16.857401	-6.513959	-16.425847
17	H	-16.261340	-4.610637	-15.552573
18	C	-15.446810	-8.406211	-15.873298
19	H	-13.770035	-7.978984	-14.581118
20	C	-16.558411	-7.878970	-16.541060
21	H	-17.716982	-6.102167	-16.944686
22	H	-15.196750	-9.457336	-15.974397
23	H	-17.180286	-8.523252	-17.154089
24	H	-14.179483	-6.687093	-12.546259
25	Ir	-13.239966	-3.375964	-14.796810
26	O	-14.787851	-0.762084	-14.310824
27	C	-16.152342	-0.306142	-13.906078
28	C	-17.071112	-1.431048	-14.519613
29	O	-11.906373	-1.032574	-16.425577
30	C	-11.224111	0.275685	-16.202036
31	C	-10.500682	0.034109	-14.824496
32	B	-14.802314	-2.162303	-14.551346
33	B	-12.145524	-1.684814	-15.183014
34	O	-11.390167	-0.980364	-14.185459

35	O	-16.155113	-2.615415	-14.503959
36	C	-10.429543	1.250791	-13.903310
37	H	-9.942002	0.973044	-12.962729
38	H	-9.843283	2.055242	-14.363828
39	H	-11.426078	1.630832	-13.670718
40	C	-9.120211	-0.624470	-14.965472
41	H	-8.381396	0.071533	-15.377987
42	H	-8.776108	-0.944203	-13.976650
43	H	-9.169857	-1.505892	-15.611748
44	C	-12.335090	1.333398	-16.132830
45	H	-11.925432	2.340637	-15.995774
46	H	-12.896113	1.312316	-17.072191
47	H	-13.033312	1.109552	-15.322206
48	C	-10.294884	0.539794	-17.385688
49	H	-10.889963	0.651938	-18.297509
50	H	-9.725792	1.465478	-17.235542
51	H	-9.593183	-0.282818	-17.539329
52	C	-17.438608	-1.183876	-15.988771
53	H	-17.943686	-2.072620	-16.380178
54	H	-18.117679	-0.330249	-16.092597
55	H	-16.544247	-1.015967	-16.593791
56	C	-18.309508	-1.780229	-13.697032
57	H	-18.986550	-0.919931	-13.630136
58	H	-18.849930	-2.599917	-14.181029
59	H	-18.046024	-2.098613	-12.686137
60	C	-16.162736	-0.278106	-12.371173
61	H	-15.353487	0.372300	-12.025720
62	H	-17.110262	0.110720	-11.981927
63	H	-15.997802	-1.277630	-11.957339
64	C	-16.370745	1.093724	-14.475457
65	H	-17.389410	1.444064	-14.269279
66	H	-15.669783	1.792670	-14.007942
67	H	-16.201851	1.113829	-15.553723
68	H	-13.842928	-3.061514	-16.200790
69	C	-11.360118	-4.034453	-15.188557
70	H	-11.113469	-3.823310	-16.208107
71	H	-10.666316	-3.537142	-14.543406
72	H	-11.309715	-5.089993	-15.020644
73	H	-13.265609	-4.530094	-15.846061

Cartesian coordinates of TS-2

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-13.831763	-5.735345	-12.948223
2	C	-13.017301	-4.882945	-12.096864
3	N	-14.164436	-5.342670	-14.143750
4	C	-11.857193	-2.852553	-11.902006
5	C	-12.699030	-5.233432	-10.779179
6	C	-11.513641	-3.148385	-10.576774
7	C	-11.936098	-4.352836	-10.006756
8	N	-12.595845	-3.703255	-12.651405
9	H	-11.549815	-1.943279	-12.407175
10	H	-10.921676	-2.439977	-10.009520
11	H	-11.679589	-4.602054	-8.983331
12	H	-13.049638	-6.175373	-10.372165
13	C	-14.955859	-6.211374	-14.966652
14	C	-16.053139	-5.670296	-15.654425
15	C	-14.647120	-7.578195	-15.079285
16	C	-16.857401	-6.513959	-16.425847
17	H	-16.261340	-4.610637	-15.552573
18	C	-15.446810	-8.406211	-15.873298
19	H	-13.770035	-7.978984	-14.581118
20	C	-16.558411	-7.878970	-16.541060
21	H	-17.716982	-6.102167	-16.944686
22	H	-15.196750	-9.457336	-15.974397
23	H	-17.180286	-8.523252	-17.154089
24	H	-14.179483	-6.687093	-12.546259
25	Ir	-13.239966	-3.375964	-14.796810
26	O	-14.787851	-0.762084	-14.310824
27	C	-16.152342	-0.306142	-13.906078
28	C	-17.071112	-1.431048	-14.519613
29	O	-11.906373	-1.032574	-16.425577
30	C	-11.224111	0.275685	-16.202036

31	C	-10.500682	0.034109	-14.824496
32	B	-14.802314	-2.162303	-14.551346
33	B	-12.145524	-1.684814	-15.183014
34	O	-11.390167	-0.980364	-14.185459
35	O	-16.155113	-2.615415	-14.503959
36	C	-10.429543	1.250791	-13.903310
37	H	-9.942002	0.973044	-12.962729
38	H	-9.843283	2.055242	-14.363828
39	H	-11.426078	1.630832	-13.670718
40	C	-9.120211	-0.624470	-14.965472
41	H	-8.381396	0.071533	-15.377987
42	H	-8.776108	-0.944203	-13.976650
43	H	-9.169857	-1.505892	-15.611748
44	C	-12.335090	1.333398	-16.132830
45	H	-11.925432	2.340637	-15.995774
46	H	-12.896113	1.312316	-17.072191
47	H	-13.033312	1.109552	-15.322206
48	C	-10.294884	0.539794	-17.385688
49	H	-10.889963	0.651938	-18.297509
50	H	-9.725792	1.465478	-17.235542
51	H	-9.593183	-0.282818	-17.539329
52	C	-17.438608	-1.183876	-15.988771
53	H	-17.943686	-2.072620	-16.380178
54	H	-18.117679	-0.330249	-16.092597
55	H	-16.544247	-1.015967	-16.593791
56	H	-18.309508	-1.780229	-13.697032
57	H	-18.986550	-0.919931	-13.630136
58	H	-18.849930	-2.599917	-14.181029
59	H	-18.046024	-2.098613	-12.686137
60	C	-16.162736	-0.278106	-12.371173
61	H	-15.353487	0.372300	-12.025720
62	H	-17.110262	0.110720	-11.981927
63	H	-15.997802	-1.277630	-11.957339
64	C	-16.370745	1.093724	-14.475457
65	H	-17.389410	1.444064	-14.269279
66	H	-15.669783	1.792670	-14.007942
67	H	-16.201851	1.113829	-15.553723
68	H	-13.842928	-3.061514	-16.200790
69	C	-11.360118	-4.034453	-15.188557
70	H	-11.113469	-3.823310	-16.208107
71	H	-10.666316	-3.537142	-14.543406
72	H	-11.309715	-5.089993	-15.020644
73	H	-13.265609	-4.530094	-15.846061

Cartesian coordinates of INT-4

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-14.458348	-5.433514	-13.016727
2	C	-13.565883	-4.696650	-12.136223
3	N	-14.687958	-5.006695	-14.224723
4	C	-12.142864	-2.845781	-11.900412
5	C	-13.349257	-5.078849	-10.806776
6	C	-11.893903	-3.177315	-10.562545
7	C	-12.500893	-4.307451	-10.007166
8	N	-12.963909	-3.590790	-12.676136
9	H	-11.693238	-1.991523	-12.394917
10	H	-11.230947	-2.554101	-9.974213
11	H	-12.320228	-4.582815	-8.974286
12	H	-13.842510	-5.960130	-10.411955
13	C	-15.560961	-5.762706	-15.075884
14	C	-16.545672	-5.079221	-15.805962
15	C	-15.441275	-7.159905	-15.174446
16	C	-17.429835	-5.808297	-16.606211
17	H	-16.608178	-4.000238	-15.713838
18	C	-16.317888	-7.874278	-15.997121
19	H	-14.647818	-7.675190	-14.642477
20	C	-17.319448	-7.202367	-16.707727
21	H	-18.203661	-5.284692	-17.158185
22	H	-16.212802	-8.950619	-16.086905
23	H	-18.001361	-7.758241	-17.343046
24	H	-14.949918	-6.324942	-12.626826
25	Ir	-13.475065	-3.192012	-14.845115
26	O	-14.661605	-0.385181	-14.422833

27	C	-15.963691	0.258648	-14.071270
28	C	-17.006218	-0.731944	-14.717675
29	O	-10.698181	0.271425	-15.666623
30	C	-9.720792	-0.245052	-14.679494
31	C	-10.385044	-1.601807	-14.235295
32	B	-14.861581	-1.771444	-14.661491
33	B	-11.982141	-0.271840	-15.444952
34	O	-11.833248	-1.324342	-14.468585
35	O	-16.265061	-2.031924	-14.665124
36	C	-10.202464	-1.965703	-12.762813
37	H	-10.726921	-2.902630	-12.546842
38	H	-9.141448	-2.109051	-12.524875
39	H	-10.607664	-1.190602	-12.109634
40	C	-10.017853	-2.787849	-15.139605
41	H	-8.977945	-3.100161	-14.993012
42	H	-10.668076	-3.634514	-14.897175
43	H	-10.162542	-2.536710	-16.194609
44	C	-9.671206	0.806958	-13.562070
45	H	-8.952847	0.532692	-12.781127
46	H	-9.362938	1.763036	-13.996205
47	H	-10.659644	0.946099	-13.116689
48	C	-8.359269	-0.380845	-15.359246
49	H	-8.005003	0.608609	-15.665172
50	H	-7.620398	-0.808042	-14.670137
51	H	-8.413858	-1.010368	-16.249977
52	C	-17.280225	-0.446265	-16.200199
53	H	-17.888894	-1.258918	-16.609204
54	H	-17.829599	0.492673	-16.331271
55	H	-16.349077	-0.408386	-16.770859
56	C	-18.311207	-0.900046	-13.942472
57	H	-18.864071	0.046393	-13.902882
58	H	-18.941765	-1.640044	-14.445461
59	H	-18.132787	-1.244960	-12.921737
60	C	-16.027835	0.298444	-12.537930
61	H	-15.149583	0.832510	-12.162838
62	H	-16.926055	0.817787	-12.185809
63	H	-16.019189	-0.711421	-12.116495
64	C	-15.963724	1.671319	-14.650819
65	H	-16.930803	2.161168	-14.484291
66	H	-15.190470	2.269336	-14.157971
67	H	-15.753220	1.660331	-15.721872
68	H	-14.079809	-3.310725	-16.278221
69	H	-12.222099	-4.024223	-15.258759
70	C	-13.387356	0.206020	-16.165729
71	H	-13.778136	-0.598162	-16.753506
72	H	-14.099247	0.477377	-15.414413
73	H	-13.195944	1.048731	-16.796681

Cartesian coordinates of INT-5

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-13.497862	-5.738790	-13.700062
2	c	-13.071552	-4.790677	-12.691467
3	N	-13.442749	-5.413773	-14.960612
4	C	-12.175296	-2.661794	-12.262139
5	C	-13.037370	-5.114050	-11.327317
6	C	-12.108432	-2.937915	-10.893759
7	C	-12.554144	-4.176149	-10.414673
8	N	-12.661418	-3.564760	-13.147279
9	H	-11.830114	-1.728579	-12.692699
10	H	-11.710830	-2.188918	-10.218926
11	H	-12.515491	-4.407389	-9.356140
12	H	-13.375784	-6.091202	-11.000841
13	C	-13.769162	-6.375170	-15.968529
14	C	-14.370898	-5.926884	-17.155588
15	C	-13.480543	-7.743663	-15.806458
16	C	-14.718981	-6.843474	-18.150172
17	H	-14.544693	-4.866045	-17.283624
18	C	-13.819504	-8.652002	-16.812978
19	H	-12.958233	-8.089098	-14.920739
20	C	-14.447729	-8.207955	-17.983133
21	H	-15.190373	-6.489818	-19.061059
22	H	-13.580771	-9.703270	-16.688071

23	H	-14.706721	-8.915279	-18.764115
24	H	-13.851108	-6.715916	-13.373399
25	Ir	-12.733932	-3.305017	-15.311165
26	O	-15.351845	-1.070858	-14.535231
27	C	-16.311206	-0.975284	-13.374861
28	C	-16.928156	-2.432694	-13.332297
29	O	-12.034610	-1.891473	-15.917082
30	C	-12.744304	-0.581167	-15.959185
31	C	-11.617403	0.391549	-16.480065
32	B	-15.048880	-2.410925	-14.754791
33	B	-10.631559	-1.695530	-15.818761
34	O	-10.374928	-0.294349	-16.013066
35	O	-15.844894	-3.258980	-13.982295
36	C	-11.639712	1.795753	-15.878080
37	H	-10.793935	2.374062	-16.264983
38	H	-12.562882	2.322314	-16.149124
39	H	-11.562347	1.764845	-14.789028
40	C	-11.525882	0.457116	-18.011452
41	H	-12.389270	0.973873	-18.445342
42	H	-10.621350	1.009178	-18.287558
43	H	-11.457218	-0.546168	-18.440731
44	C	-13.198197	-0.285327	-14.522162
45	H	-13.761163	0.653165	-14.461716
46	H	-13.846692	-1.100127	-14.185999
47	H	-12.344613	-0.239749	-13.840706
48	C	-13.950989	-0.729766	-16.885138
49	H	-14.647707	-1.458336	-16.458700
50	H	-14.479936	0.224999	-16.996286
51	H	-13.653926	-1.086511	-17.873263
52	C	-18.166806	-2.604581	-14.219383
53	H	-18.410666	-3.668721	-14.285636
54	H	-19.030761	-2.076928	-13.801964
55	H	-17.986884	-2.233090	-15.232409
56	C	-17.170919	-2.998997	-11.936405
57	H	-17.916047	-2.399681	-11.400690
58	H	-17.553068	-4.020856	-12.020091
59	H	-16.252388	-3.026506	-11.347161
60	C	-15.464824	-0.623509	-12.146958
61	H	-14.927367	0.308640	-12.342909
62	H	-16.093848	-0.480439	-11.261874
63	H	-14.726641	-1.399994	-11.931258
64	C	-17.301082	0.142781	-13.691988
65	H	-18.057629	0.224378	-12.902900
66	H	-16.765640	1.094831	-13.751169
67	H	-17.804028	-0.021439	-14.646527
68	H	-12.651674	-3.288862	-16.909697
69	C	-7.510157	-4.366276	-15.616292
70	C	-7.409756	-3.621168	-14.232885
71	B	-9.199940	-2.683146	-15.495037
72	C	-6.194118	-4.515343	-16.376020
73	H	-5.485228	-5.131706	-15.809876
74	H	-6.379277	-5.006432	-17.336945
75	H	-5.734084	-3.544944	-16.574149
76	C	-8.248460	-5.709508	-15.532082
77	H	-8.454985	-6.063620	-16.546899
78	H	-7.648303	-6.467744	-15.016786
79	H	-9.202839	-5.598345	-15.009096
80	C	-6.314086	-2.546201	-14.196380
81	H	-6.449390	-1.937444	-13.297637
82	H	-5.313270	-2.991654	-14.167797
83	H	-6.380682	-1.885416	-15.065773
84	C	-7.318114	-4.527392	-13.007029
85	H	-6.399737	-5.126601	-13.033508
86	H	-7.298884	-3.913823	-12.100967
87	H	-8.175289	-5.200438	-12.940905
88	O	-8.396574	-3.446097	-16.395660
89	O	-8.715372	-2.895548	-14.177686
90	H	-14.462252	-2.770441	-15.782506

Cartesian coordinates of TS-3

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-12.522559	-5.602415	-12.889516

2	c	-11.947830	-4.550219	-12.066522
3	N	-12.966147	-5.333184	-14.083204
4	C	-11.360636	-2.282873	-11.922785
5	c	-11.527280	-4.780300	-10.750988
6	C	-10.929979	-2.453444	-10.600959
7	C	-11.010954	-3.715918	-10.006238
8	N	-11.861047	-3.311607	-12.645417
9	H	-11.311848	-1.334212	-12.446345
10	H	-10.536499	-1.603917	-10.055506
11	H	-10.681397	-3.869983	-8.984984
12	H	-11.610740	-5.773654	-10.324231
13	C	-13.513899	-6.394520	-14.877998
14	C	-14.725897	-6.174015	-15.550502
15	C	-12.857831	-7.633750	-14.978438
16	C	-15.291800	-7.213629	-16.293907
17	H	-15.204244	-5.204808	-15.458742
18	H	-13.423811	-8.657484	-15.744733
19	H	-11.898234	-7.780369	-14.492890
20	C	-14.645654	-8.453726	-16.396752
21	H	-16.237745	-7.052171	-16.800627
22	H	-12.907326	-9.607430	-15.836708
23	H	-15.085614	-9.250113	-16.988222
24	H	-12.600732	-6.604561	-12.467734
25	Ir	-12.603117	-3.204874	-14.781468
26	O	-14.776914	-1.081981	-14.299362
27	C	-16.206617	-0.993820	-13.873077
28	C	-16.806329	-2.331944	-14.452511
29	O	-12.046211	-0.380427	-16.015661
30	C	-12.004813	1.097433	-15.912329
31	C	-11.090214	1.315044	-14.649207
32	B	-14.425848	-2.440831	-14.520613
33	B	-11.777256	-0.986335	-14.769320
34	O	-11.326001	0.057318	-13.880288
35	O	-15.610536	-3.233019	-14.439545
36	C	-11.477305	2.495142	-13.759551
37	H	-10.806396	2.540743	-12.895068
38	H	-11.389358	3.441663	-14.306617
39	H	-12.500162	2.395490	-13.391524
40	C	-9.590282	1.349349	-14.978339
41	H	-9.312390	2.272742	-15.498490
42	H	-9.020180	1.295933	-14.045314
43	H	-9.305633	0.496856	-15.602256
44	C	-13.460859	1.534645	-15.696470
45	H	-13.549086	2.624964	-15.628969
46	H	-14.058275	1.190573	-16.546351
47	H	-13.872622	1.078145	-14.792704
48	C	-11.453961	1.667200	-17.218536
49	H	-12.139446	1.427836	-18.037639
50	H	-11.362852	2.758788	-17.159922
51	H	-10.476339	1.245791	-17.462155
52	C	-17.249581	-2.217259	-15.917074
53	H	-17.508912	-3.214635	-16.286070
54	H	-18.131134	-1.574481	-16.018550
55	H	-16.440920	-1.831069	-16.542413
56	C	-17.895564	-2.979519	-13.600215
57	H	-18.774166	-2.326633	-13.531152
58	H	-18.208669	-3.921290	-14.061984
59	H	-17.541258	-3.198694	-12.590695
60	C	-16.199298	-0.941281	-12.338797
61	H	-15.584534	-0.094601	-12.018726
62	H	-17.209389	-0.808416	-11.935601
63	H	-15.770219	-1.854385	-11.914954
64	C	-16.795246	0.288513	-14.456732
65	H	-17.866763	0.362167	-14.234580
66	H	-16.295749	1.155762	-14.013083
67	H	-16.655010	0.332519	-15.538390
68	H	-13.187458	-3.590669	-16.175494
69	C	-8.645615	-5.784252	-15.788109
70	C	-8.177031	-4.358481	-16.041135
71	B	-10.377861	-4.253944	-14.941702
72	C	-8.661629	-6.590074	-17.100357
73	H	-7.658640	-6.727365	-17.446859
74	H	-9.112982	-7.544647	-16.927236
75	H	-9.224393	-6.058098	-17.838733
76	C	-7.679467	-6.502390	-14.827674

77	H	-7.986497	-7.520397	-14.708111
78	H	-6.688766	-6.473658	-15.230891
79	H	-7.691856	-6.012081	-13.876704
80	C	-7.976456	-4.119370	-17.549179
81	H	-7.882224	-3.069752	-17.734446
82	H	-7.088671	-4.620127	-17.874723
83	H	-8.819112	-4.502094	-18.086164
84	C	-6.819720	-4.107475	-15.358272
85	H	-6.099057	-4.805756	-15.729685
86	H	-6.492798	-3.110895	-15.570052
87	H	-6.924239	-4.231373	-14.300621
88	O	-10.040583	-5.718154	-15.183332
89	O	-9.234811	-3.412279	-15.491232
90	H	-14.142626	-3.469191	-14.919255

Cartesian coordinates of INT-6

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-12.522559	-5.602415	-12.889516
2	c	-11.947830	-4.550219	-12.066522
3	N	-12.966147	-5.333184	-14.083204
4	C	-11.360636	-2.282873	-11.922785
5	c	-11.527280	-4.780300	-10.750988
6	C	-10.929979	-2.453444	-10.600959
7	C	-11.010954	-3.715918	-10.006238
8	N	-11.861047	-3.311607	-12.645417
9	H	-11.311848	-1.334212	-12.446345
10	H	-10.536499	-1.603917	-10.055506
11	H	-10.681397	-3.869983	-8.984984
12	H	-11.610740	-5.773654	-10.324231
13	C	-13.513899	-6.394520	-14.877998
14	C	-14.725897	-6.174015	-15.550502
15	C	-12.857831	-7.633750	-14.978438
16	C	-15.291800	-7.213629	-16.293907
17	H	-15.204244	-5.204808	-15.458742
18	H	-13.423811	-8.657484	-15.744733
19	H	-11.898234	-7.780369	-14.492890
20	C	-14.645654	-8.453726	-16.396752
21	H	-16.237745	-7.052171	-16.800627
22	H	-12.907326	-9.607430	-15.836708
23	H	-15.085614	-9.250113	-16.988222
24	H	-12.600732	-6.604561	-12.467734
25	Ir	-12.603117	-3.204874	-14.781468
26	O	-14.776914	-1.081981	-14.299362
27	C	-16.206617	-0.993820	-13.873077
28	C	-16.806329	-2.331944	-14.452511
29	O	-12.046211	-0.380427	-16.015661
30	C	-12.004813	1.097433	-15.912329
31	C	-11.090214	1.315044	-14.649207
32	B	-14.425848	-2.440831	-14.520613
33	B	-11.777256	-0.986335	-14.769320
34	O	-11.326001	0.057318	-13.880288
35	O	-15.610536	-3.233019	-14.439545
36	C	-11.477305	2.495142	-13.759551
37	H	-10.806396	2.540743	-12.895068
38	H	-11.389358	3.441663	-14.306617
39	H	-12.500162	2.395490	-13.391524
40	C	-9.590282	1.349349	-14.978339
41	H	-9.312390	2.272742	-15.498490
42	H	-9.020180	1.295933	-14.045314
43	H	-9.305633	0.496856	-15.602256
44	C	-13.460859	1.534645	-15.696470
45	H	-13.549086	2.624964	-15.628969
46	H	-14.058275	1.190573	-16.546351
47	H	-13.872622	1.078145	-14.792704
48	C	-11.453961	1.667200	-17.218536
49	H	-12.139446	1.427836	-18.037639
50	H	-11.362852	2.758788	-17.159922
51	H	-10.476339	1.245791	-17.462155
52	C	-17.249581	-2.217259	-15.917074
53	H	-17.508912	-3.214635	-16.286070
54	H	-18.131134	-1.574481	-16.018550
55	H	-16.440920	-1.831069	-16.542413

56	C	-17.895564	-2.979519	-13.600215
57	H	-18.774166	-2.326633	-13.531152
58	H	-18.208669	-3.921290	-14.061984
59	H	-17.541258	-3.198694	-12.590695
60	C	-16.199298	-0.941281	-12.338797
61	H	-15.584534	-0.094601	-12.018726
62	H	-17.209389	-0.808416	-11.935601
63	H	-15.770219	-1.854385	-11.914954
64	C	-16.795246	0.288513	-14.456732
65	H	-17.866763	0.362167	-14.234580
66	H	-16.295749	1.155762	-14.013083
67	H	-16.655010	0.332519	-15.538390
68	H	-13.187458	-3.590669	-16.175494
69	C	-8.645615	-5.784252	-15.788109
70	C	-8.177031	-4.358481	-16.041135
71	B	-10.377861	-4.253944	-14.941702
72	C	-8.661629	-6.590074	-17.100357
73	H	-7.658640	-6.727365	-17.446859
74	H	-9.112982	-7.544647	-16.927236
75	H	-9.224393	-6.058098	-17.838733
76	C	-7.679467	-6.502390	-14.827674
77	H	-7.986497	-7.520397	-14.708111
78	H	-6.688766	-6.473658	-15.230891
79	H	-7.691856	-6.012081	-13.876704
80	C	-7.976456	-4.119370	-17.549179
81	H	-7.882224	-3.069752	-17.734446
82	H	-7.088671	-4.620127	-17.874723
83	H	-8.819112	-4.502094	-18.086164
84	C	-6.819720	-4.107475	-15.358272
85	H	-6.099057	-4.805756	-15.729685
86	H	-6.492798	-3.110895	-15.570052
87	H	-6.924239	-4.231373	-14.300621
88	O	-10.040583	-5.718154	-15.183332
89	O	-9.234811	-3.412279	-15.491232
90	H	-14.142626	-3.469191	-14.919255

Cartesian coordinates of TS-4

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	-12.522559	-5.602415	-12.889516
2	C	-11.947830	-4.550219	-12.066522
3	N	-12.966147	-5.333184	-14.083204
4	C	-11.360636	-2.282873	-11.922785
5	C	-11.527280	-4.780300	-10.750988
6	C	-10.929979	-2.453444	-10.600959
7	C	-11.010954	-3.715918	-10.006238
8	N	-11.861047	-3.311607	-12.645417
9	H	-11.311848	-1.334212	-12.446345
10	H	-10.536499	-1.603917	-10.055506
11	H	-10.681397	-3.869983	-8.984984
12	H	-11.610740	-5.773654	-10.324231
13	C	-13.513899	-6.394520	-14.877998
14	C	-14.725897	-6.174015	-15.550502
15	C	-12.857831	-7.633750	-14.978438
16	C	-15.291800	-7.213629	-16.293907
17	H	-15.204244	-5.204808	-15.458742
18	C	-13.423811	-8.657484	-15.744733
19	H	-11.898234	-7.780369	-14.492890
20	C	-14.645654	-8.453726	-16.396752
21	H	-16.237745	-7.052171	-16.800627
22	H	-12.907326	-9.607430	-15.836708
23	H	-15.085614	-9.250113	-16.988222
24	H	-12.600732	-6.604561	-12.467734
25	Ir	-12.603117	-3.204874	-14.781468
26	O	-14.776914	-1.081981	-14.299362
27	C	-16.206617	-0.993820	-13.873077
28	C	-16.806329	-2.331944	-14.452511
29	O	-12.046211	-0.380427	-16.015661
30	C	-12.004813	1.097433	-15.912329
31	C	-11.090214	1.315044	-14.649207
32	B	-14.425848	-2.440831	-14.520613
33	B	-11.777256	-0.986335	-14.769320
34	O	-11.326001	0.057318	-13.880288

35	O	-15.610536	-3.233019	-14.439545
36	C	-11.477305	2.495142	-13.759551
37	H	-10.806396	2.540743	-12.895068
38	H	-11.389358	3.441663	-14.306617
39	H	-12.500162	2.395490	-13.391524
40	C	-9.590282	1.349349	-14.978339
41	H	-9.312390	2.272742	-15.498490
42	H	-9.020180	1.295933	-14.045314
43	H	-9.305633	0.496856	-15.602256
44	C	-13.460859	1.534645	-15.696470
45	H	-13.549086	2.624964	-15.628969
46	H	-14.058275	1.190573	-16.546351
47	H	-13.872622	1.078145	-14.792704
48	C	-11.453961	1.667200	-17.218536
49	H	-12.139446	1.427836	-18.037639
50	H	-11.362852	2.758788	-17.159922
51	H	-10.476339	1.245791	-17.462155
52	C	-17.249581	-2.217259	-15.917074
53	H	-17.508912	-3.214635	-16.286070
54	H	-18.131134	-1.574481	-16.018550
55	H	-16.440920	-1.831069	-16.542413
56	C	-17.895564	-2.979519	-13.600215
57	H	-18.774166	-2.326633	-13.531152
58	H	-18.208669	-3.921290	-14.061984
59	H	-17.541258	-3.198694	-12.590695
60	C	-16.199298	-0.941281	-12.338797
61	H	-15.584534	-0.094601	-12.018726
62	H	-17.209389	-0.808416	-11.935601
63	H	-15.770219	-1.854385	-11.914954
64	C	-16.795246	0.288513	-14.456732
65	H	-17.866763	0.362167	-14.234580
66	H	-16.295749	1.155762	-14.013083
67	H	-16.655010	0.332519	-15.538390
68	H	-13.187458	-3.590669	-16.175494
69	C	-8.645615	-5.784252	-15.788109
70	C	-8.177031	-4.358481	-16.041135
71	B	-10.377861	-4.253944	-14.941702
72	C	-8.661629	-6.590074	-17.100357
73	H	-7.658640	-6.727365	-17.446859
74	H	-9.112982	-7.544647	-16.927236
75	H	-9.224393	-6.058098	-17.838733
76	C	-7.679467	-6.502390	-14.827674
77	H	-7.986497	-7.520397	-14.708111
78	H	-6.688766	-6.473658	-15.230891
79	H	-7.691856	-6.012081	-13.876704
80	C	-7.976456	-4.119370	-17.549179
81	H	-7.882224	-3.069752	-17.734446
82	H	-7.088671	-4.620127	-17.874723
83	H	-8.819112	-4.502094	-18.086164
84	C	-6.819720	-4.107475	-15.358272
85	H	-6.099057	-4.805756	-15.729685
86	H	-6.492798	-3.110895	-15.570052
87	H	-6.924239	-4.231373	-14.300621
88	C	-10.040583	-5.718154	-15.183332
89	O	-9.234811	-3.412279	-15.491232
90	H	-14.142626	-3.469191	-14.919255

5.6.2. Ir^I-Ir^{III}-Ir^I Catalytic Cycle of Pym-UiO-IrH Catalyzed Monoborylation of Methane

In pym-UiO-IrH catalyzed monoborylation of methane, a Ir^I-Ir^{III}-Ir^I catalytic cycle (Figure 5.20) could be an alternative pathway compared to the Ir^{III}-Ir^V-Ir^{III} catalytic cycle as described in Figure 4 in the main manuscript. According to this cycle, Ir^{III}(diboryl)hydride (INT-A) undergoes reductive elimination of a B–H bond, resulting in the formation of the Ir^I boryl intermediate (INT-B), instead of oxidative addition to form a 7 coordinate, 18-electron Ir^V intermediate (INT-2, Figure 5.4). Subsequent oxidative addition of methane yields Ir^{III}(boryl)(methyl)hydride (INT-C), and further reductive elimination of MeBpin and oxidative addition of B₂pin₂ regenerates INT-A.

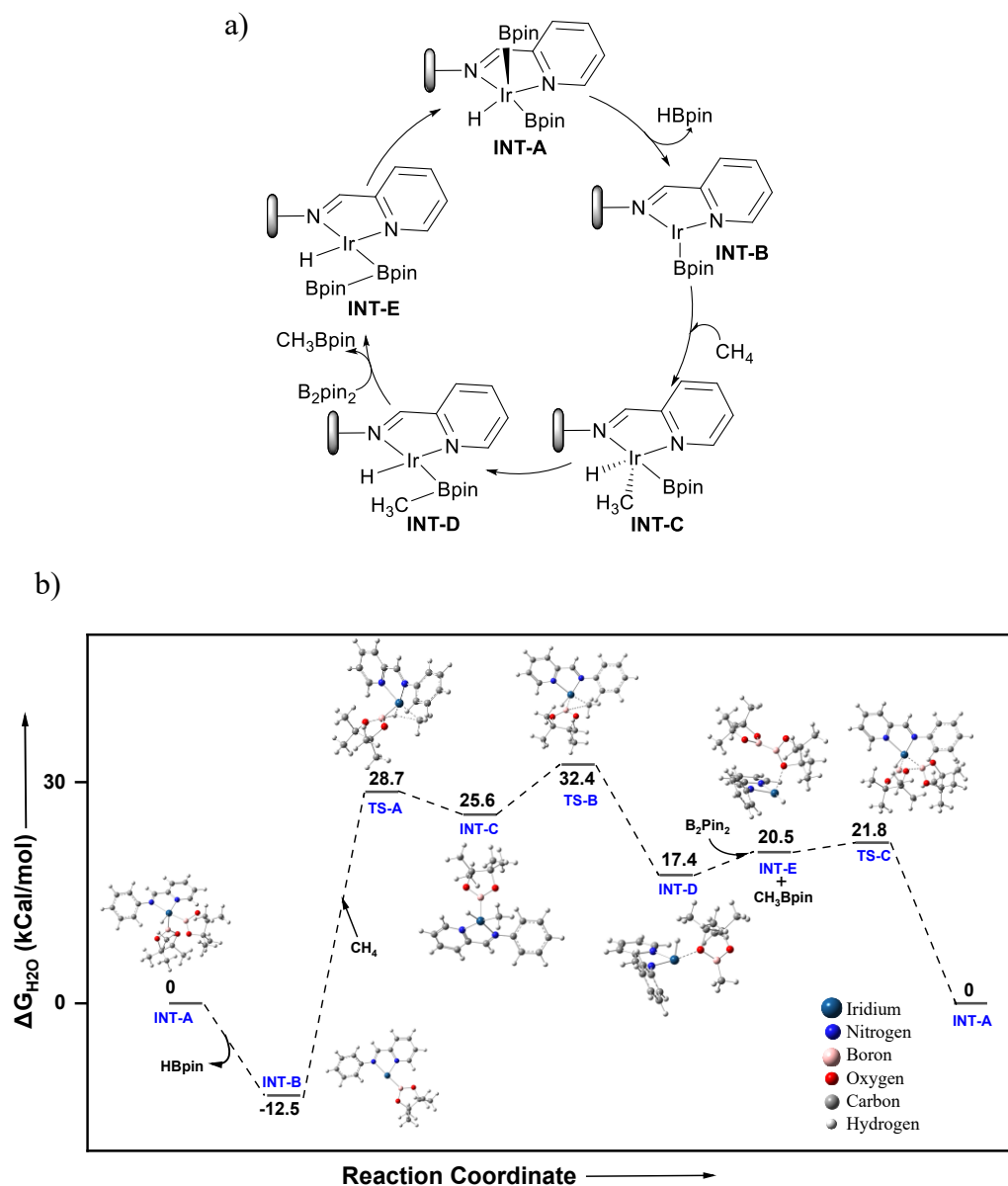


Figure 5.20. (a) Ir^I-Ir^{III}-Ir^I catalytic cycle of pyrim-UiO-IrH catalyzed monoborylation of methane. (b) DFT-calculated free energy profile at 403 K for Ir^I-Ir^{III}-Ir^I catalytic cycle of pyrim-UiO-IrH catalyzed methane borylation reaction. We used the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) as the default SCRF method by using cyclohexane as the solvent for all the molecules in this DFT calculation at 403 K.

Alternatively, pyrim-Ir^I(Bpin) (INT B) reacts with CH₄ to form pyrim-Ir^I(Bpin)(CH₃)(H) (INT-C), which could undergo reductive elimination to give pyrim-Ir^I-CH₃ species. Then, pyrim-Ir^I-CH₃ reacts with B₂pin₂ to give pyrim-Ir^{III}(CH₃)(Bpin)₂, which then gives CH₃Bpin and regenerates INT-B. However, these above two pathways via Ir^I-Ir^{III}-Ir^I catalytic cycle are unlikely due to the high barrier associated with the transformation of INT-B to INT-C, involving CH₄ C-H activation. DFT calculations reveal that the activation energy for methane mono borylation via Ir^I-Ir^{III}-Ir^I cycle is significantly higher compared to that of Ir^{III}-Ir^V-Ir^{III} catalytic cycle, as depicted in Figure 5.4 of the manuscript. Therefore, based on the DFT calculation, we propose that pyrim-UiO-IrH catalyzed methane borylation reaction likely occurs via Ir^{III}-Ir^V-Ir^{III} catalytic cycle.

5.7. XAS Analysis

5.7.1. X-ray Absorption Spectroscopic Analysis

X-ray Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) measurements have been carried out at the Energy-Scanning EXAFS beamLine (BL-9) at the Indus-2 Synchrotron Source at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.²²⁰ All the measurements were performed at room temperature. This beamLine operates in the energy range of 4 keV to 25 keV. The beamLine optics consist of a Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si (111) based double crystal monochromator (DCM). The second crystal of the DCM is a sagittal cylindrical crystal which is used for horizontal focusing of the beam while another Rh/Pt coated bendable post mirror facing downward is used for vertical focusing of the beam at the sample position. Two ionization chambers (300 mm length each) have been used for data collection in the transmission mode; one ionization chamber for measuring incident flux, the second one for measuring transmitted flux. For energy calibration, standard metal foils were used. Appropriate gas pressure and gas mixture have been chosen to achieve 10-20% absorption in the first ionization chamber and 70-90% absorption in the second ionization chamber to obtain a better signal-to-noise ratio. Pellets were made from powder samples for recording absorption spectra. Sample powder was mixed homogeneously with

cellulose powder in appropriate proportion and pressed (2 Ton) into a 15 mm diameter disc. The amount of the sample was estimated such that to get a reasonable edge jump at a particular absorption edge of the element to be probed. Spectra were collected at the iridium L₃-edge in transmission mode and were calibrated against the reference spectrum of metallic iridium (11215 eV). Data were processed using Demeter software.²²¹ Metallic iridium pellet standard was used as a reference for energy calibration and was measured simultaneously with experimental samples.

5.7.2. XANES Analysis

The oxidation states of the Ir species within pyrim-UiO-IrCl₃(THF) and pyrim-UiO-IrH were determined by the comparison of the energy of its L₃-edge positions to that of Ir(0) and IrO₂. The positions of the L₃-edge of pyrim-UiO-IrCl₃(THF) (11219.5 eV) was ~1.5 eV lower than IrO₂ (11221.0 eV), while L₃-edge of pyrim-UiO-IrH (11216.5 eV) was ~1.5 eV higher in energy to Ir(0) (11215 eV). We, therefore, conclude that Ir in pyrim-UiO-IrCl₃(THF) has +3 oxidation state and in pyrim-UiO-IrH has +1 oxidation state.

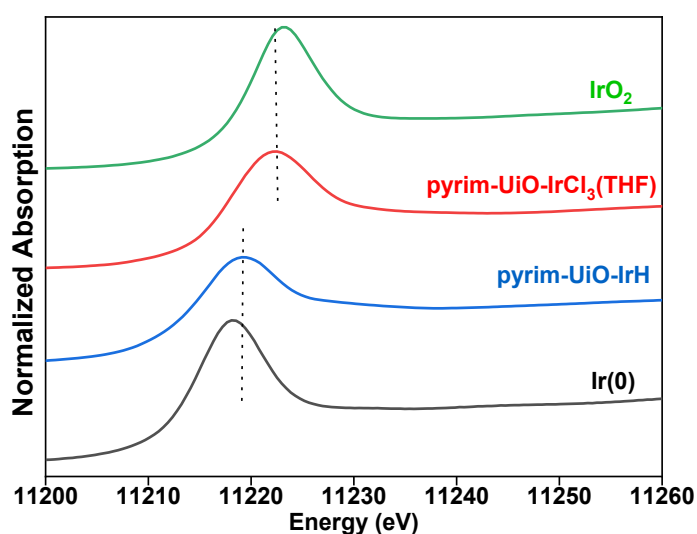


Figure 5.21. Ir L₃-edge XANES spectra of Ir(0) (black), pyrim-UiO-IrH (blue), pyrim-UiO-IrCl₃(THF) (red) and IrO₂(green).

5.7.3. EXAFS Fitting using DFT Optimized Structures

The spectra were calibrated against the reference spectra and aligned to the first peak in the smoothed first derivative of the absorption spectrum, the background noise was removed, and

the spectra were processed to obtain a normalized unit edge step. The fitting parameters of pyrim-UiO-IrCl₃ and pyrim-UiO-IrH are summarized in Table 5.5, and Table 5.6, respectively.

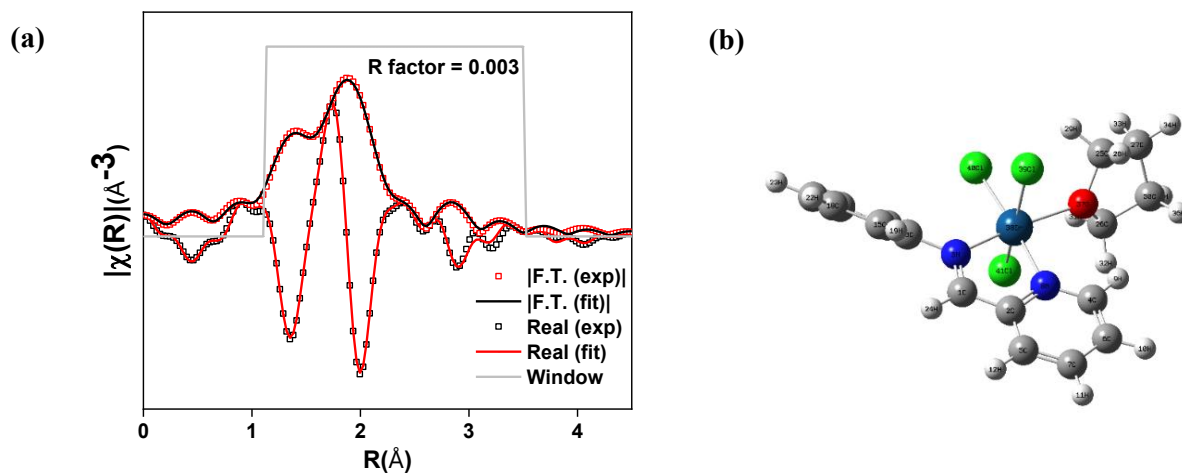


Figure 5.22. (a) EXAFS spectra (red and black hollow squares) and fits (red and black solid lines) of pyrim-UiO-IrCl₃ in the R space from 1.15 - 3.5 Å. (b) DFT optimised structure of (pyrim)IrCl₃(THF) molecule.

Table 5.5. Summary of the EXAFS fitting parameters of pyrim-UiO-IrCl₃.

Sample	Pyrim-IrCl ₃ (THF)	Fitting range	k 3-11 Å ⁻¹ R 1.15-3.5 Å
Independent points	11	R-factor	0.003
Variables	10	S_o^2	0.55
Reduced chi-square	621	ΔE_0 (eV)	6.18
R(Ir-H26) (Å)	1.56±0.06	σ^2 (Ir-H3) (Å ²)	0.005±0.001
R(Ir-N3) (Å)	1.99±0.07	σ^2 (Ir-N3) (Å ²)	0.003±0.004
R(Ir-N8) (Å)	1.99±0.07	σ^2 (Ir-N8) (Å ²)	0.003±0.004
R(Ir-Cl39) (Å)	2.37±0.08	σ^2 (Ir-Cl39) (Å ²)	0.006±0.006
R(Ir-Cl40) (Å)	2.37±0.08	σ^2 (Ir-Cl40) (Å ²)	0.006±0.006
R(Ir-Cl41) (Å)	2.37±0.08	σ^2 (Ir-Cl41) (Å ²)	0.006±0.004
R(Ir-C1) (Å)	2.80±0.04	σ^2 (Ir-C1) (Å ²)	0.002±0.004
R(Ir-C2) (Å)	2.80±0.04	σ^2 (Ir-C2) (Å ²)	0.002±0.001
R(Ir-C13) (Å)	3.02±0.05	σ^2 (Ir-C13) (Å ²)	0.002±0.001
R(Ir-C4) (Å)	3.02±0.05	σ^2 (Ir-C4) (Å ²)	0.002±0.001

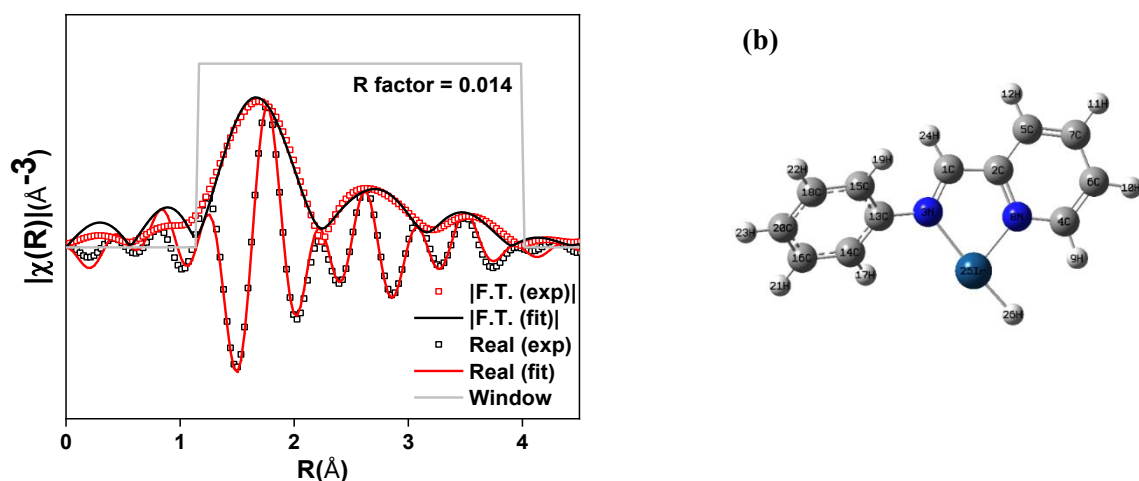


Figure 5.23. (a) EXAFS spectra (red and black hollow squares) and fits (red and black solid lines) of pyrim-UiO-IrH in the R space from 1.15 - 4.0 Å. (b) DFT optimised structure of pyrim-IrH.

Table 5.6. Summary of the EXAFS fitting parameters of pyrim-IrH.

Sample	Pyrim-IrH	Fitting range	k 3-10.5 Å ⁻¹ R 1.15-4.0 Å
Independent points	13	R-factor	0.017
Variables	11	S_o^2	0.81
Reduced chi-square	889	ΔE_0 (eV)	9.65
R(Ir-N3) (Å)	1.99±0.06	σ^2 (Ir-N3) (Å ²)	0.008±0.004
R(Ir-N8) (Å)	1.99±0.06	σ^2 (Ir-N8) (Å ²)	0.008±0.004
R(Ir-C1) (Å)	2.70±0.08	σ^2 (Ir-C1) (Å ²)	0.009±0.006
R(Ir-C2) (Å)	2.70±0.08	σ^2 (Ir-C2) (Å ²)	0.009±0.006
R(Ir-C13) (Å)	3.01±0.07	σ^2 (Ir-C13) (Å ²)	0.009±0.004
R(Ir-C4) (Å)	3.01±0.07	σ^2 (Ir-C4) (Å ²)	0.009±0.004
R(Ir-C14) (Å)	3.26±0.09	σ^2 (Ir-C14) (Å ²)	0.003±0.001
R(Ir-C15) (Å)	4.31±0.05	σ^2 (Ir-C15) (Å ²)	0.005±0.001
R(Ir-C5) (Å)	4.31±0.05	σ^2 (Ir-C5) (Å ²)	0.005±0.001
R(Ir-C4) (Å)	4.32±0.05	σ^2 (Ir-C4) (Å ²)	0.005±0.001

5.8. XPS Analysis

All the binding energies were corrected with reference to the C1s peak at 284.8 eV. MULTIPAK software was used for peak analysis and de-convolution studies.

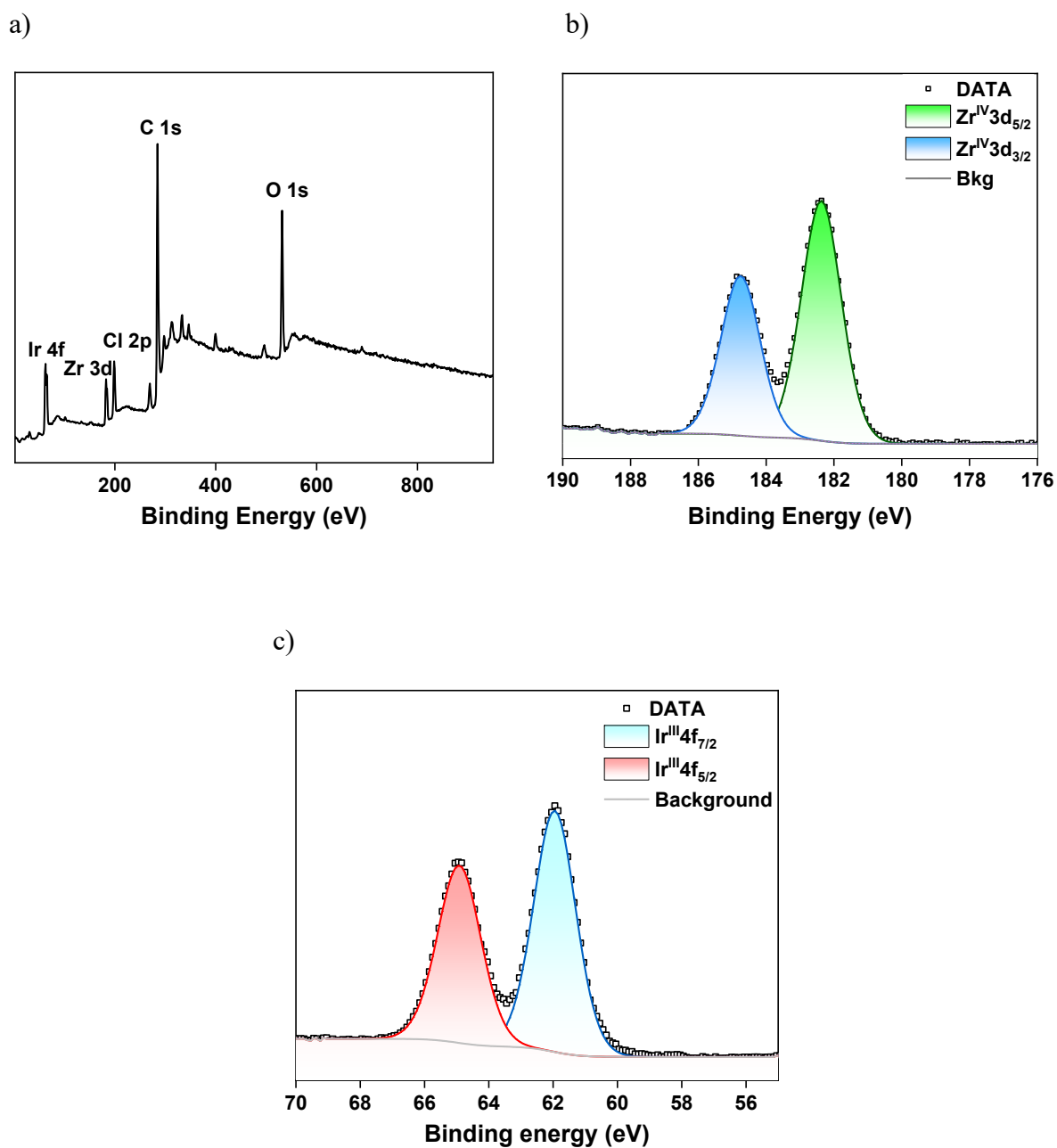


Figure 5.24. a) Raw XPS data of pyrim-UiO-IrCl₃; b) Zr 3d XPS spectrum of pyrim-UiO-IrCl₃; c) Ir 4f XPS spectrum of pyrim-UiO-IrCl₃.

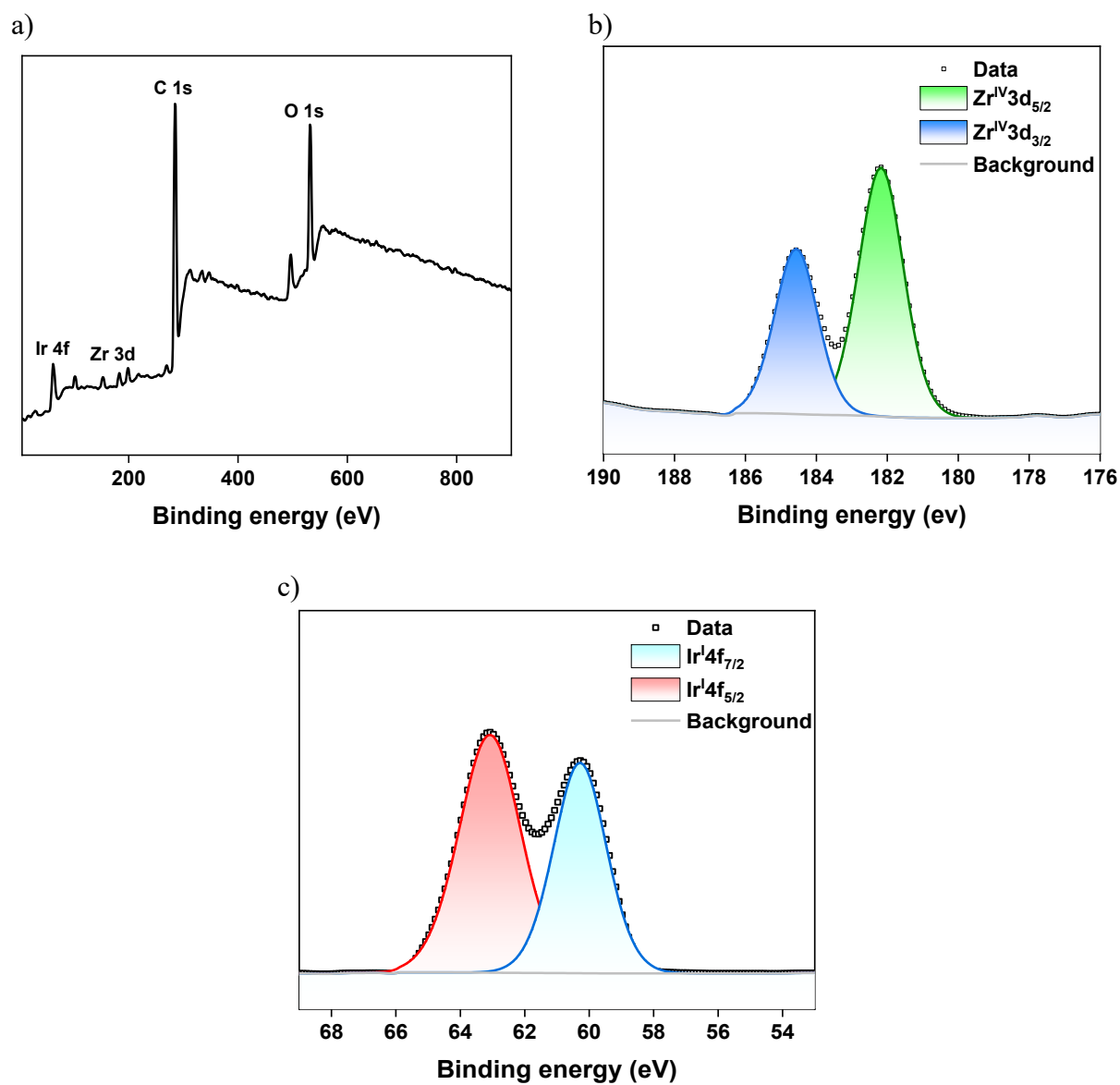


Figure 5.25. a) Raw XPS data of pyrim-UiO-IrH; b) Zr 3d XPS spectrum of pyrim-UiO-IrH; c) Ir 4f XPS spectrum of pyrim-UiO-IrH.

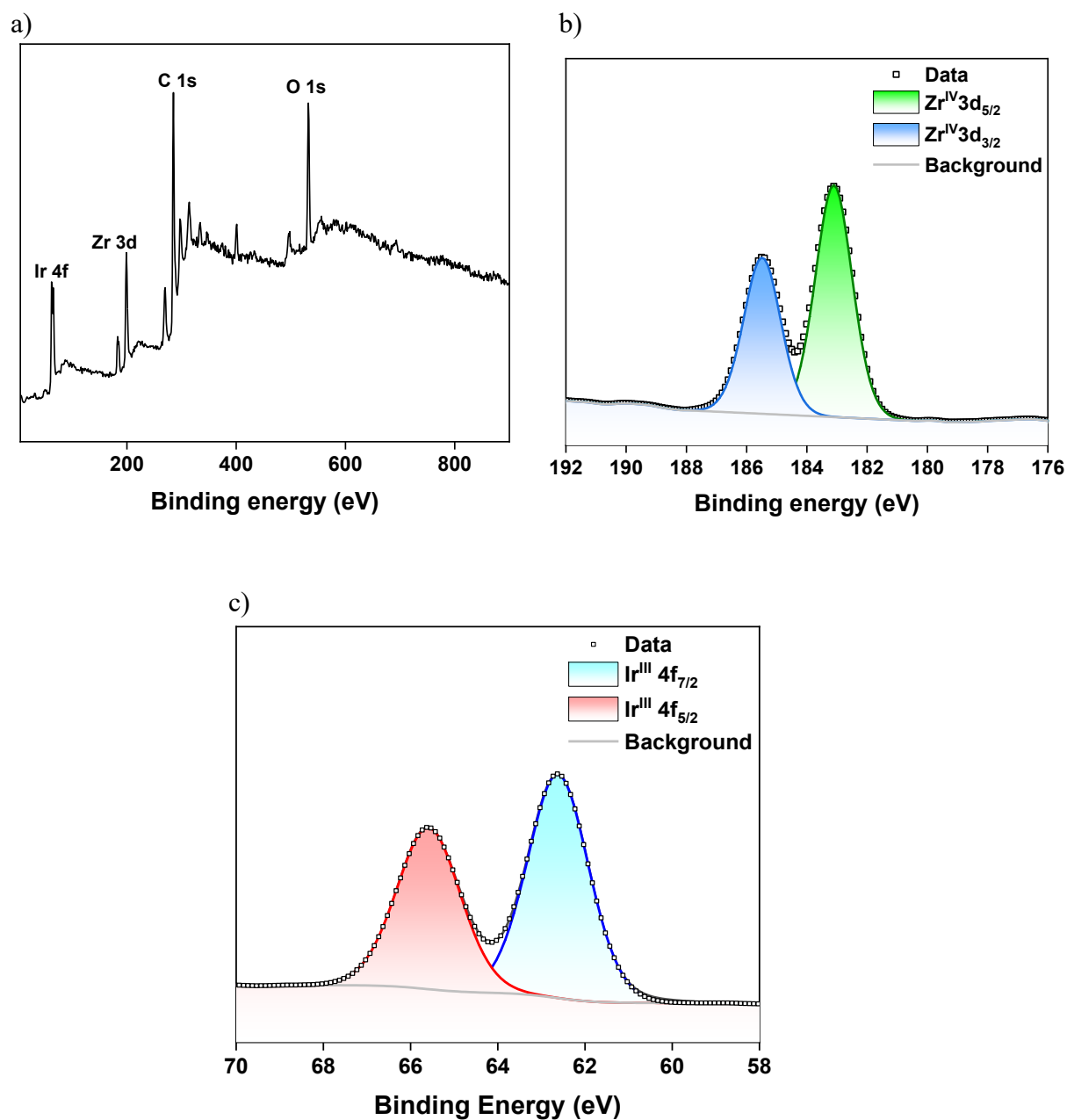


Figure 5.26. a) Raw XPS data of pyrim-UiO-IrH(Bpin)₂; b) Zr 3d XPS spectrum of pyrim-UiO-IrH(Bpin)₂; c) Ir 4f XPS spectrum of pyrim-UiO-IrH(Bpin)₂.

Table 5.7. Comparison of catalytic activity of pyrim-UiO-IrH with that of other reported catalysts in borylation of CH₄.

Catalysts	CH ₄ pressure	Temp. (Time h)	Yield (TON) of CH ₃ Bpin	Reference
[Ir(COD)Cl] ₂ + dmpe	34.47 bar	150 °C (16)	52% (104)	<i>Science</i> 2016 , 351, 1424.
(MesH)Ir(Bpin) ₃ + 3,4,7,8-tetramethylphenanthroline	35 bar	150 °C (14)	45% (15)	<i>Science</i> 2016 , 351, 1421-1424.
(dmpe)Ir(COD)Cl	500 psi	150 °C (16)	31% (153)	<i>ACS Catal.</i> 2018 , 8, 10021.
UiO-67-Mix-Ir (0.49)	34 bar	150 °C (14)	19.5% (67)	<i>Nat. Catal.</i> 2018 , 1 (5), 356.
Zr-P1-Ir (0.3)	50 bar	110 °C (15)	38% (127)	<i>J. Am. Chem. Soc.</i> 2019 , 141, 11196–11203.
CAL-3-Ir	34 bar	150 °C (9)	29% (126)	<i>Angew. Chem. Int. Ed.</i> 2019 , 58, 10671–10676.
[(dmpe)Ir(cod)]-SiO ₂ (0.069)	34.47 bar	150 °C (16)	82.8% (1204)	<i>J. Am. Chem. Soc.</i> 2023 , 145, 7992–8000.
Pyrim-UiO-IrH (0.5)	40 bar	130 °C (24)	98% (196)	This work

5.9. Conclusion

In conclusion, we have developed a porous MOF-supported iridium catalyst for chemoselective monoborylation of methane, affording CH₃Bpin in up to 98% yield, which is significantly higher than previously reported systems. As a heterogeneous catalyst, pyrim-UiO-IrH exhibits excellent structural stability and recyclability, maintaining consistent catalytic activity for at least five catalytic cycles without noticeable changes in crystallinity or framework integrity, resulting in a cumulative turnover number (TON) of up to 980. Importantly, pyrim-UiO-IrH demonstrates at least 24 times higher catalytic activity than the corresponding homogeneous analogue, [Ph(pyrim)(PhCO₂Me)₂]IrH, highlighting the beneficial role of MOF confinement and active-site isolation in stabilizing reactive Ir–H species and preventing bimolecular catalyst decomposition. Mechanistic investigations suggest that oxidative addition of methane to the Ir(III)(Bpin)₂(H) intermediate generates a high-valent Ir(V)(Bpin)₂(CH₃)(H)₂ species as the turnover-limiting step. The MOF framework provides a confined coordination environment that stabilizes key catalytic intermediates and promotes efficient C–H activation under relatively mild conditions. Overall, this work demonstrates the importance of MOFs as an effective platform for designing robust heterogeneous catalysts with well-defined single active sites, enabling highly selective functionalization of methane and other light hydrocarbons into value-added chemical building blocks.

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

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Abstract: 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.

6.1 Introduction

Direct transformation of methane into methylborane via chemoselective monoborylation of a methane C–H bond is highly appealing due to the abundance of methane as the inexpensive carbon feedstock and the application of organoborane products as versatile reagents and intermediates for organic synthesis.^{297–299} However, methane activation under mild conditions is extremely difficult owing to its high C–H bond dissociation energy (104 kcal/mol), large HOMO-LUMO gap, low acidity and poor solubility in any solvent.^{300–302} In addition, borylation of methane often suffers from poor selectivity because of over-borylation of methane, competitive solvent C–H borylation, and boron-byproducts generation (Figure 6.1a).

To date, all the reported catalysts for methane C–H borylation are based on late transition metals, such as Ir, Rh and Ru, which activate methane by oxidative addition (Figures 1b and 1c).^{304,305,312–315,320,323} In addition, bis(pinacolato)diboron (B_2pin_2) is used as the borylating agent because the reaction between CH_4 and B_2pin_2 to form CH_3Bpin and pinacolborane ($HBpin$) is thermodynamically downhill.²⁹⁹ In 2016, Sanford³²⁴ and Mindiola³²⁵ reported homogeneous 1,10-phenanthroline- and diphosphine-ligated Ir, Rh and Ru catalysts for borylation of methane using B_2pin_2 , yielding a mixture of monoborylated (CH_3Bpin) and diborylated [$CH_2(Bpin)_2$] products with selectivity spanning 2:1 to 31:1. Later, Farha and co-workers developed a heterogeneous iridium(III) catalyst confined within a porous metal–organic framework (MOF) to facilitate the selective monoborylation over multiborylation via shape-selective catalysis, affording CH_3Bpin in 99% chemoselectivity with a turnover number (TON) of 67.⁵⁶ Despite notable advances, all these catalytic reactions employ toxic precious metals and have a low boron atom economy (typically <50%) due to the formation of an equivalent amount of $HBpin$. Moreover, methane borylation often faces challenges such as poor selectivity due to over-borylation of methane, competitive solvent C–H borylation, and the generation of boron byproducts such as $HOBpin$ and $pinBOBpin$ (Figure 6.1a).

As porous and tunable molecular materials, MOFs^{17,35,41} have been recently employed to develop robust and active base-metal catalysts for methane activation, owing to their structural diversity, high surface area, isorecticular nature, tunable pores and ease of post-synthetic modification.^{188,267,274} The rigid MOF framework stabilizes homogeneously inaccessible and highly active base-metal species via active-site isolation by preventing multinuclear deactivation pathways.^{64,306,319} Herein, we report the development of a heterogeneous earth-abundant metal catalyst employing MOFs for selective monoborylation

of methane using HBpin as the borylating agent (Figure 6.1d). The MOF catalyst (bpy-UiO-NiH₂), consists of zirconium UiO-67 MOF³¹⁸ as a porous and robust solid support with monomeric bipyridyl Ni(II)-dihydride catalytic species at its linkers within the pores. The zirconium UiO-67 MOFs, constructed from Zr₆(μ₃-O)₄(μ₃-OH)₄ secondary building units (SBUs) and linear dicarboxylate bridging linkers, are thermally and chemically robust under various reaction conditions. The uniform and rigid pores of UiO-67 framework with an aperture size of 0.8 nm and an octahedral cavity of 1.1 nm³ allow diffusion for only CH₄ (0.38 nm), HBpin (0.73 × 0.59 nm) and CH₃Bpin (0.88 × 0.73 nm, linear), however, restrict the formation of larger and thermodynamically more favoured multiborylated products such as CH₂(Bpin)₂ (1.39 × 0.8 nm, bent),⁵⁶ leading to the formation of only CH₃Bpin in 98% selectivity via shape-selective catalysis.

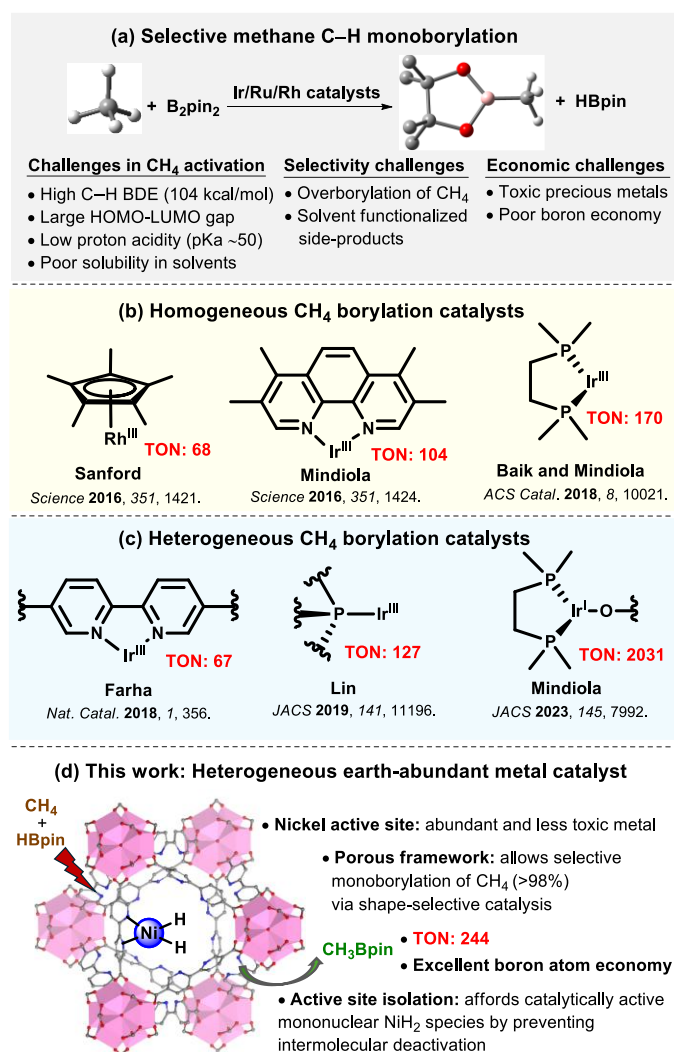


Figure 6.1. (a) Methane C–H monoborylation using B₂pin₂. (b–c) Types of reported homogeneous and heterogeneous catalysts for methane monoborylation. (d) This work: selective monoborylation of methane by base-metal catalysts using HBpin.

6.2. Results and Discussion

6.2.1. Synthesis and Characterization of Bpy-UiO-NiH₂

Bpy-UiO-NiH₂ MOF was synthesized by post-synthetic metalation of the bipyridine moiety of the pristine bpy-UiO-67 MOF, which is built from Zr₆O₄(OH)₄ nodes and 2,2'-bipyridine-5,5'-dicarboxylate (bpy) bridging linkers. Stirring a slurry of bpy-UiO in THF solution of NiBr₂ at room temperature afforded bpy-UiO-NiBr₂ MOF bearing bipyridyl-NiBr₂ species at its linkers (Figure 6.2a). The UiO-67 topology of bpy-UiO MOF, as well as the retention of the MOF's structure and crystallinity upon metalation, were confirmed by the similarity in powder X-ray diffraction (PXRD) patterns between simulated UiO-67, pristine bpy-UiO and bpy-UiO-NiBr₂ (Figure 6.2b). X-ray photoelectron spectroscopy (XPS) analysis of bpy-UiO-NiBr₂ displayed Ni 2p_{3/2} and 2p_{1/2} binding energy peaks at 855.5 eV and 873.2 eV, respectively, indicating +2 oxidation state of Ni ion (Figure 6.2c). The X-ray absorption near-edge structure (XANES) of bpy-UiO-NiBr₂ showed that the Ni K-edge energy at 8347.8 eV is closely aligned with that of NiBr₂ (8347 eV) and ~15 eV higher than Ni(0) foil, further confirming the presence of Ni²⁺ species (Figure 6.2d). The extended X-ray absorption fine structure (EXAFS) of bpy-UiO-NiBr₂ at the Ni K-edge fitted well with the DFT-optimized structure of a tetrahedral bipyridyl-NiBr₂ complex, suggesting that Ni²⁺ ion in bpy-UiO-NiBr₂ is tetrahedrally coordinated with two nitrogen atoms of bipyridine and two bromides (Figure 6.2e). Next, the treatment of bpy-UiO-NiBr₂ with NaEt₃BH in THF at room temperature yielded bpy-UiO-NiH₂ bearing mononuclear bipyridyl-nickel dihydride species at the linkers. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis of the digested bpy-UiO-NiH₂ MOF revealed a Ni-loading of ~25% with respect to the bipyridyl linkers, giving a molecular formula of Zr₆(μ₃-O)₄(μ₃-OH)₄(bpy)₆Ni_{1.5}H₃. Scanning electron microscopy (SEM) of bpy-UiO-NiH₂ revealed octahedral particles with average sizes of 250 nm, while energy dispersive X-ray (EDX) mapping showed a uniform distribution of Ni and Zr throughout the MOF particles (Figures 6.6-6.7). Bpy-UiO-NiH₂ displays a BET surface area of 1260 m²/g and a pore diameter of 0.68 nm (Figure 6.9). The reduction in surface area and pore sizes, compared to 2247 m²/g and 0.75 nm for pristine bpy-UiO MOF, is attributed to the incorporation of the NiH₂ moiety within the MOF's pore. The infrared (IR) spectrum (KBr) of bpy-UiO-NiH₂ exhibited a characteristic ν_{Ni-H} stretching frequency at 1948 cm⁻¹ (Figure 6.10).³²⁶ The XPS spectrum of bpy-UiO-NiH₂ showed Ni 2p_{3/2} and 2p_{1/2} binding energies at 855.1 eV and 872.8 eV, respectively, confirming the presence of Ni²⁺ ion after NaEt₃BH treatment (Figure 6.2c).

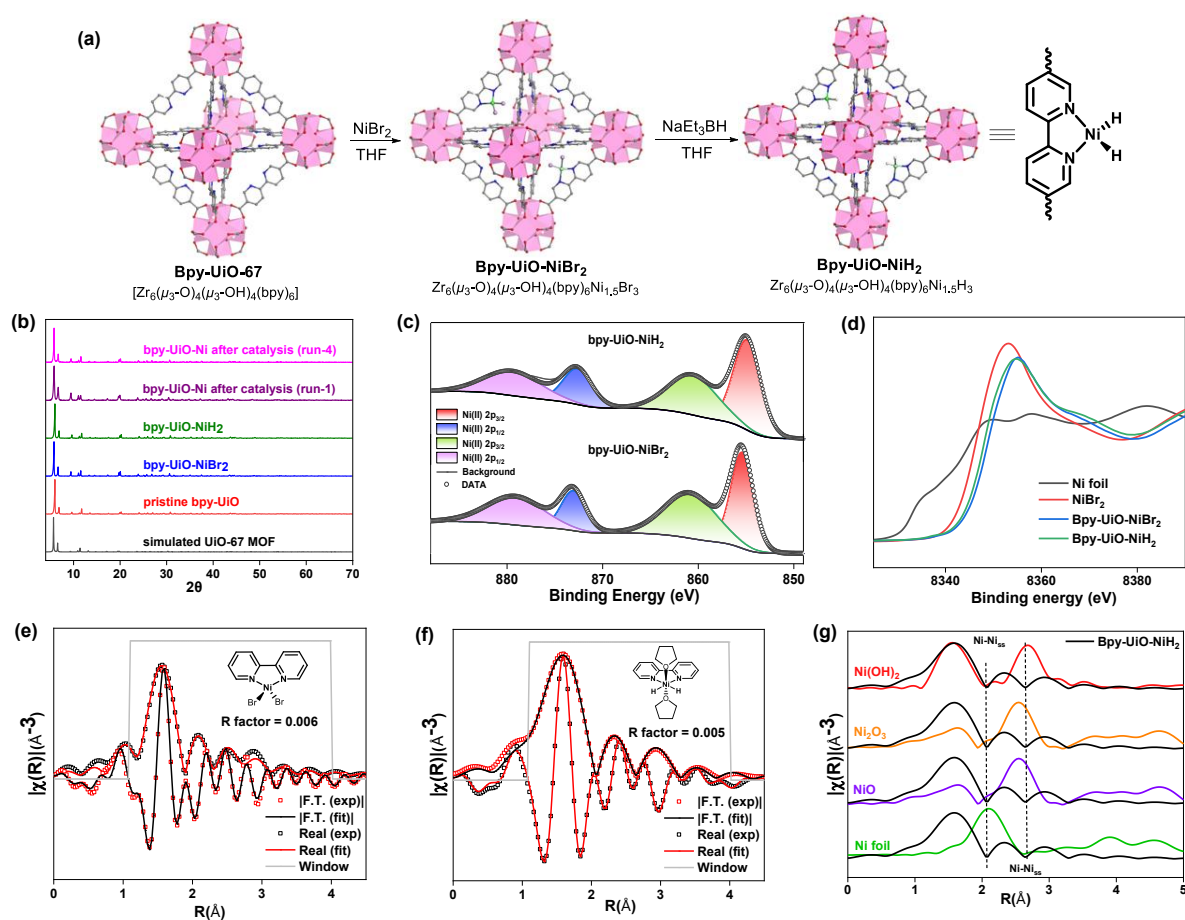


Figure 6.2. (a) Synthesis of bpy-Uio-NiH₂ by post-synthetic modification of the pristine bpy-Uio MOF. (b) PXRD patterns of simulated UiO-67 MOF (black), pristine bpy-Uio MOF (red), bpy-Uio-NiBr₂ (blue), bpy-Uio-NiH₂ (green), recovered bpy-Uio-Ni after run-1 of catalysis (purple) and recovered bpy-Uio-Ni after run-4 of catalysis (magenta). (c) Nickel 2p XPS spectra of bpy-Uio-NiBr₂ and bpy-Uio-NiH₂. (d) $\mu(E)$ XAS spectra of Ni foil (black), NiBr₂ (red), bpy-Uio-NiBr₂ (blue) and bpy-Uio-NiH₂ (green). (e) EXAFS spectrum (red and black squares) and fits (black and red lines) of bpy-Uio-NiBr₂ in the R space from 1.1–4.0 Å. (f) EXAFS spectrum (red and black squares) and fits (black and red lines) of bpy-Uio-NiH₂(THF)₂ in the R space from 1.1–4.0 Å. (g) Comparison of k^2 -weighted Ni-EXAFS $\chi(R)$ spectra of Ni foil (green), NiO (violet), Ni₂O₃ (orange) and Ni(OH)₂ (red) with that of bpy-Uio-NiH₂ (black).

Furthermore, XANES of bpy-Uio-NiH₂ revealed a Ni K-edge energy of 8347.4 eV, approximately 0.4 eV higher than that of NiBr₂ and 0.4 eV lower compared to bpy-Uio-NiBr₂, reinforcing the presence of Ni in the +2 oxidation state. The EXAFS data of bpy-Uio-NiH₂ at the Ni K-edge, fitted with the Density Functional Theory (DFT)-optimized model of bpy-Uio-NiH₂(THF)₂, revealed that the Ni ion is octahedrally coordinated by two nitrogen atoms from the bipyridine moiety (1.94, 1.94 Å), two hydrides, and two axial THF molecules (2.34, 2.34 Å) (Figure 6.2f). In the raw phase uncorrected k^2 -weighted Ni-EXAFS $\chi(R)$ spectrum of bpy-Uio-NiH₂, Ni···Ni scattering features of metallic Ni (Ni foil), Ni₂O₃ and Ni(OH)₂ at 2.1 Å and 2.55 Å are absent, which rules out the existence of any Ni(0) or Ni-oxide nanoparticles within bpy-Uio-NiH₂ (Figure 6.2g). To further investigate any minor percentages of Ni nanoparticles

that might co-exist with bpy-UiO-NiH₂, EXAFS fitting with different percentages of Ni(0) nanoparticles was conducted, which resulted in significant misfits (Figure 6.24). Moreover, the possible coordination of the Ni ion at the metal-oxo nodes of bpy-UiO MOF was excluded by fitting the raw EXAFS data of bpy-UiO-NiH₂ with the DFT-optimized structure of NiH₂ supported at μ_3 -OH nodes (Figure 6.25). The EXAFS analysis thus revealed that bpy-UiO-NiH₂ contains single-site, monomeric (bpy)Ni^{II}(H)₂ species, with no neighbouring Ni atoms.

6.2.2. Bpy-UiO-NiH₂ Catalyzed Borylation of Methane

Bpy-UiO-NiH₂ was utilized as a heterogeneous catalyst for methane borylation, with HBpin serving both as the borylating agent and the limiting reagent. The borylation reactions were first screened in a high-pressure batch reactor by varying reaction temperature, CH₄ pressure, reaction time and catalyst loading to optimize the yield of monoborylated product, CH₃Bpin. At a 0.25 mol% of Ni-loading, bpy-UiO-NiH₂ catalyzed CH₄ borylation in THF and 200 °C under 20 bar of CH₄ primarily produced borylated THF, and CH₃Bpin was afforded only in 9% yield (entry 1, Table 6.1). Reactions in hydrocarbon solvents, such as heptane, toluene, dodecane and methyl cyclohexane gave low yields (28-50%) of CH₃Bpin, due to the formation of various byproducts, including borylated solvents, pinBOBpin and HOBpin (entries 2-5, Table 6.1). Borylation in cyclohexane furnished the highest CH₃Bpin yield of 61% (entry 6, Table 6.1). Importantly, excellent selectivity (96-98%) for CH₃Bpin over CH₂(Bpin)₂ was achieved in all the reactions. The borylation of methane did not occur below 150 °C, and the formation of a substantial amount of boron-byproducts was detected at 250 °C (entries 7-9, Table 6.1).

Table 6.1. Variations of reaction temperature and solvents for bpy-UiO-NiH₂ catalyzed borylation of methane.^[a]

$$\text{CH}_4 + \text{H}-\text{B}(\text{pin})_2 \xrightarrow[\text{T, solvent}]{\text{Bpy-UiO-NiH}_2 \text{ (0.25 mol\% Ni)}} \text{CH}_3\text{Bpin} + \text{CH}_2(\text{Bpin})_2 + \text{H}_2$$

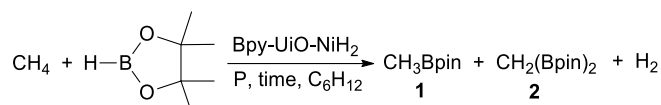
1
2

Entry	Solvent	Temp. (°C)	Conv. of HBpin	%Yield of 1 ^[b] (Selectivity) ^[c]	TON ^[d]
1	THF	200	100	9 (97)	36
2	Heptane	200	100	48 (97)	192
3	Toluene	200	100	28 (96)	112
4	C ₁₂ H ₂₆	200	100	50 (98)	200
5	CH ₃ C ₆ H ₁₁	200	100	38 (97)	152
6	C ₆ H ₁₂	200	100	61 (98)	244
7	C ₆ H ₁₂	100	3	0	--
8	C ₆ H ₁₂	150	35	20 (98)	80
9	C ₆ H ₁₂	250	100	36 (92)	144

^[a]Reaction conditions: 2 mg of bpy-UiO-NiH₂ (1.37 μ mol Ni, 0.25 mol% of Ni), HBpin (0.55 mmol), 2 mL solvent, 20 bar CH₄, 10 h. ^[b]Yield was determined by GC-FID using mesitylene as an internal standard, calculated as [moles (CH₃Bpin)/initial moles of HBpin] $\times$ 100. ^[c]CH₃Bpin selectivity = [moles of (CH₃Bpin)/moles of {CH₃Bpin + CH₂(Bpin)₂}] $\times$ 100. ^[d]TON = %Yield of CH₃Bpin/%Ni-loading.

Reactions under 10 bar and 30 bar of CH₄ afforded CH₃Bpin in only 24% and 46% yields, respectively, due to the lesser solubility of CH₄ at lower pressure and the formation of more diborylated product at higher pressure (entries 3-6, Table 6.2). Increasing the nickel-loading from 1.37 μ mol to 2.7 μ mol (entry 8, Table 6.2) resulted in the complete conversion of HBpin in lesser time but yielded CH₃Bpin in poor quantity, because of the competing borylation of the cyclohexane solvent. Under the optimized reaction conditions of 200 °C, 20 bar of CH₄ and 10 h of reaction time in cyclohexane solvent with 0.25 mol% Ni-loading, bpy-UiO-NiH₂ selectively monoborylated methane to afford CH₃Bpin in 61% yield with 100% HBpin conversion and a TON of 244 (entry 6, Table 6.1). The recyclability of the heterogeneous MOF catalyst was confirmed by consistent activity over at least six consecutive cycles, giving a cumulative TON of 1388. Notably, using B₂pin₂ instead of HBpin resulted in a negligible yield of CH₃Bpin (entry 10, Table 6.2).

Table 6.2. Variations of catalyst loading, pressure and reaction time for the borylation of methane.^[a]



Entry	Ni-loading (mol%)	P (bar)	Time (h)	Conv. of HBpin	%Yield of 1 (Selectivity)	TON
1	0.25	20	6	74	45 (98)	180
2	0.25	5	18	100	22 (98)	88
3	0.25	10	10	100	24 (98)	96
4	0.25	10	24	100	28 (98)	88
5	0.25	30	10	100	46 (90)	184
6	0.25	40	10	100	38 (78)	152
7	0.12	20	10	76	30 (98)	250
8	0.5	20	10	100	48 (98)	96
9 ^[b]	0.25	20	10	8	0	--
10 ^[c]	0.25	20	10	13	0	--
11 ^[d]	0.25	20	10	84	51 (98)	204
12 ^[e]	0.25	20	10	100	60 (98)	240

^[a]Reaction conditions: bpy-UiO-NiH₂, HBpin (0.55 mmol), 200 °C, 2 mL C₆H₁₂. ^[b]Nitrogen was used instead of methane. ^[c]B₂pin₂ was used as borylating agent. ^[d]1.2 equivalent of tricyclohexylphosphine w.r.t. Ni was added in the feed. ^[e]Catalysis was performed in the presence of a drop of Hg.

6.3. Control Experiments

We attempted to synthesize the homogeneous control to investigate the role of the MOF in stabilizing molecular bipyridyl-NiH₂ catalyst and its selectivity for borylated products. The reaction between 5,5'-dimethyl-2,2'-bipyridine (Me₂bpy) and NiBr₂ in 1:1 molar ratio in a polar solvent such as CH₃OH, THF always gave [(Me₂bpy)₂NiBr(H₂O)]Br, which was isolated and characterized by single-crystal X-ray crystallography (Figure 6.3a). The formation of (Me₂bpy)₂NiBr₂ is presumably due to the intermolecular disproportionation between the two putative (Me₂bpy)NiBr₂ intermediate molecules. In contrast, such intermolecular interaction is prohibited in bpy-UiO-Ni MOF due to the isolation of the active Ni-sites. Importantly, (Me₂bpy)₂NiBr₂, upon treatment with NaEt₃BH, was barely active in methane borylation, affording a mixture of CH₃Bpin and CH₂(Bpin)₂ in only 4% yield (Entry 9, Table 6.7). Similarly, the nickel complexes prepared from 1,10-phenanthroline or bulkier N-donor ligand, such as 4,4'-tert-butyl-2,2'-bipyridine in 1:1 molar ratio of ligand to Ni yielded only 12% and 17% of CH₃Bpin, respectively (Figure 6.4a). The lack of catalytic activity of the homogeneous controls underscores the crucial role of the MOF in stabilizing the mono-bipyridyl nickel(II) hydride catalyst via active site isolation by preventing intermolecular degradation pathways.

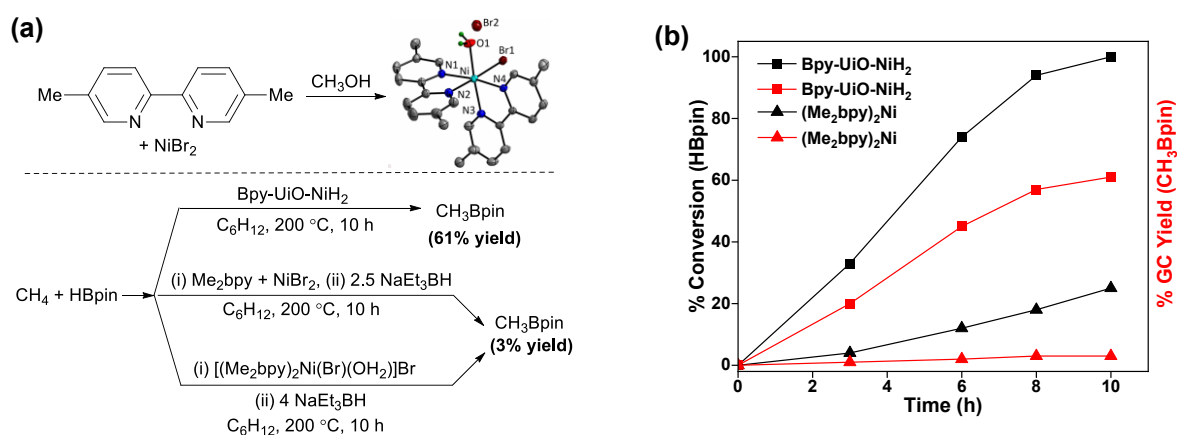


Figure 6.3. (a) CH₄ borylation using homogeneous control of bpy-UiO-Ni. (b) Time evaluation studies of CH₄ borylation reactions using bpy-UiO-NiH₂ and its homogenous control [(Me₂bpy)₂Ni] under identical conditions.

The control experiment with 20 bar of N₂ instead of CH₄ under optimized conditions did not generate any CH₃Bpin, indicating CH₄ as the sole carbon source in CH₃Bpin formation (Section 6.5.2.2). CH₃Bpin formation ceased upon removing the solid MOF from the reaction mixture, indicating that the catalytic species is embedded within the MOF (Figure 6.15). The rate of bpy-UiO-NiH₂-catalyzed borylation of methane remained unchanged in the presence of a drop of Hg, ruling out the involvement of Ni-nanoparticles or any leached Ni species as the

potential catalysts (Figure 6.16). The borylation reactions of methane (a) without bpy-UiO-NiH₂ catalyst and (b) with pristine bpy-UiO MOF, NiBr₂, Ni(OH)₂ or NiO gave no methylated product (Figure 6.4a). In addition, Ni-nanoparticles and Ni(0)@UiO-67 were barely active in methane borylation, confirming the active role of monomeric (bpy)Ni^{II}H₂ species within MOF (Figure 6.4a). To confirm that the chemoselective methane borylation occurring within the pores of bpy-UiO-NiH₂, an experiment with bulky phosphine such as tricyclohexylphosphine was performed to poison the surface nickel active-sites.⁵⁶ The addition of 1.2 equivalent of tricyclohexylphosphine per nickel ion of the bpy-UiO-NiH₂ catalyst resulted in a drop of conversion to ~84%, while the chemoselectivity for the monoborylated product remained unaltered, suggesting that the nickel active sites are mostly embedded within the MOF framework, leading to selective methane monoborylation via size-selective catalysis (entry 11, Table 6.2).

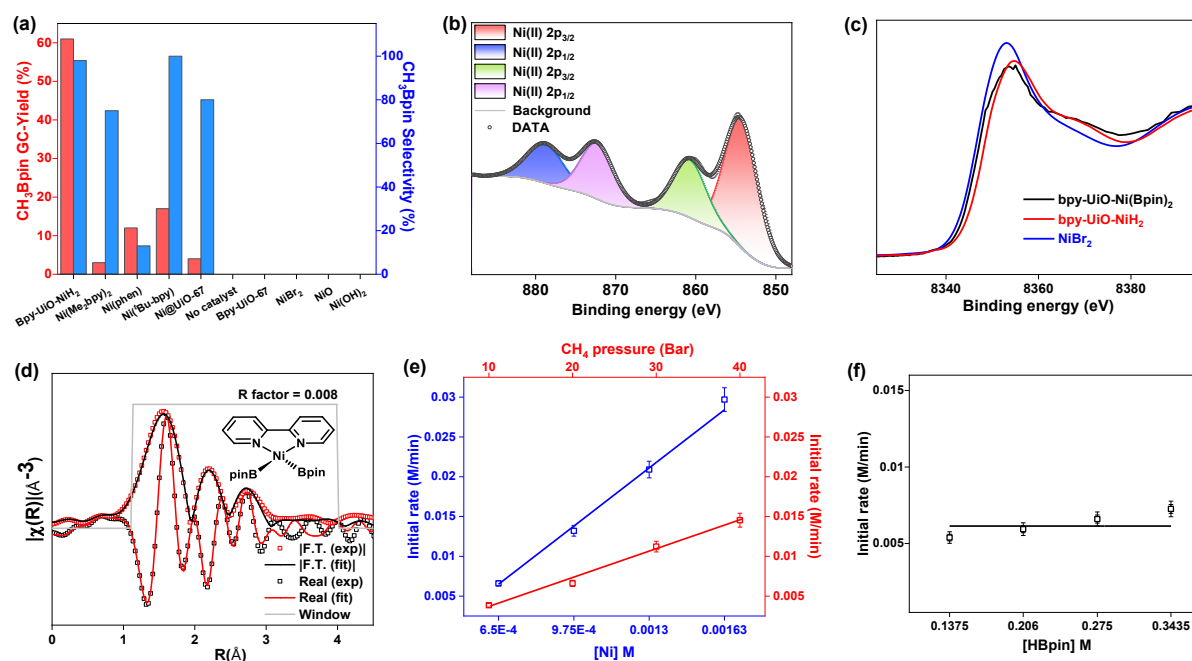


Figure 6.4. (a) Comparison of the catalytic activity for the conversion of CH₄ to CH₃Bpin over bpy-UiO-NiH₂ with other catalysts under identical reaction conditions. Reaction conditions: 2 mg of bpy-UiO-NiH₂ (1.37 μ mol Ni, 0.25 mol% of Ni), HBpin (0.55 mmol), 2 mL solvent, 20 bar CH₄, 10 h. Selectivity is mentioned w.r.t. CH₂(Bpin)₂. (b) Nickel 2p XPS spectrum of bpy-UiO-Ni after catalysis. (c) $\mu(E)$ XAS spectra of NiBr₂ (blue), bpy-UiO-NiH₂ (red) and bpy-UiO-Ni(Bpin)₂ (black). (d) EXAFS spectrum (red and black squares) and fits (black and red lines) of bpy-UiO-Ni(Bpin)₂ in the R space from 1.1 - 4.0 Å. (e-f) Kinetic plots of initial rates for borylation of methane *versus* initial concentrations of nickel, HBpin and initial pressure of CH₄ (bar) for the first 5 min (<15% conversion).

The PXRD, SEM, XPS, and ICP analyses of the used catalyst demonstrated the durability of the UiO framework and the catalytic component after catalysis. The bpy-UiO-Ni maintained its crystallinity and structural integrity during borylation reaction, as indicated by the PXRD patterns and SEM images of the recovered MOF (Figure 6.2b, 6.11). The XPS spectrum of bpy-UiO-Ni following catalysis exhibited Ni 2p_{3/2} and 2p_{1/2} binding energies at 855.0 eV and 872.7 eV, respectively, confirming the retention of the Ni ion in the +2-oxidation state after catalysis (Figure 6.4b). The bpy-UiO-NiH₂ catalyst was recyclable for at least six catalytic runs without any significant drop-in activity and selectivity, achieving a cumulative TON of 1388. ICP-OES analysis of the reaction mixture after catalysis revealed minimal leaching of Ni and Zr, with 0.011% and 0.02%, respectively.

6.4. Mechanistic Analysis of Bpy-UiO-NiH₂ Catalysed Methane Borylation

The reaction of bpy-UiO-NiH₂ with HBpin (2.5 equivalents w.r.t. Ni) in cyclohexane produced bpy-UiO-Ni(Bpin)₂ and 2 equivalent of H₂, and this reaction is exergonic by 4.4 kcal/mol as calculated by density functional theory (DFT). XANES analysis of bpy-UiO-Ni(Bpin)₂ showed a Ni K-edge energy at 8347.2 eV, confirming presence of Ni⁺² ion (Figure 6.4c). The disappearance of the Ni–H stretching band in the IR spectrum of bpy-UiO-Ni(Bpin)₂ indicated the replacement of hydrides with Bpin moiety (Figure 6.10). Electron paramagnetic resonance (EPR) spectrum of bpy-UiO-Ni(Bpin)₂ exhibited a Ni²⁺ signal centered at *g* ~ 2.01, suggesting the presence of tetrahedral Ni²⁺ species within MOF (Figure 6.12). The EXAFS analysis of bpy-UiO-Ni(Bpin)₂ at the Ni K-edge suggested the existence of tetrahedral (bpy)Ni^{II}(Bpin)₂ species (Figure 6.4d). Catalytic testing revealed that bpy-UiO-Ni(Bpin)₂ exhibited similar activity to bpy-UiO-NiH₂ in methane borylation, suggesting its role as a potential catalytic intermediate. To gain a deeper understanding of bpy-UiO-NiH₂ catalyzed methane borylation and to identify the turnover-limiting step (TLS), we determined the empirical rate law by kinetic experiments using the initial rate method. The rate of CH₃Bpin formation had a linear correlation with the amounts of bpy-UiO-NiH₂ (6.5×10⁻⁴-1.63×10⁻³ M of Ni) and CH₄ (10-40 bar), suggesting a first-order dependence on both variables (Figure 4e). Conversely, the rate of CH₃Bpin formation remained independent of the HBpin concentration (0.1375–0.3435 M), indicating a zero-order dependence with respect to [HBpin] (Figure 6.4f). The empirical rate law; $r = k[\text{bpy-UiO-NiH}_2]^1[\text{CH}_4]^1[\text{HBpin}]^0$, indicates that only CH₄ and Ni catalyst are involved in the turnover-limiting step (TLS) of the catalytic cycle.

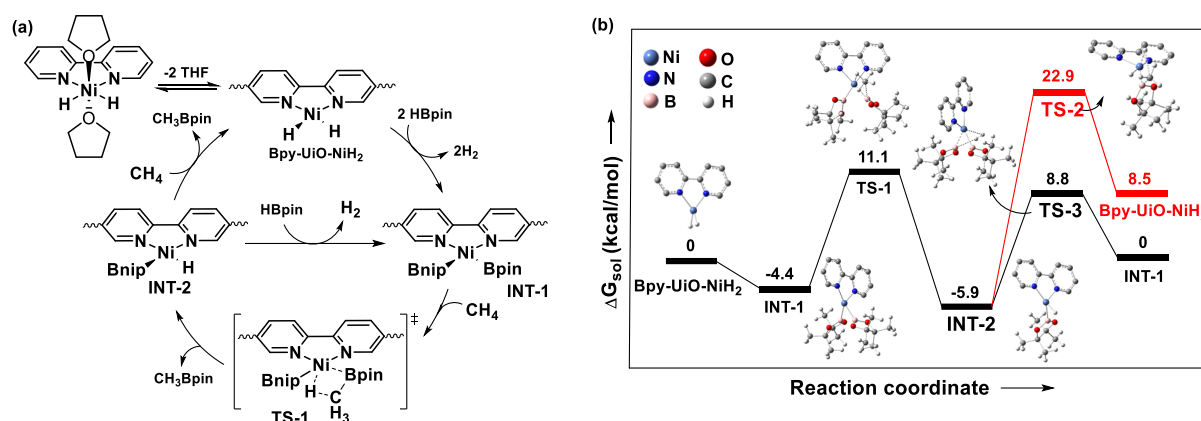


Figure 6.5. (a) Proposed catalytic cycle of bpy-UiO-NiH_2 catalyzed monoborylation of methane. (b) DFT-calculated free energy profile diagram at 473 K.

Based on the above spectroscopic and kinetic data, we propose a catalytic cycle, which begins with the transformation of the octahedral $(\text{bpy})\text{NiH}_2(\text{THF})_2$ species in $\text{bpy-UiO-NiH}_2(\text{THF})_2$ to a tetrahedral $(\text{bpy})\text{NiH}_2$ after dissociating two coordinated THF molecules (Figure 6.5a). Then, the reaction between the $(\text{bpy})\text{NiH}_2$ and HBpin yields tetrahedral bpy-Ni(Bpin)_2 intermediate (INT-1). INT-1 reacts with CH_4 to give bpy-Ni(Bpin)(H) (INT-2) and CH_3Bpin via σ -bond metathesis between the Ni-Bpin bond and a methane C-H bond in the transition state (TS-1). DFT calculations using B3LYP-D3 method and 6-311G(d,p) basis set revealed that the transformation of INT-1 to INT-2 via TS-1 has an activation free energy of 15.5 kcal/mol (Figure 6.5b). Subsequently, INT-2 is either converted to $(\text{bpy})\text{Ni(Bpin)}_2$ species (INT-1) through σ -bond metathesis between the Ni-H bond and HBpin , or regenerate $(\text{bpy})\text{NiH}_2$ via σ -bond metathesis between the Ni-Bpin bond and CH_4 . The former process has a free energy barrier of 14.7 kcal/mol, while the latter involves a higher free energy barrier of 28.8 kcal/mol. The empirical rate law, with first-order dependence on methane and Ni, and zero-order dependence on HBpin , suggests that the transformation of INT-1 to INT-2 via TS-1 is the turnover-limiting step (TLS), which is further supported by the DFT-calculated energy profile diagram (Figure 6.5). The DFT calculation revealed that the methane C-H activation by $(\text{bpy})\text{NiH}_2$ via σ -bond metathesis is unlikely due to the requirement of a very high activation energy of 20.5 kcal/mol (Figure 6.26).

6.5. Experimental Section

6.5.1. Synthesis and Characterisation of bpy-UiO-NiH_2

6.5.1.1. Synthesis of 2,2'-bipyridine-5,5'-dicarboxylic acid²⁷⁸

2,2'-bipyridine-5,5'-dicarboxylic acid was synthesised by a modified reported procedure. 5,5'-Dimethyl-2,2'-bipyridyl (0.500 g, 2.72 mmol), NaOH (0.030 g, 0.75 mmol), and deionized water (12 mL) were placed in a round-bottom flask. The mixture was stirred at 70 °C. Then 1.48 g of NaOH (0.037 mol) was added slowly into the mixture (pH = 12). The resulting mixture became clear, and after it stayed 1 h, finely powdered KMnO₄ (2.140 g, 0.0135 mol) was added into the flask in small portions. After it stirred at 90 °C, the mixture was cooled at room temperature and filtered. The filtrate was acidified with 12 M HCl. After that, a white precipitate formed, which was subsequently filtered and dried, resulting in the formation of 0.208 g (0.85 mmol, 31% yield) of white solid of 2,2'-bipyridine-5,5'-dicarboxylic acid and is analyzed by ¹H NMR (Figure 6.31). ¹H NMR (500 MHz, DMSO-*d*₆): δ 13.55 (s, 2 H), 9.16 (s, 2 H), 8.54 (d, ³J_{H-H} = 8.8 Hz, 2 H), 8.45 (d, ³J_{H-H} = 8.4 Hz, 2 H).

6.5.1.2. Synthesis of bpy-UiO

2,2'-bipyridine-5,5'-dicarboxylic acid (0.026 g, 0.106 mmol) and ZrCl₄ (0.026 g, 0.112 mmol) were dissolved in 13 mL DMF. After sonication for 30 minutes, TFA (0.040 mL, 0.523 mmol) was added, and the resultant mixture was heated in a sealed 15 mL glass vial at 100 °C for 4 days in an oven. The reaction mixture was allowed to cool at room temperature, and the white crystalline solid was isolated after centrifugation to afford bpy-UiO MOF in 35% yield. The MOF was washed with DMF multiple times, followed by THF and stored in THF at room temperature.

6.5.1.3. Analysis of digested bpy-UiO-MOF by ¹H NMR

Digestion of bpy-UiO MOF was carried out by charging the synthesized bpy-UiO MOF into a vial containing 0.5 mL of DMSO-*d*₆ and then followed by the addition of saturated solution of K₃PO₄ in D₂O with periodic shaking of the resulting mixture. After allowing 2 hours for separation, the upper organic layer of DMSO-*d*₆ was isolated and subjected to analysis via ¹H NMR. The ¹H NMR spectrum of digested bpy-UiO MOF in Figure 6.32 showed that bpy-UiO MOF is constructed from [2,2'-bipyridine]-5,5'-dicarboxylate linkers.

6.5.1.4. Synthesis of bpy-UiO-NiH₂

A solution of NiBr₂ (0.005 g, 0.024 mmol) in THF was added to bpy-UiO MOF and kept overnight with periodic shaking at room temperature inside the glovebox. The resulting solid was centrifuged out of the solution and washed 8-10 times with THF to give bpy-UiO-NiBr₂

MOF. Bpy-UiO-NiBr₂ has 25% nickel loading with respect to bipyridyl-moiety at the linkers of bpy-UiO MOF as analyzed by ICP-OES of the digested bpy-UiO-NiH₂ MOF. NaEt₃BH (35 μ L, 1 M in toluene) was added dropwise to the vial containing slurry of bpy-UiO-NiBr₂ (0.015 g, 0.006 mmol) in 3 mL THF inside the glovebox and was kept at room temperature for 1 hour. The resultant black solid of bpy-UiO-NiH₂ was separated via centrifugation and washed several times with THF to remove excess NaEt₃BH. The bpy-UiO-NiBr₂ has 30% solvent weight analysed by thermogravimetric analysis and 25% nickel loading with respect to bpy-moiety of the digested bpy-UiO-NiH₂ MOF as analyzed by ICP-OES.

Table 6.3. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) data of the digested bpy-UiO-NiH₂.

Formula	Zr(ppm)	Ni(ppm)
$\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{bpy})_6\text{Ni}_{6x}\text{H}_{12x}$	2.34	0.38

Calculation of Ni loading w.r.t bpy-moiety is as follows:

Amount of Zr in digested bpy-UiO-NiH₂ MOF = 2.34 ppm

Amount of Ni in digested bpy-UiO-NiH₂ MOF = 0.38 ppm

Mol. weight of Zr = 91.224 g/mol

Mol. weight of Ni = 58.69 g/mol.

Amt. of Zr/ Mol. weight of Zr = $2.34/91.224 = 0.0256$

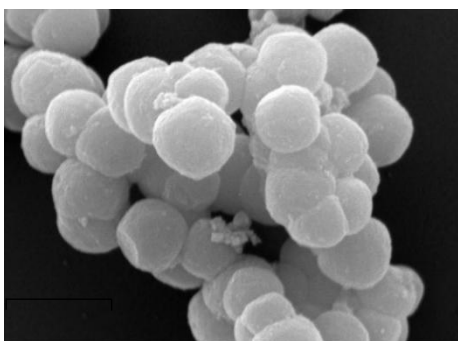
Amt. of Ni/ Mol. weight of Ni = $0.38/58.69 = 0.0065$

Therefore, 0.0256 of Zr = 0.0065 of Ni

1 Zr = 1 bpy linker = 0.2539 Ni

Hence, % Ni (% x) = $6/6 \times 0.2539 \times 100 = 25.39\% \approx 25\%$

a)



b)

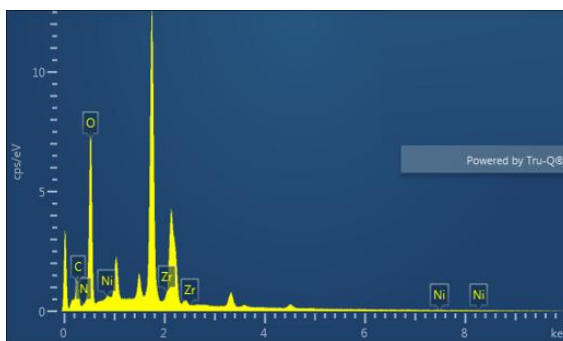


Figure 6.6. a) SEM image and (b) SEM-EDX analysis of bpy-UiO-NiH₂. SEM image displayed octahedron particles of bpy-UiO-NiH₂ with an average size of 250 nm.

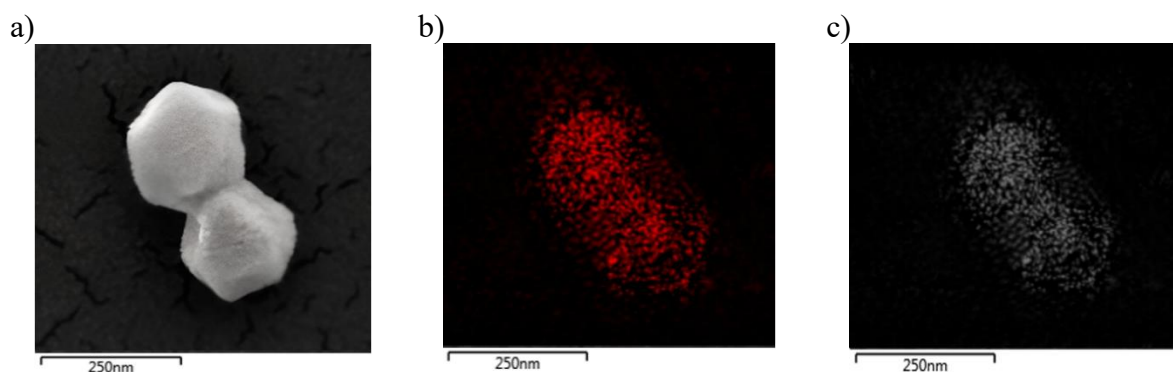


Figure 6.7. (a) SEM image of bpy-UiO-NiH₂ particles along with EDX mapping of (b) Zr and (c) Ni of the respective particles. Uniform distribution of Zr and Ni throughout the bpy-UiO-NiH₂ particles is observed.

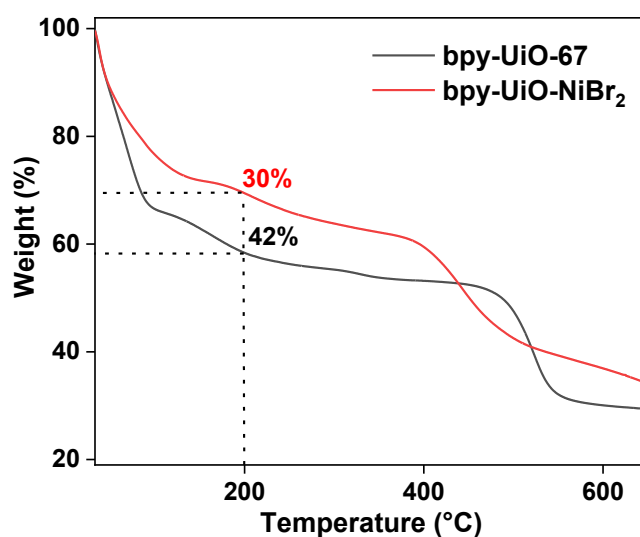


Figure 6.8. TGA curve of freshly prepared bpy-UiO-67 (black) and bpy-UiO-NiBr₂ (red). A solvent weight loss of 42% was observed in bpy-UiO-67 and 30% in bpy-UiO-NiBr₂ at the range of temperature from 40 °C to 200 °C. The increased weight of metalated MOF is due to the presence of nickel within the MOF.

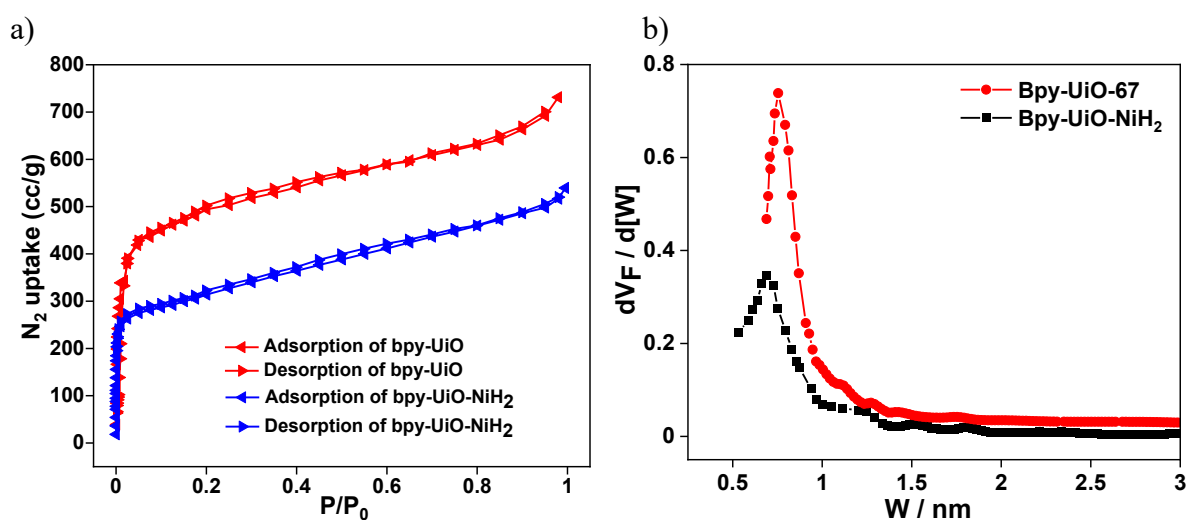


Figure 6.9. a) Brunauer–Emmett–Teller (BET) nitrogen sorption isotherms of bpy-UiO and bpy-UiO-NiH₂ measured at 77 K. Bpy-UiO and bpy-UiO-NiH₂ have a BET surface area of 2247 m²/g and 1260 m²/g respectively. b) HK pore distribution plot of bpy-UiO and bpy-UiO-NiH₂. Pore size for bpy-UiO and bpy-UiO-NiH₂ was determined to be 0.75 nm and 0.68 nm respectively.

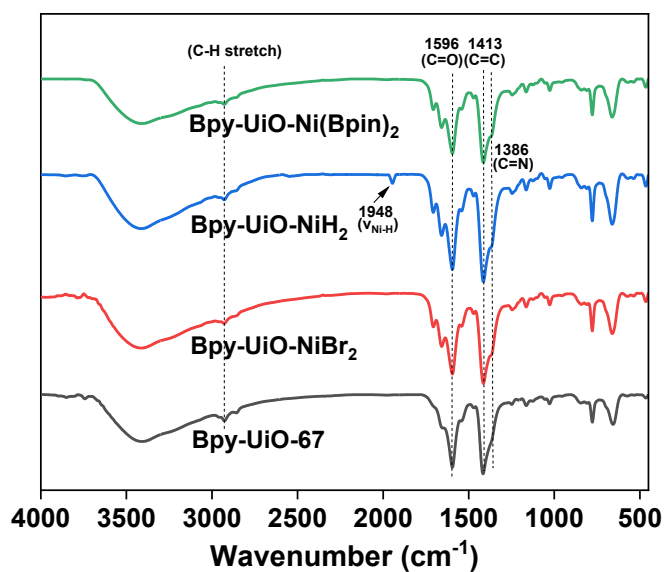


Figure 6.10. IR spectra of freshly prepared bpy-UiO-67 (black), bpy-UiO-NiBr₂ (red), bpy-UiO-NiH₂ (blue) and bpy-UiO-Ni(Bpin)₂ (green). A characteristic peak of Ni hydride stretching frequency was detected at 1948 cm⁻¹.

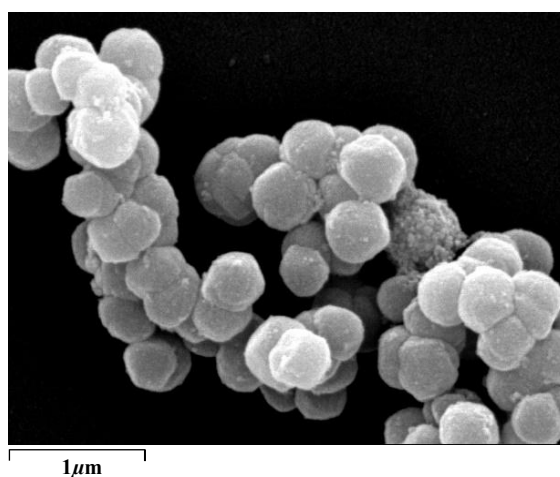


Figure 6.11. SEM image of bpy-UiO-Ni particles after catalysis. Reaction conditions: 2 mg of bpy-UiO-Ni (1.37 μmol Ni), 2 mL C₆H₁₂, 20 bar CH₄, 10 h at 200 °C. After catalysis SEM image shows bpy-UiO-Ni particles maintains its structure.

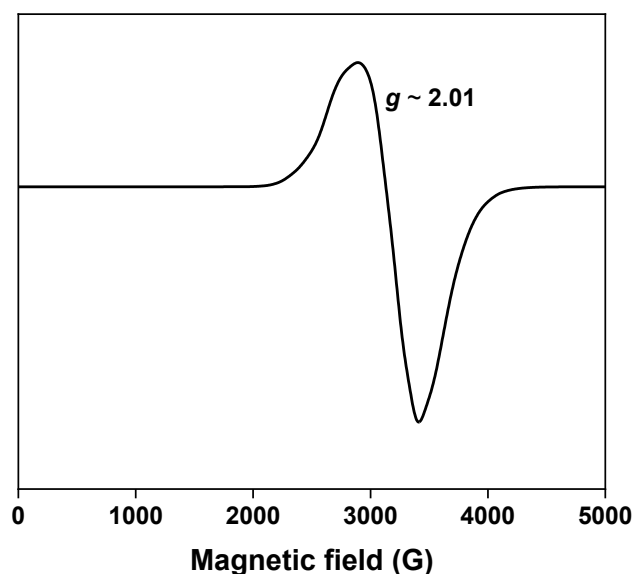


Figure 6.12. Room temperature X-band EPR spectra of bpy-UiO-Ni(Bpin)₂. The signal centered at $g \sim 2.01$ indicates the existence of tetrahedral and paramagnetic (bpy)Ni^{II}(Bpin)₂ species, not a diamagnetic Ni(II) square-planar species.³²⁷

6.5.1.5. Synthesis of homogeneous bipyridyl-nickel complex³²⁸

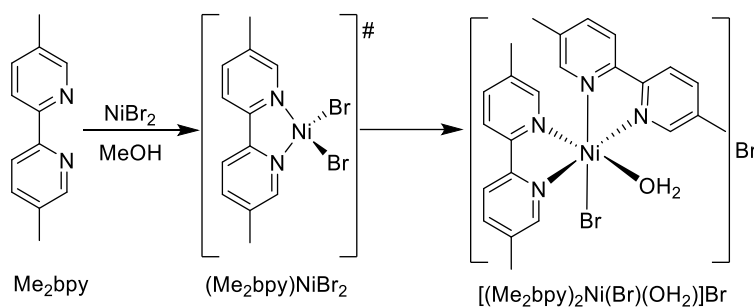


Figure 6.13. Synthesis of homogeneous bipyridyl-nickel complex, [(Me₂bpy)₂Ni(Br)(OH₂)]Br.

In a 25 mL Schlenk flask, NiBr₂ (293 mg, 1.34 mmol) and 5,5'-dimethyl-2,2'-bipyridyl (250 mg, 1.34 mmol) were added. After degassing, methanol (15 mL) was added cautiously under nitrogen atmosphere and the Schlenk flask was immersed in an oil bath at 70 °C overnight under stirring. Following this, the reaction mixture was allowed to cool to room temperature and the solvent was evaporated under vacuum. The mixture was subsequently filtered and the resulting solid was dried under vacuum to yield product. Crystals suitable for X-ray crystallography were grown via MeOH/diethyl ether vapor diffusion at room temperature. Analysis of the single crystal data disclosed a six-coordinate nickel complex, [(Me₂bpy)₂Ni(Br)(OH₂)]Br with nickel coordinated with four nitrogen atoms of two bipyridine ligands, one bromide and one water molecule with one bromide as a counter anion (Figure 6.14).

6.5.1.5.1. X-Ray structure determination

Single crystals of complex $C_{24}H_{26}Br_2N_4NiO$ [M_BPY_0m_a] were selected from the methanol solution containing single crystals and immersed in paratone oil, followed by mounting on a nylon loop. A suitable crystal was selected and data collections were performed on a Bruker APEX-II CCD diffractometer. The crystal was kept at 295.00 K during data collection. Using Olex2,³²⁹ the structure was solved with the olex2.solve³³⁰ structure solution program using Charge Flipping and refined with the XL³³¹ refinement package using Least Squares minimisation. Diagrams for the complexes were prepared using Mercury software.³³² Crystallographic data of the complex is given in Table S3 and bond parameters are mentioned in Table 6.4.

Table 6.4. Crystallographic parameters of $C_{24}H_{26}Br_2N_4NiO$.

Identification code	M_BPY_0m_a
Empirical formula	$C_{24}H_{26}Br_2N_4NiO$
Formula weight	605.02
Temperature/K	295.00
Crystal system	triclinic
Space group	P-1
a/Å	11.432(4)
b/Å	11.663(4)
c/Å	12.093(4)
$\alpha/^\circ$	117.667(10)
$\beta/^\circ$	93.518(11)
$\gamma/^\circ$	90.250(11)
Volume/Å ³	1424.4(8)
Z	2
ρ_{calc}/cm^3	1.411
μ/mm^{-1}	3.506
F(000)	608.0
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	3.572 to 56.704
Index ranges	$-15 \leq h \leq 15, -15 \leq k \leq 15, -16 \leq l \leq 16$
Reflections collected	55843
Independent reflections	7082 [$R_{int} = 0.0360, R_{sigma} = 0.0205$]
Data/restraints/parameters	7082/0/294
Goodness-of-fit on F^2	1.037
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0266, wR_2 = 0.0719$
Final R indexes [all data]	$R_1 = 0.0310, wR_2 = 0.0739$
Largest diff. peak/hole / e Å ⁻³	0.82/-0.85

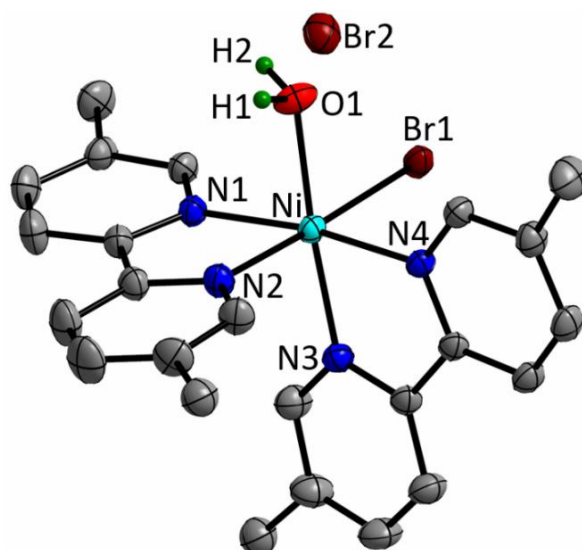


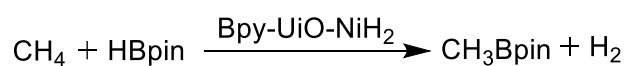
Figure 6.14. Molecular structure of $C_{24}H_{26}Br_2N_4NiO$ (CCDC no. 2361306). Thermal ellipsoids are shown at the 30% probability level and all hydrogen atoms are omitted for clarity except H1 and H2.

Table 6.5. Selected bond length and bond angle of complex $C_{24}H_{26}Br_2N_4NiO$.

Bond length (Å)	$C_{24}H_{26}Br_2N_4NiO$
Br1-Ni	2.6030(9)
Ni-N1	2.0710(16)
Ni-N2	2.0900(18)
Ni-N3	2.0793(17)
Ni-O1	2.1009(16)
Ni-N4	2.0680(15)
Bond Angle (°)	
N1-Ni-N2	78.76(6)
N1-Ni-O1	88.07(7)
N1-Ni-Br1	97.21(5)
N1-Ni-N4	170.92(6)
N1-Ni-N3	96.47(7)
N4-Ni-O1	96.30(7)
N4-Ni-N3	79.26(7)
N4-Ni-N2	93.15(6)
N4-Ni-Br1	90.87(4)
O1-Ni-Br1	88.61(5)
N3-Ni-Br1	90.37(5)
N2-Ni-N3	90.15(7)

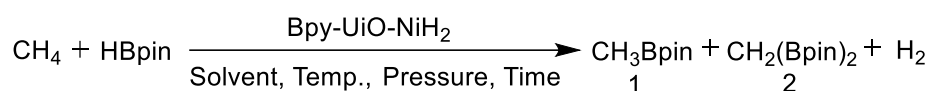
6.5.2. Catalytic Reactions with bpy-UiO-NiH₂

6.5.2.1. General procedure for bpy-UiO-NiH₂ catalysed borylation of methane



In the glovebox, bpy-UiO-NiH₂ (0.25 mol% of Ni) dissolved in 2 mL of solvent was transferred to a glass liner. HBpin was then added to the liner, which was securely placed into a high-pressure reactor and sealed. After sealing, the Parr reactor was taken out from the glovebox and purged with CH₄ two to three times. Following this, the Parr reactor was pressurized to 5-40 bar with CH₄ and heated to a temperature between 100-250 °C, maintaining it for 2 to 24 hours. Upon completion of the reaction, the reactor was cooled, and pressure was released. The resulting mixture was centrifuged to separate the MOF and the supernatant was analyzed using GC-MS/FID to determine the conversion and yield of CH₃Bpin and the H₂ produced was subjected to analysis using Gas Chromatography with Thermal Conductivity Detector (GC-TCD) following the catalytic reaction.

Table 6.6. Optimization of reaction conditions for borylation of methane catalyzed by bpy-UiO-NiH₂.^a

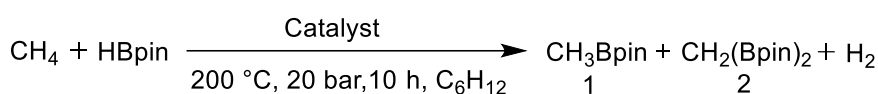


Entry No.	Temp. (°C)	Pressure (bar)	Time (h)	Solvent	% Conv. (HBpin)	% Yield of 1 ^b	% Selectivity of 1 ^c	TON
1	200	20	6 h	C ₆ H ₁₂	74	45	98	180
2	200	20	10 h	C ₆ H ₁₂	100	61	98	244
3	200	5	18 h	C ₆ H ₁₂	100	22	98	88
4	200	10	10 h	C ₆ H ₁₂	100	24	98	96
5	200	10	24 h	C ₆ H ₁₂	100	28	98	88
6	200	30	10 h	C ₆ H ₁₂	100	46	90	184
7	200	40	10 h	C ₆ H ₁₂	100	38	78	152
8	100	20	10 h	C ₆ H ₁₂	3	0	--	--
9	150	20	10 h	C ₆ H ₁₂	35	20	98	80
10	250	20	10 h	C ₆ H ₁₂	100	36	92	144
11 ^d	200	20	10 h	C ₆ H ₁₂	100	48	98	96
12 ^e	200	20	10 h	THF	100	9	97	36
13	200	20	10 h	Toluene	100	28	96	112
14	200	20	10 h	CH ₃ C ₆ H ₁₁	100	38	97	152
15	200	20	10 h	Heptane	100	48	97	192
16	200	20	10 h	C ₁₂ H ₂₆	100	50	98	200
17 ^f	200	20	10 h	C ₆ H ₁₂	100	60	98	240

18 ^g	200	20	10 h	C ₆ H ₁₂	13	0	--	--
19 ^h	200	20	10 h	C ₆ H ₁₂	84	51	98	204
20 ⁱ	200	20	10 h	C ₆ H ₁₂	100	57	96	228

^aReaction conditions: 2 mg of bpy-UiO-NiH₂ (0.25 mol% of Ni), 0.55 mmol HBpin, 2 mL solvents. ^bYield of CH₃Bpin was determined by GC using mesitylene as an internal standard, calculated as [moles (CH₃Bpin)/initial moles of HBpin] × 100. ^cCH₃Bpin selectivity, calculated as [moles (CH₃Bpin)/moles {CH₃Bpin + CH₂(Bpin)₂}] × 100. ^d4 mg of bpy-UiO-NiH₂ (0.5 mol% of Ni) was used as the catalyst. ^eLower yield is attributed to the predominance of borylated THF as the main product. ^fCatalysis was performed in the presence of a drop of Hg. ^gB₂pin₂ was used as borylating agent. ^h1.2 equiv. of bulky coordinated tricyclohexylphosphine per Ni was added. ⁱbpy-UiO-Ni(Bpin)₂ was used as the catalyst.

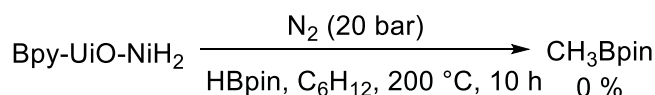
Table 6.7. Control experiments for methane borylation reaction.^a



Entry No.	Catalyst	% Conv. (HBpin)	CH ₃ Bpin ^b (%)	CH ₂ (Bpin) ₂ (%)	HOBpin (%)	pinBOBpin (%)	SolBpin (%)	TON
1	Bpy-UiO-NiH ₂	100	61	1	17	1	20	244
2 ^c	Bpy-UiO-NiH ₂	8	0	0	0	2	6	--
3	No catalyst	17	0	0	5	1	11	--
4	Bpy-UiO-67	24	0	0	5	3	16	--
5	NiBr ₂	43	0	0	7	11	25	--
6	Ni@UiO-67	38	4	1	4	5	24	16
7	NiO	30	0	0	3	6	21	--
8	Ni(OH) ₂	32	0	0	16	4	12	--
9	(Me ₂ bpy) ₂ Ni	25	3	1	10	0	11	12

^aReaction conditions: Ni catalyst (0.25 mol% of Ni), 0.55 mmol HBpin, 200 °C, 20 bar CH₄, 10 h and 2 mL C₆H₁₂. ^bYield of CH₃Bpin was determined by GC using mesitylene as an internal standard, calculated as [moles (CH₃Bpin)/initial moles of HBpin] × 100. ^cNitrogen was used instead of methane.

6.5.2.2. Blank reaction of bpy-UiO-NiH₂ with HBpin under N₂ without methane



In the glovebox, a solution containing bpy-UiO-NiH₂ (2 mg, 0.25 mol% of Ni) in 2 mL cyclohexane was transferred into a glass liner. HBpin (0.55 mmol) was then added to the liner, which was securely placed into a high-pressure reactor and sealed. The sealed Parr reactor was taken out of the glovebox and purged with nitrogen gas two to three times. Nitrogen gas

was then pressurized to 20 bar inside the reactor, followed by heating at 200 °C for 10 hours without mechanical stirring. After cooling the reactor and releasing the pressure, the MOF was separated from the reaction mixture via centrifugation. The resulting supernatant was analyzed using GC-MS/FID to determine the conversion and yield of CH₃Bpin. No CH₃Bpin was detected, indicating that CH₄ was the only carbon source for CH₃Bpin in the bpy-UiO-NiH₂ catalyzed methane borylation reaction.

6.5.2.3. Test for “heterogeneity” of bpy-UiO-NiH₂ in borylation of CH₄

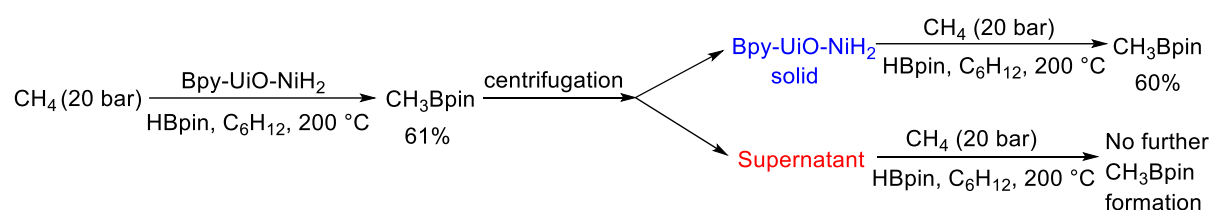


Figure 6.15. Heterogeneity test of bpy-UiO-NiH₂ for the borylation of methane.

In the glovebox, a solution containing bpy-UiO-NiH₂ (2 mg, 0.25 mol% of Ni) in 2 mL of cyclohexane was transferred into a glass liner. Subsequently, HBpin (0.55 mmol) was added to the liner. The liner was securely fitted into a high-pressure reactor and sealed. After removing the sealed Parr reactor from the glovebox, it was purged with CH₄ two to three times. Then, the reactor was pressurized with 20 bar of methane and heated at 200 °C for 10 hours without mechanical stirring. After cooling the system and releasing the pressure, the solid MOF was separated from the suspension, inside the glovebox, and washed with cyclohexane multiple times.

Two reactions were set up separately in two different Parr reactors, one with the solid and the other with the supernatant recovered from the previous reaction. The extracted solid and supernatant were added into two separate liners, along with HBpin (0.55 mmol) in each liner. Then 2 mL of C₆H₁₂ was added to the glass liner containing solid MOF. Both liners were fitted into two separate Parr reactors and sealed. After removing the sealed Parr reactors from the glovebox, purged with CH₄ gas two times. The Parr reactors were pressurized to 20 bar of CH₄ and stirred at 200 °C for 10 hours. After completion of the reaction, the pressure of the reactors was released. The reactions were analyzed with GC-MS/FID, revealing that the reaction with the solid MOF yielded 60%, while the reaction with the supernatant gave no further formation of CH₃Bpin. This experiment ruled out the potential of any leached Ni-

species responsible for catalysis and confirmed that the solid bpy-UiO-NiH₂ was the actual catalyst for the borylation of methane.

6.5.2.4. Hg test of bpy-UiO-NiH₂ in borylation of CH₄

The catalytic process of methane borylation using bpy-UiO-NiH₂ was subjected to examination in the presence of a trace amount of Hg. This addition aimed to elucidate the potential involvement of any leached Ni nanoparticles that might have formed during the reaction and acted as catalysts.³³³ The results revealed that the rate of bpy-UiO-NiH₂-catalyzed methane borylation remained unaffected in the presence of Hg⁰. This observation suggests that any potential leached Ni nanoparticles did not contribute significantly to the catalytic activity. Therefore, it can be inferred that bpy-UiO-NiH₂ itself serves as actual catalyst in this reaction. The details of the experiments are as follows:

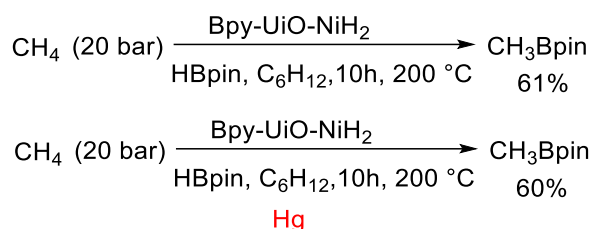


Figure 6.16. Hg test in the borylation of methane catalysed by bpy-UiO-NiH₂.

Bpy-UiO-NiH₂ (1.37 μmol of Ni) as a slurry in 1 mL C₆H₁₂ was charged into two separate glass liners. To glass liners, 1 mL C₆H₁₂ and 0.55 mmol HBpin were added. In one of the reaction mixtures, a drop of mercury was added. The liners were sealed in two separate Parr reactors. The reactors were purged with methane gas. The reactors were pressurized with 20 bar methane and then heated at 200 °C for 10 h without stirring. The reactors were cooled to room temperature, and the solid was centrifuged out of the reaction mixtures. The reactions were analyzed with GC-MS/FID. Almost same results were obtained for both reactions. We thus conclude that any leached Ni-particles were not responsible for the catalytical activity, and bpy-UiO-NiH₂ was the actual catalyst.

6.5.2.5. Recycling of bpy-UiO-NiH₂ for the borylation of methane

The recycle and reuse experiment was conducted to check the stability of bpy-UiO-NiH₂ MOF-catalyst (Table 6.8). The detailed procedure of recycling experiment was given below. In the glovebox, bpy-UiO-NiH₂ (10 mg, 0.25 mol% of Ni) in 2 mL cyclohexane was transferred into

glass liner. HBpin (2.75 mmol) was subsequently added to the liner, which was then securely fitted into a high-pressure reactor and sealed. The sealed Parr reactor was then removed from the glovebox and purged with CH₄ two to three times. The reactor was pressurized with 20 bar methane and then heated at 200 °C for 10 h without any mechanical stirring.

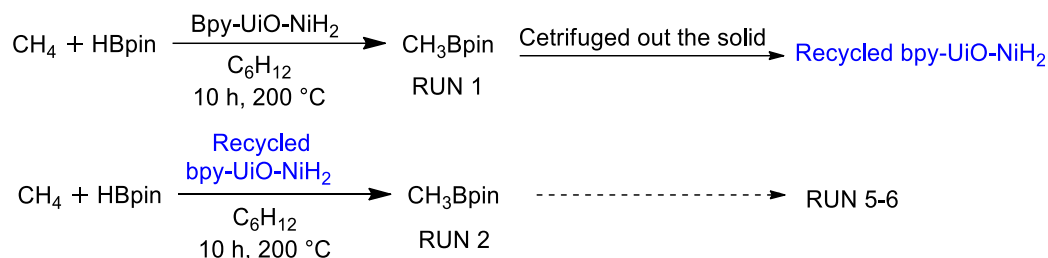


Figure 6.17. Recycle and reuse of bpy-UiO-NiH₂ in borylation of methane.

The system was subsequently cooled, and the pressure was released. The solid MOF was removed from suspension to separate the solid and the supernatant, inside the glove box and washed with cyclohexane multiple times. The yield of CH₃Bpin was determined by GC-MS/FID analysis. The solid MOF was then recycled.

Inside the glovebox, the recovered MOF-catalyst was again added to the glass liner. 2 mL cyclohexane and HBpin (2.75 mmol) were added to the glass liner and sealed it in a Parr reactor. The Parr reactor was taken out from the glovebox and was purged with the CH₄ gas and then pressurized it to 20 bar of CH₄. The reactor was heated at 200 °C for 10 h. After the reaction, the solution was analyzed in the same way as mentioned previously in run 1. The recycling and reuse experiments were performed up to 5 times in total.

Table 6.8. %GC-Yield of CH₃Bpin and other boron products and the leaching of Ni and Zr at various runs of the recycling of bpy-UiO-NiH₂ in the borylation of methane.

Run	Time	CH ₃ Bpin (%)	CH ₂ (Bpin) ₂ (%)	HOBpin (%)	pinBOBpin (%)	SolBpin (%)	%Leaching (Ni, Zr)
1	10 h	61	1	17	1	20	0.011, 0.02
2	10 h	59	1	16	3	21	
3	10 h	58	1	17	4	20	0.03, 0.05
4	10 h	57	1	16	5	21	
5	10 h	56	1	14	5	24	
6	10 h	56	1	13	5	25	0.04, 0.06

6.5.2.6. Methane borylation using Ni(0) and Ni@UiO-67

6.5.2.6.1. Ni(0) catalyzed borylation of methane

Inside the glovebox, NiBr₂ (0.001 g, 0.005 mmol) was charged into a glass vial containing 2 mL of THF. Then, NaBEt₃H (10 μ L, 1 M in toluene) was added to the vial and stirred gently for an hour to form black coloured Ni-nanoparticles.³³⁴ The black solid was washed 3-4 times with THF and dried. Now, 0.1 mg of Ni nanoparticles (1.37 μ mol of Ni) in 2 mL cyclohexane was transferred into glass liner inside the glovebox. HBpin (0.55 mmol) was subsequently added to the liner, which was then securely fitted into a high-pressure reactor and sealed. The sealed Parr reactor was then removed from the glovebox and purged with CH₄ two to three times. The reactor was pressurized with 20 bar methane and then heated at 200 °C for 10 h without any mechanical stirring. The system was subsequently cooled, and the pressure was released. The GC-MS/FID analysis showed nickel nanoparticles yielded negligible amount of CH₃Bpin.

6.5.2.6.2. Ni@UiO-67 catalyzed borylation of methane

In a 25 mL round bottom flask, NiBr₂ (39 mg, 0.18 mmol) was dissolved in 2 mL of ethyl acetate, followed by the addition of 100 mg of UiO-67 MOF which was prepared by combining 50 mg of biphenyl-dicarboxylic acid linker dissolved in 1 mL of DMF with a solution containing 69 mg of ZrCl₄ in 1 mL of DMF, followed by hydrothermal treatment at 120°C for 24 hours in a 10 mL Teflon-lined autoclave.²⁶⁸ Then the mixture was heated at 50 °C for 48 hours. After centrifugation, the solid was collected, washed thoroughly and dried to yield UiO-67-NiBr₂. Subsequently, NaBH₄ (10 mg) was dissolved in 6 mL of deionized water in another round-bottom flask, followed by the addition of 80 mg of UiO-67-NiBr₂. The pH was maintained between 6 and 8 during the addition of NaBH₄. The resulting mixture was stirred for 30 minutes and then filtered. The collected solid was washed extensively with deionized water to obtain a black powder of Ni@UiO-67.³³⁵ Finally, the Ni@UiO-67 was activated at 150 °C for 12 hours under high vacuum. Now, inside the glovebox, 2.8 mg of Ni@UiO-67 (1.37 μ mol of Ni) was transferred into a glass liner containing 2 mL of C₆H₁₂. HBpin (0.55 mmol) was subsequently added to the liner, which was then securely fitted into a high-pressure reactor and sealed. The sealed Parr reactor was then removed from the glovebox and purged with CH₄ three times. The reactor was pressurized with 20 bar methane and then heated at 200 °C for 10 h without any mechanical stirring. The system was subsequently cooled, and the

pressure was released. The GC-MS/FID analysis indicated that the synthesized Ni@UiO-67 resulted in a 4% CH₃Bpin yield.

6.5.2.7. C–H borylation of methane using bpy-UiO-NiH₂ and its homogeneous control as catalysts under identical conditions to compare their catalytic activities

Three Parr reactors were set-up within a glovebox. In the first reactor, 80 μ L (0.55 mmol) of HBpin, along with 0.0006 g (0.0013 mmol) of (Me₂bpy)₂Ni which is formed by reacting [(Me₂bpy)₂Ni(Br)(OH₂)]Br with 4 equiv. NaEt₃BH in THF, followed by drying and then 2 mL of cyclohexane was added. Meanwhile, the second reactor was charged with 80 μ L (0.55 mmol) of HBpin, 2 mg (0.25 mol% Ni) of bpy-UiO-NiH₂, and 2 mL of cyclohexane. In the third reactor, 80 μ L (0.55 mmol) of HBpin was combined with the catalyst, which is prepared by reacting a mixture of NiBr₂ and Me₂bpy (in a 1:1 ratio) with 2.5 equiv. of NaEt₃BH in THF, followed by drying. Subsequently, 2 mL of cyclohexane was added to the mixture. All reactors were purged twice with CH₄ and then pressurized with 20 bar of CH₄ each. The reaction mixtures were stirred at 200 °C for 10 hours. Upon completion of the reaction, the system was cooled and pressure in the reactors was released and the yield (%) of the products was monitored using GC-MS/FID. Similar homogeneous controls were also established using nickel complexes of 1,2-phenanthroline and [4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine].

Table 6.9. Comparison of bpy-UiO-NiH₂ with its homogeneous control in the borylation of methane under similar condition.^a

Catalyst	Ni (μ mol)	Conv. (%)	CH ₃ Bpin (%)	CH ₂ (Bpin) ₂ (%)	HOBpin (%)	pinBOBpin (%)	SolBpin (%)	TON
Bpy-UiO-NiH ₂	1.37	100	61	1	17	1	20	244
(Me ₂ bpy) ₂ Ni	1.37	25	3	1	10	0	11	12
Me ₂ bpy + NiBr ₂ + 2.5 NaEt ₃ BH	1.37	25	3	1	9	0	12	12
(phen)NiBr ₂ + NaEt ₃ BH	1.37	96	12	78	0	0	6	48
(^t Bu-bpy)NiBr ₂ + NaEt ₃ BH	1.37	100	17	0	0	0	83	68

^aReaction conditions: 2 mL of C₆H₁₂, HBpin (0.55 mmol), 200 °C, 20 bar CH₄ and 10 h.

6.5.2.8. Determination of rate law for bpy-UiO-NiH₂ catalysed methane borylation

The empirical rate law was established through kinetic experiments utilizing the initial rate method at low conversions of HBpin (<15%). In the glovebox, bpy-UiO-NiH₂ (0.25 mol% of

Ni) as a slurry in 2 mL of solvent was transferred to a glass liner. HBpin was then added to the liner, which was securely placed into a high-pressure reactor and sealed. After sealing, the Parr reactor was taken out from the glovebox and purged with CH₄ two to three times. Following this, the Parr reactor was pressurized with CH₄ and heated to 200 °C for 5 minutes. The reactor was subsequently cooled and the resulting mixture was centrifuged to separate the MOF and the supernatant was analyzed using GC-MS/FID to determine the yield of CH₃Bpin. To investigate the kinetic dependence of the reaction on the amount of HBpin, yield of CH₃Bpin was measured over various HBpin amounts ranging from 0.1375–0.3435 M. Additionally, the effects of varying catalyst amounts and methane pressure on CH₃Bpin yield were assessed by conducting reactions with 6.5×10^{-4} – 1.63×10^{-3} M of Ni and 10–40 bar of CH₄ (Figure 6.4e-f).

6.6. Analysis and Quantification of CH₃Bpin by GC-MS and GC-FID

The conversions and yields of the reactions were determined by Agilent 7890B gas chromatograph equipped with a flame ionisation detector (FID) and a mass detector (Agilent 5977B GC/MSD) and a HP-5MS Ultra Inert 30m-250µm-0.25µm column. GC conditions: Inj: 220 °C; Det: 250 °C; Column temp: 40 °C followed by a ramp of 5 °C/min to 240 °C; Column flow: 1.0 mL/min.

We employed two distinct methodologies to determine the yield of CH₃Bpin, outlined as follows.

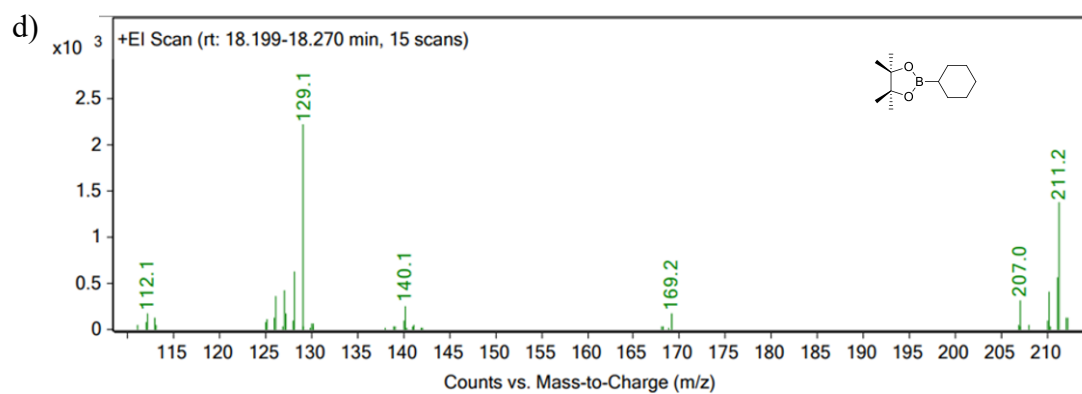
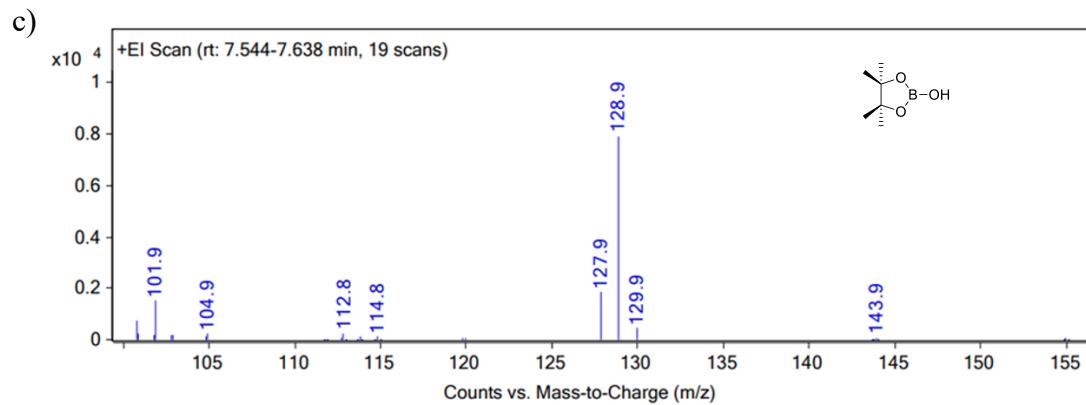
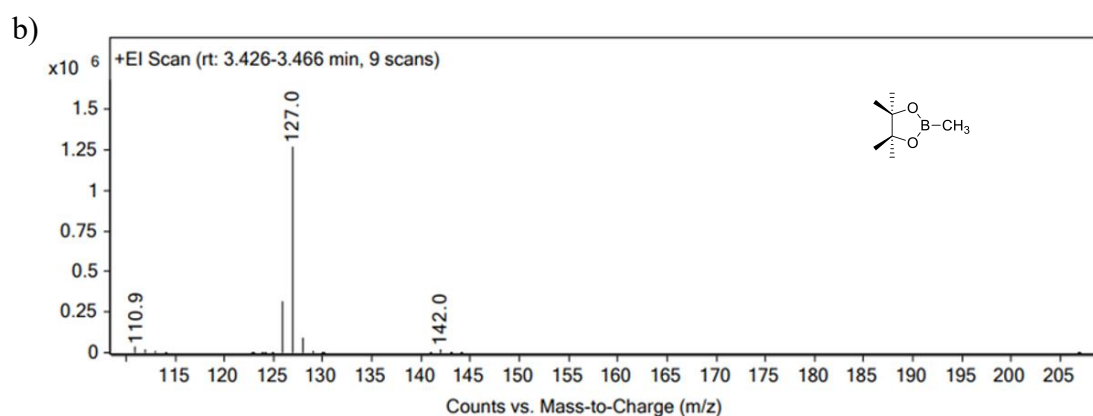
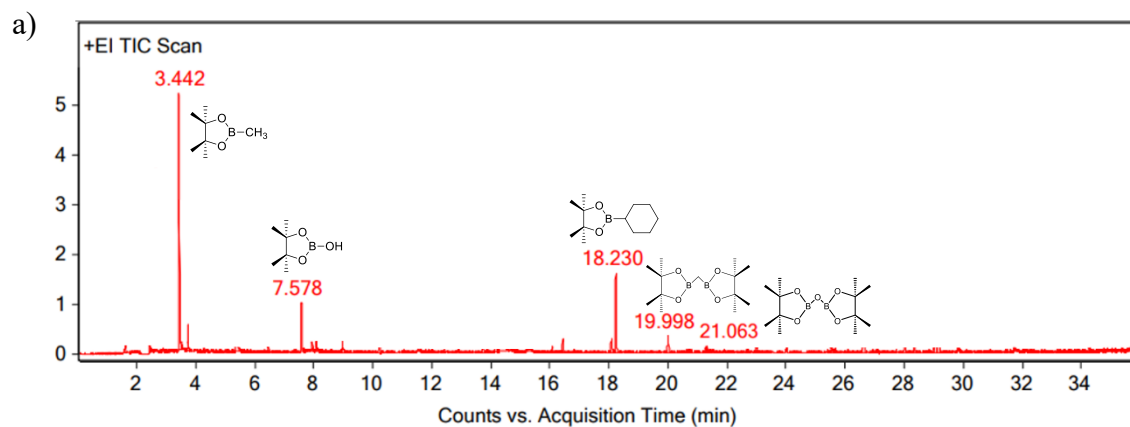
A) The conversion and yield of CH₃Bpin were determined for each reaction run by measuring the relative amount of Boron species through the corrected integration of GC-MS peaks as follows.

$$\text{Conversion\%} = \left[1 - \frac{\text{HBpin remaining}}{(\text{HBpin} + \text{CH}_3\text{Bpin} + \text{CH}_2(\text{Bpin})_2 + \text{SolBpin} + \text{etc})} \right] \times 100\%$$

$$\text{Yield of CH}_3\text{Bpin\%} = \left[\frac{\text{CH}_3\text{Bpin}}{(\text{HBpin} + \text{CH}_3\text{Bpin} + \text{CH}_2(\text{Bpin})_2 + \text{SolBpin} + \text{etc})} \right] \times 100\%$$

$$\text{TON of CH}_3\text{Bpin} = \frac{\% \text{ Yield of CH}_3\text{Bpin}}{\% \text{ Ni Loading}}$$

$$\text{TON of CH}_3\text{Bpin} = \frac{\text{mmol of CH}_3\text{Bpin}}{\text{mmol of Ni}}$$



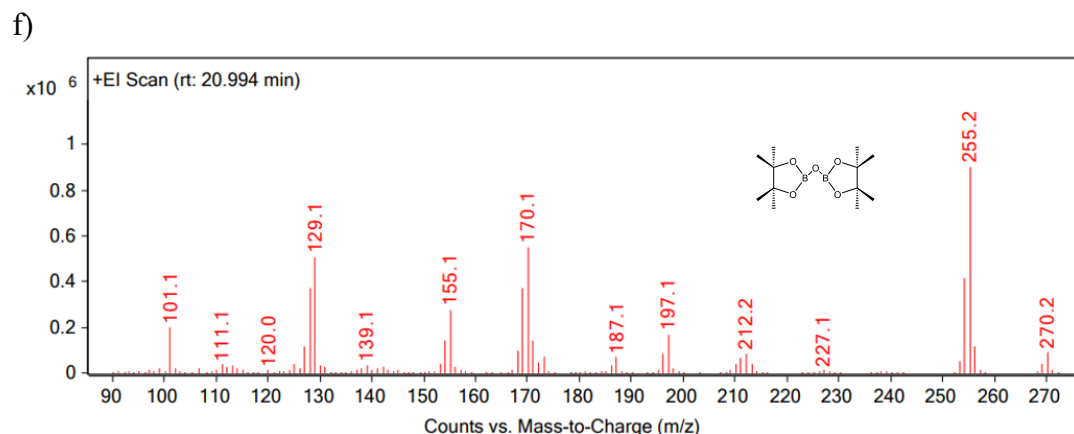
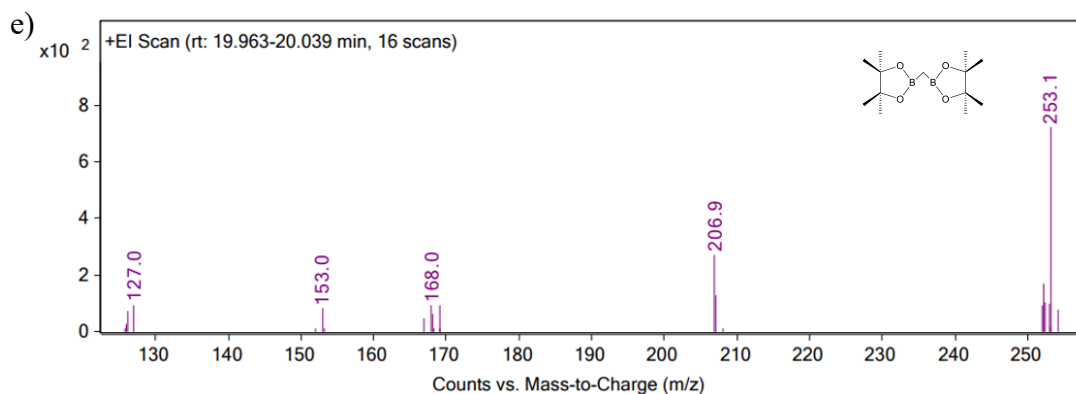


Figure 6.18. The GC-MS spectra of the crude reaction mixture after 10 h of catalysis (100% HBpin conversion) using bpy-UiO-NiH₂. Reaction conditions: 2 mg of bpy-UiO-NiH₂ (1.37 μ mol of Ni), 2 mL of C₆H₁₂, HBpin (0.55 mmol), 200 $^{\circ}$ C, 20 bar CH₄ and 10 h.

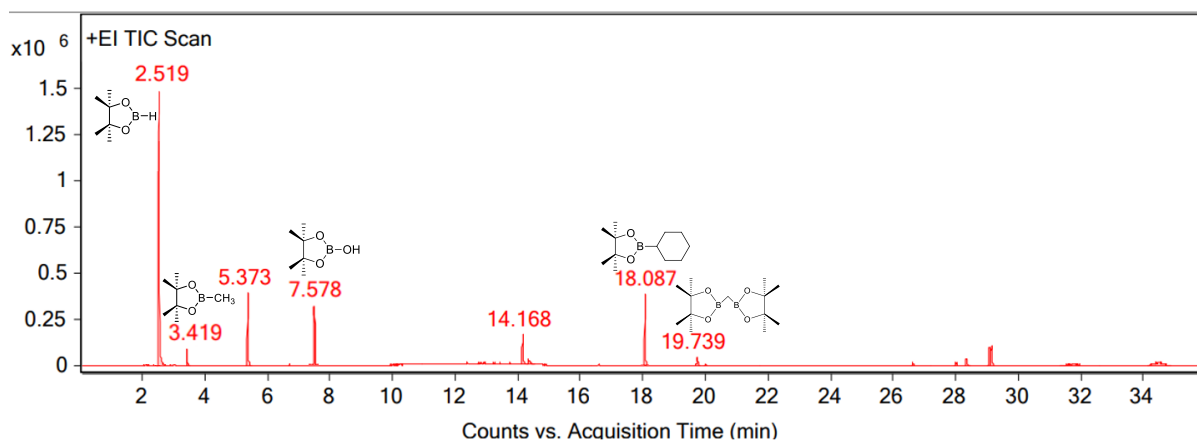


Figure 6.19. The GC spectra of the crude reaction mixture after 10 h of catalysis (25% HBpin conversion) using [(Me₂bpy)₂Ni(Br)(OH₂)]Br + 4 NaEt₃BH. Reaction conditions: (Me₂bpy)₂Ni (1.37 μ mol of Ni), 2 mL of C₆H₁₂, HBpin (0.55 mmol), 200 $^{\circ}$ C, 20 bar CH₄ and 10 h.

B) The yield of CH₃Bpin was also determined by GC analysis using mesitylene as an internal standard. First, we made a GC-calibration curve using known quantities of CH₃Bpin with mesitylene as an internal standard (I.S.) as shown below.

Calculation for the determination of %yield of CH₃Bpin:

Reaction conditions: 2 mg of bpy-UiO-NiH₂ (1.37 μ mol of Ni), 2 mL of C₆H₁₂, HBpin (0.55 mmol), 200 °C, 20 bar CH₄ and 10 h.

$$[\text{Mesitylene}] = 0.07188618 \text{ M (10 } \mu\text{L)}$$

$$\% \text{GC-Area of CH}_3\text{Bpin peak} = 67.68\%$$

$$\% \text{GC-Area of Mesitylene peak} = 32.32\%$$

$$[\text{CH}_3\text{Bpin}] = ?$$

From the calibration plot, slope = 0.89882

Now,

$$\% \text{GC-Area of CH}_3\text{Bpin} / \% \text{GC-Area of I.S.} = \text{Slope} \times [\text{CH}_3\text{Bpin}] / [\text{I.S.}]$$

$$\Rightarrow 67.68 / 32.32 = 0.89882 \times [\text{CH}_3\text{Bpin}] / 0.07188618$$

$$\Rightarrow [\text{CH}_3\text{Bpin}] = 0.1675 \text{ M}$$

$$M = n / V$$

$$n \text{ (mmol)} = M \times V \text{ (mL)}$$

$$\text{mmol of CH}_3\text{Bpin produced} = 0.1675 \times 2 = 0.335 \text{ mmol [Since 2 mL of solvent was used]}$$

$$\begin{aligned} \% \text{ Yield (CH}_3\text{Bpin)} &= [\text{mmol of product (CH}_3\text{Bpin)} / \text{mmol of reactant taken}] \times 100 \% \\ &= (0.335/0.55) \times 100\% = 61\% \end{aligned}$$

6.7. X-ray Absorption Spectroscopic Analysis

X-ray Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) measurements have been carried out at the Energy-Scanning EXAFS beamLine (BL-9) at the Indus-2 Synchrotron Source at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.²²⁰ All the measurements were performed at room temperature. This beamLine operates in the energy range of 4 keV to 25 keV. The beamLine optics consist of a Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si (111) based double crystal monochromator (DCM). The second crystal of the DCM is a sagittal cylindrical crystal which is used for horizontal focusing of the beam while another Rh/Pt coated bendable post mirror facing downward is used for vertical focusing of the beam at the sample position. Two ionization chambers (300 mm length each)

have been used for data collection in the transmission mode; one ionization chamber for measuring incident flux, the second one for measuring transmitted flux. For energy calibration, standard metal foils were used. Appropriate gas pressure and gas mixture have been chosen to achieve 10-20% absorption in the first ionization chamber and 70-90% absorption in the second ionization chamber to obtain a better signal-to-noise ratio. Pellets were made from powder samples for recording absorption spectra. Sample powder was mixed homogeneously with cellulose powder in appropriate proportion and pressed (2 Ton) into a 15 mm diameter disc. The amount of the sample was estimated such that to get a reasonable edge jump at a particular absorption edge of the element to be probed. Spectra were collected at the nickel K-edge in transmission mode and were calibrated against the reference spectrum of metallic nickel (8333 eV). Data were processed using Demeter software.²²¹ A metallic nickel foil standard was used as a reference for energy calibration and was measured simultaneously with experimental samples.

6.7.1. XANES Analysis

The oxidation states of the Ni species within bpy-UiO-NiBr₂ and bpy-UiO-NiH₂ were determined by the comparison of the energy of its K-edge positions to that of NiBr₂. The positions of the Ni K-edge of bpy-UiO-NiBr₂ (8347.8 eV) and bpy-UiO-NiH₂ (8347.4 eV) aligned well with that of NiBr₂ (8347 eV). We, therefore, concluded that Ni ion in bpy-UiO-NiBr₂ and bpy-UiO-NiH₂ has +2 oxidation state.

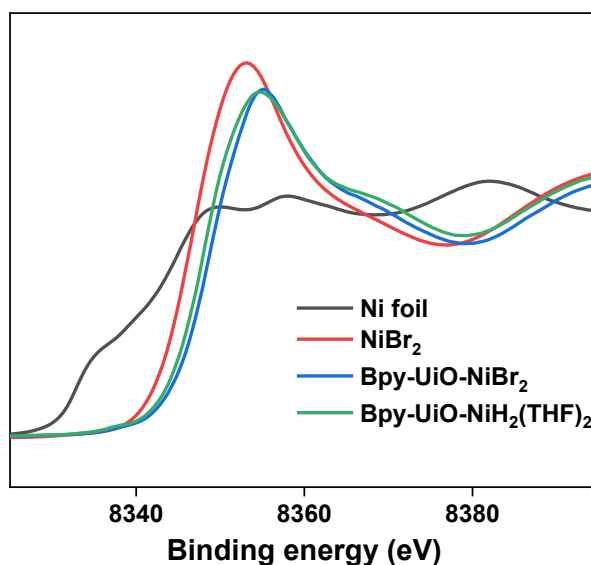


Figure 6.20. $\mu(E)$ XAS spectra of Ni foil (black), NiBr₂ (red), bpy-UiO-NiBr₂ (blue) and bpy-UiO-NiH₂(THF)₂ (green). The spectra indicates that Ni ion in bpy-UiO-NiBr₂ and bpy-UiO-NiH₂(THF)₂ have +2 oxidation state.

6.7.2. EXAFS Fitting using DFT Optimized Structures

The spectra were calibrated against the reference spectra and aligned to the first peak in the smoothed first derivative of the absorption spectrum, the background noise was removed, and the spectra were processed to obtain a normalized unit edge step. The fitting parameters of Ni-K-edge of bpy-UiO-NiBr₂, bpy-UiO-NiH₂(THF)₂ and bpy-UiO-Ni(Bpin)₂ are summarized in Table 6.10, Table 6.11 and Table 6.12 respectively.

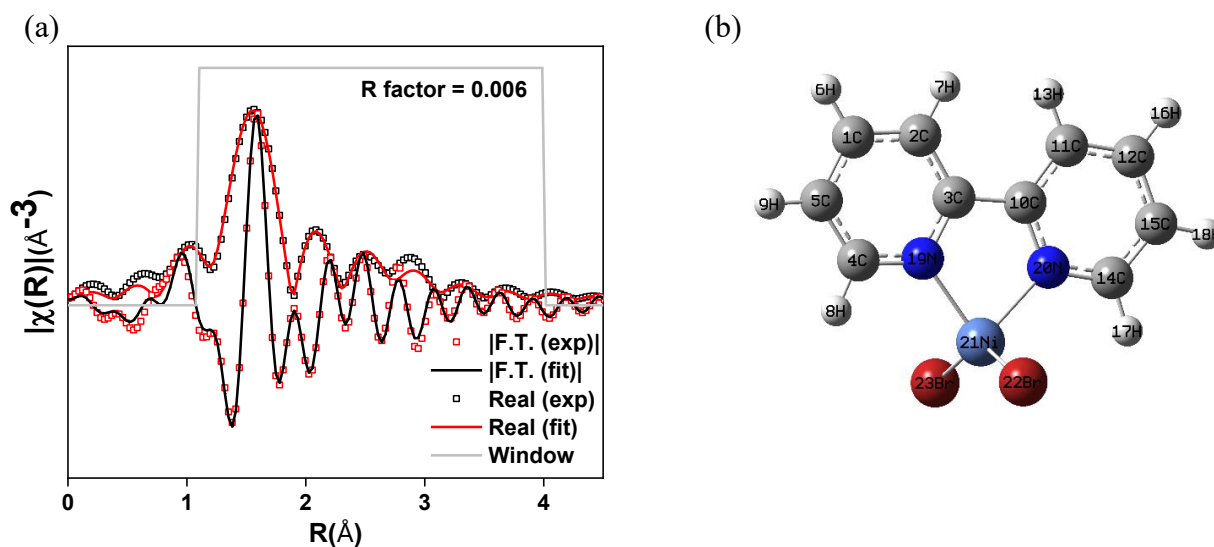


Figure 6.21. (a) EXAFS spectrum (red and black squares) and fits (black and red lines) of bpy-UiO-NiBr₂ in the R space from 1.1 - 4.0 Å. (b) DFT optimised structure of bpy-NiBr₂.

Table 6.10. Summary of EXAFS fitting parameters of bpy-UiO-NiBr₂.

Sample	Bpy-UiO-NiBr ₂	Fitting range	k 3-11.5 Å ⁻¹ R 1.15-4.0 Å
Independent points	14	R-factor	0.006
Variables	10	S_o^2	0.77
Reduced chi-square	291	ΔE_0 (eV)	6.85
R(Ni-N19) (Å)	1.94±0.02	σ^2 (Ni-N19) (Å ²)	0.01±0.004
R(Ni-N20) (Å)	1.94±0.02	σ^2 (Ni-N20) (Å ²)	0.01±0.004
R(Ni-Br22) (Å)	2.34±0.001	σ^2 (Ni-Br22) (Å ²)	0.01±0.002
R(Ni-Br23) (Å)	2.34±0.001	σ^2 (Ni-Br23) (Å ²)	0.01±0.002
R(Ni-C3) (Å)	2.82±0.09	σ^2 (Ni-C3) (Å ²)	0.002±0.0008
R(Ni-C10) (Å)	2.82±0.09	σ^2 (Ni-C10) (Å ²)	0.002±0.0008
R(Ni-C14) (Å)	2.90±0.08	σ^2 (Ni-C14) (Å ²)	0.003±0.001
R(Ni-C4) (Å)	2.90±0.08	σ^2 (Ni-C4) (Å ²)	0.003±0.001

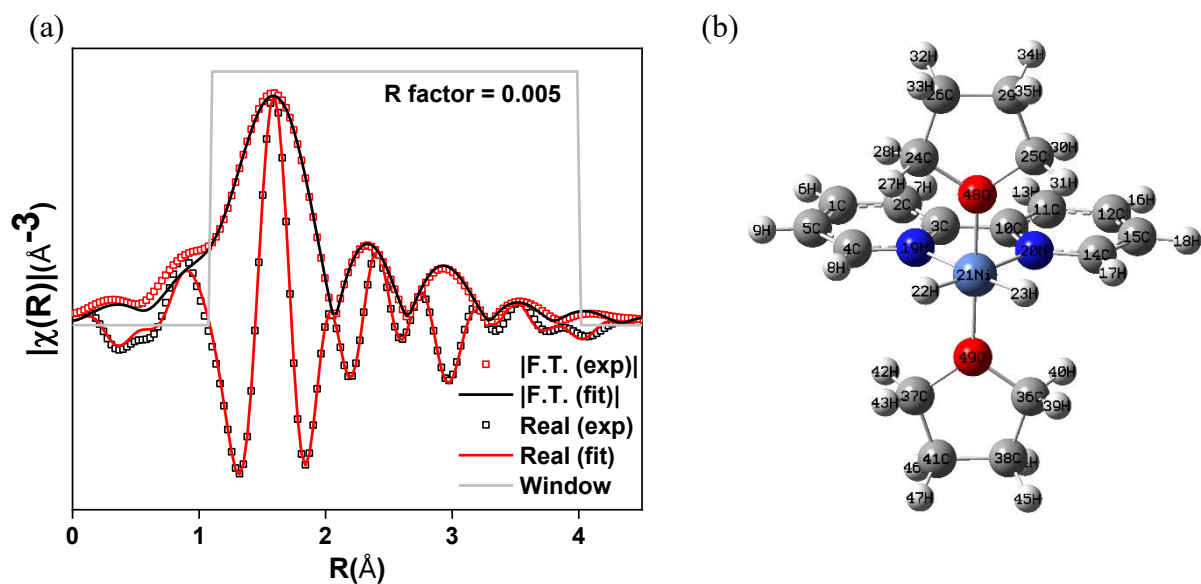


Figure 6.22. (a) EXAFS spectrum (red and black squares) and fits (black and red lines) of bpy-UiO-NiH₂(THF)₂ in the R space from 1.1 - 4.0 Å. (b) DFT optimised structure of bpy- NiH₂(THF)₂.

Table 6.11. Summary of EXAFS fitting parameters of bpy-UiO-NiH₂(THF)₂.

Sample	Bpy-UiO-NiH ₂ (THF) ₂	Fitting range	k 3-10.5 Å ⁻¹ R 1.15-4.0 Å
Independent points	13	R-factor	0.005
Variables	11	S _o ²	0.75
Reduced chi-square	334	ΔE ₀ (eV)	1.25
R(Ni-N19) (Å)	1.94±0.01	σ ² (Ni-N19) (Å ²)	0.009±0.004
R(Ni-N20) (Å)	1.94±0.01	σ ² (Ni-N20) (Å ²)	0.009±0.004
R(Ni-O48) (Å)	2.10±0.001	σ ² (Ni-O48) (Å ²)	0.008±0.002
R(Ni-O49) (Å)	2.10±0.001	σ ² (Ni-O49) (Å ²)	0.008±0.002
R(Ni-C3) (Å)	2.82±0.09	σ ² (Ni-C3) (Å ²)	0.001±0.0005
R(Ni-C10) (Å)	2.82±0.09	σ ² (Ni-C10) (Å ²)	0.001±0.0005
R(Ni-C14) (Å)	2.90±0.09	σ ² (Ni-C14) (Å ²)	0.001±0.0004
R(Ni-C4) (Å)	2.90±0.09	σ ² (Ni-C4) (Å ²)	0.001±0.0004
R(Ni-C24) (Å)	3.25±0.06	σ ² (Ni-C24) (Å ²)	0.001±0.0007
R(Ni-C25) (Å)	3.25±0.06	σ ² (Ni-C25) (Å ²)	0.001±0.0007
R(Ni-C36) (Å)	3.25±0.06	σ ² (Ni-C36) (Å ²)	0.001±0.0007
R(Ni-C37) (Å)	3.25±0.06	σ ² (Ni-C37) (Å ²)	0.001±0.0007

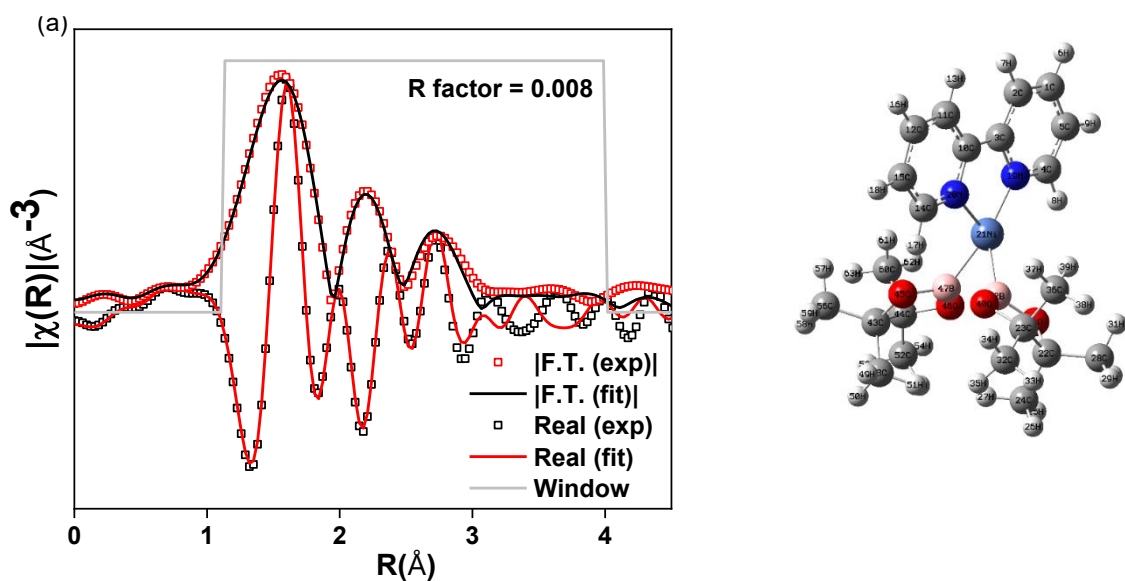


Figure 6.23. (a) EXAFS spectrum (red and black squares) and fits (black and red lines) of bpy-UiO-Ni(Bpin)₂ in the R space from 1.1 - 4.0 Å. (b) DFT optimised structure of bpy-Ni(Bpin)₂.

Table 6.12. Summary of EXAFS fitting parameters of bpy-UiO-Ni(Bpin)₂.

Sample	Bpy-UiO-Ni(Bpin) ₂	Fitting range	k 3-10.5 Å ⁻¹ R 1.11-4.0 Å
Independent points	13	R-factor	0.008
Variables	10	S _o ²	0.88
Reduced chi-square	244	ΔE ₀ (eV)	3.48
R(Ni-B42) (Å)	1.98±0.09	σ ² (Ni-B42) (Å ²)	0.009±0.004
R(Ni-B47) (Å)	1.98±0.09	σ ² (Ni-B47) (Å ²)	0.009±0.004
R(Ni-N19) (Å)	1.94±0.08	σ ² (Ni-N19) (Å ²)	0.009±0.004
R(Ni-N20) (Å)	1.96±0.08	σ ² (Ni-N20) (Å ²)	0.009±0.004
R(Ni-O45) (Å)	2.98±0.02	σ ² (Ni-O45) (Å ²)	0.008±0.002
R(Ni-O40) (Å)	2.98±0.02	σ ² (Ni-O40) (Å ²)	0.008±0.002
R(Ni-O41) (Å)	2.85±0.02	σ ² (Ni-O41) (Å ²)	0.008±0.002
R(Ni-O46) (Å)	2.85±0.02	σ ² (Ni-O46) (Å ²)	0.008±0.002
R(Ni-C3) (Å)	2.88±0.01	σ ² (Ni-C3) (Å ²)	0.001±0.0005
R(Ni-C10) (Å)	2.88±0.01	σ ² (Ni-C10) (Å ²)	0.001±0.0005
R(Ni-C4) (Å)	2.99±0.01	σ ² (Ni-C4) (Å ²)	0.001±0.0004
R(Ni-C14) (Å)	2.99±0.01	σ ² (Ni-C14) (Å ²)	0.001±0.0004
R(Ni-C44) (Å)	3.44±0.09	σ ² (Ni-C44) (Å ²)	0.001±0.0007
R(Ni-C43) (Å)	3.44±0.09	σ ² (Ni-C43) (Å ²)	0.001±0.0007
R(Ni-C23) (Å)	3.78±0.09	σ ² (Ni-C23) (Å ²)	0.001±0.0007
R(Ni-C22) (Å)	3.78±0.09	σ ² (Ni-C22) (Å ²)	0.001±0.0007

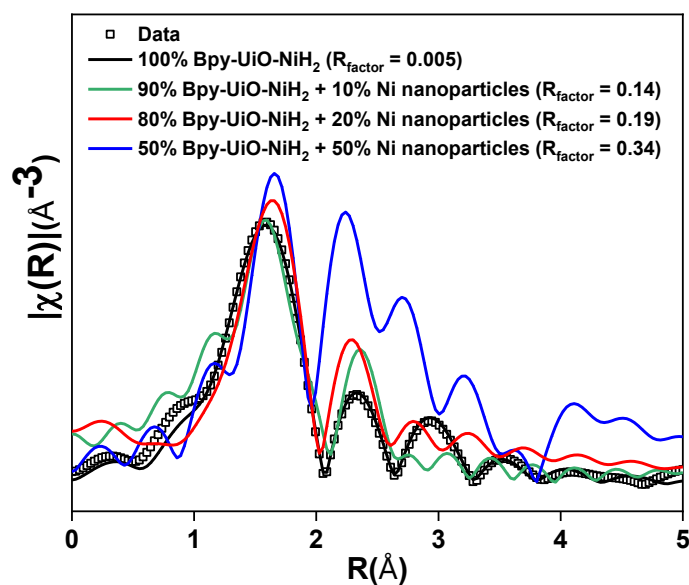


Figure 6.24. (a) EXAFS spectra of bpy-UiO-NiH₂ fitted with 100% bpy-UiO-NiH₂ (black); 10% Ni nanoparticles and 90% bpy-UiO-NiH₂ (green); 20% Ni nanoparticles and 80% bpy-UiO-NiH₂ (red); 50% Ni nanoparticles and 50% bpy-UiO-NiH₂ (blue). The spectra suggest that there are no nanoparticles present inside of bpy-UiO-NiH₂.

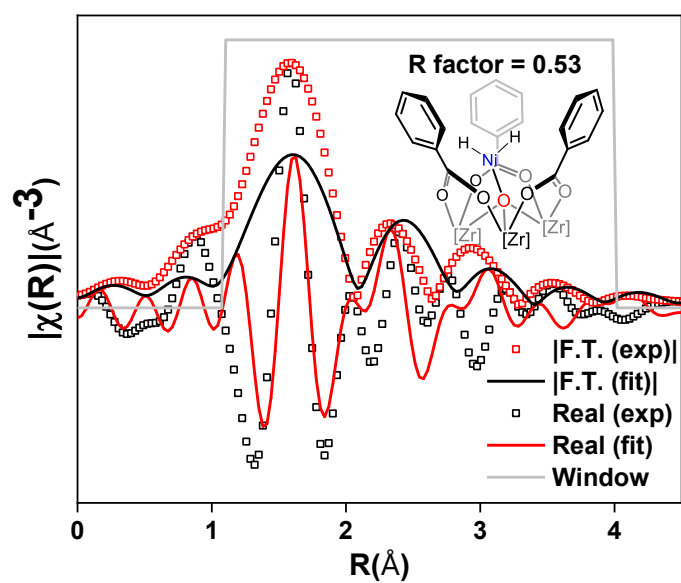


Figure 6.25. (a) Raw EXAFS spectra of bpy-UiO-NiH₂ fitted with DFT-optimized model of nickel coordinated with the μ_3 -OH of the SBUs. The misfit indicates the absence of such coordination environment for nickel.

6.8. DFT Calculations

All quantum chemical calculations were done using the density functional theory (DFT) functional B3LYP-D3/6-311G(d,p) as implemented in the Gaussian 16 software suite.^{294,295,336–338} Electronic structure complexes were optimized at the unrestricted level. Dispersion interactions were considered by incorporating the D3 scheme of Grimme.³³⁹ All calculations were performed in the solvated state and at 473.15 K. We used the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) as the default SCRF method by using cyclohexane as the solvent in this DFT calculation. Each structure was first optimized, and then frequency calculation was performed to confirm its geometry and to obtain the thermochemical data. To reduce the computational costs, a simplified bipyridyl ligand was used in these calculations.

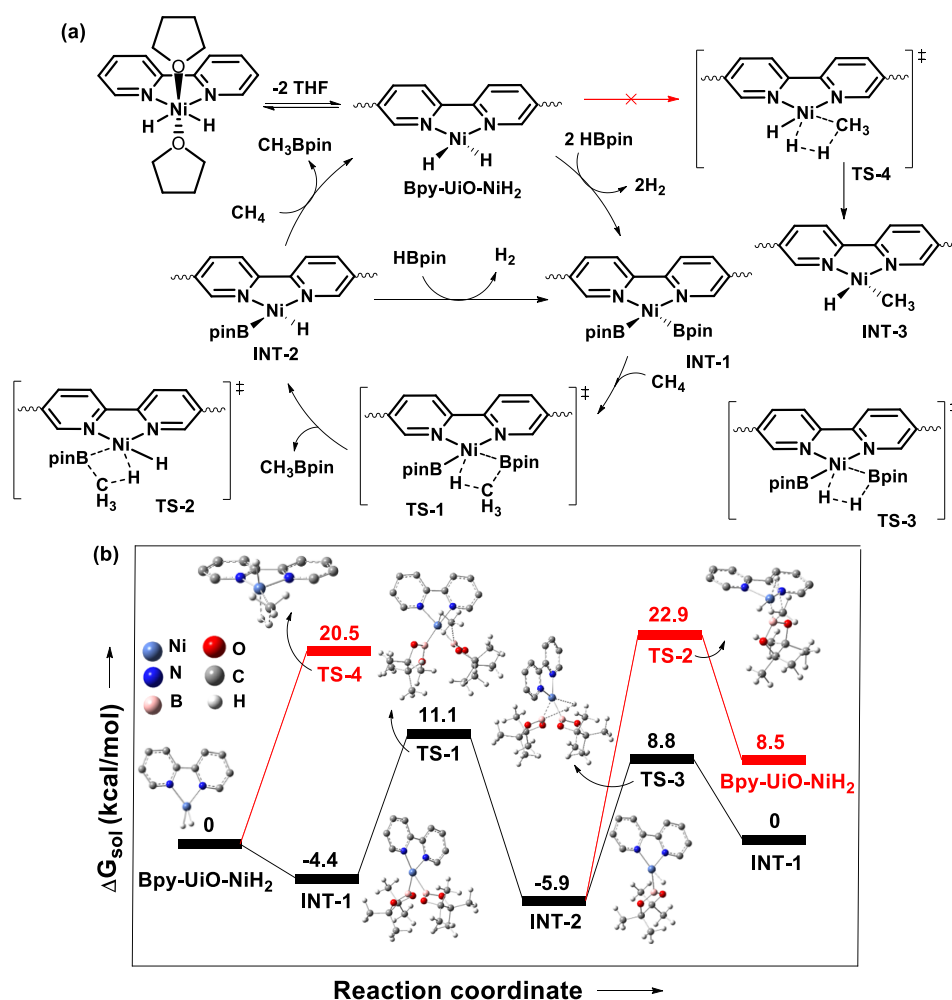
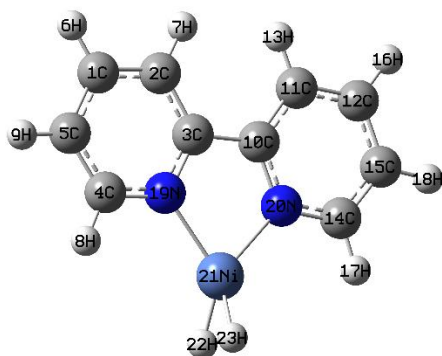
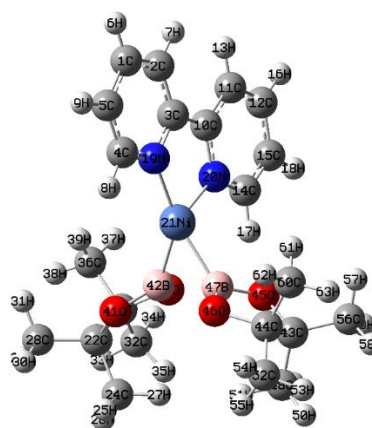


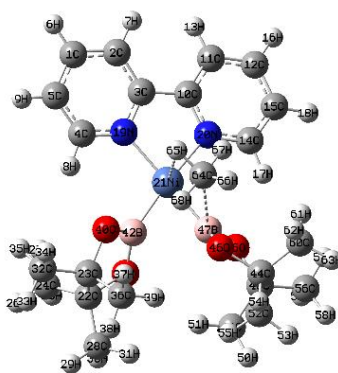
Figure 6.26. (a) Proposed catalytic cycle of bpy-UiO-NiH₂ catalyzed monoborylation of methane. (b) DFT calculated free energy diagram for bpy-UiO-NiH₂ catalyzed methane borylation in cyclohexane at 473.15 K.



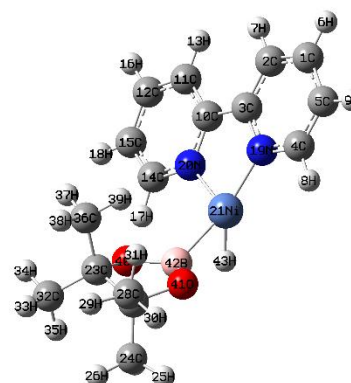
Bpy-NiH₂



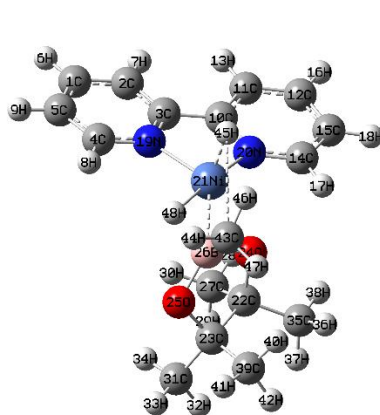
INT-1



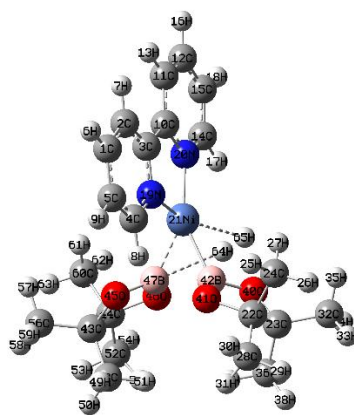
TS-1



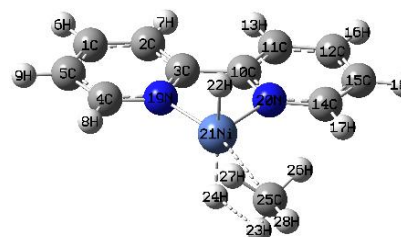
INT-2



TS-2



TS-3



TS-4

Figure 6.27. DFT-optimized structures of intermediates and transition states of the catalytic cycle in bpy-UiO-NiH₂ catalyzed methane borylation.

6.8.1. Cartesian Coordinates of the DFT-Optimized Structures

Cartesian coordinates of bpy-UiO-NiH₂

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	1.470635	3.517961	-1.283598
2	C	2.858298	3.555791	-1.361375
3	C	3.604276	3.562395	-0.183612
4	C	1.661074	3.494524	1.096403
5	C	0.857123	3.487086	-0.035510
6	H	0.877050	3.512107	-2.189276
7	H	3.345733	3.577877	-2.325732
8	H	1.238231	3.470156	2.093204
9	H	-0.219341	3.456873	0.066053
10	C	5.085602	3.601417	-0.135505
11	C	5.903452	3.657315	-1.262982
12	C	7.283492	3.688818	-1.097699
13	H	5.476383	3.678169	-2.255513
14	C	6.944613	3.610491	1.265027
15	C	7.817492	3.663941	0.186490
16	H	7.932086	3.733055	-1.963755
17	H	7.305866	3.592046	2.285613
18	H	8.885509	3.687122	0.356294
19	N	2.995455	3.531249	1.021468
20	N	5.617331	3.580289	1.106049
21	Ni	4.256752	3.535297	2.599847
22	H	4.247699	2.417523	3.523426
23	H	4.205446	4.628085	3.551521

Cartesian coordinates of INT-1

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	2.301513	5.119880	-1.671581
2	C	3.315413	4.098441	-1.768299
3	C	4.316539	3.966762	-0.682519
4	C	3.206575	5.671071	0.536650
5	C	2.251011	5.876927	-0.539434
6	H	1.585849	5.247820	-2.473646
7	H	3.277886	3.353060	-2.548681
8	H	3.292213	6.366353	1.359040
9	H	1.504512	6.652979	-0.412843
10	C	5.403068	3.079114	-0.763394
11	C	5.692989	2.226190	-1.870452
12	C	6.760187	1.364075	-1.820676
13	H	5.066525	2.266684	-2.751096
14	C	7.252970	2.181307	0.398629
15	C	7.561700	1.320993	-0.650705
16	H	6.984087	0.719474	-2.662072
17	H	7.834938	2.178532	1.313952
18	H	8.399611	0.642297	-0.562927

19	N	4.215455	4.708999	0.456882
20	N	6.239746	3.046995	0.371189
21	Ni	5.633889	4.332782	1.772049
22	C	3.607780	3.316112	5.255059
23	C	4.177622	1.918441	4.820354
24	C	4.375592	3.949169	6.418130
25	H	4.059379	4.988785	6.521030
26	H	4.179547	3.429645	7.358697
27	H	5.450439	3.942108	6.225803
28	C	2.108657	3.348215	5.517932
29	H	1.850889	2.681876	6.345578
30	H	1.806105	4.362346	5.786359
31	H	1.541894	3.047706	4.637380
32	C	4.787926	1.093129	5.944311
33	H	4.033927	0.856475	6.700055
34	H	5.174288	0.155541	5.539746
35	H	5.611964	1.619916	6.424331
36	C	3.183835	1.082417	4.010277
37	H	3.713100	0.229142	3.582674
38	H	2.365741	0.713251	4.632830
39	H	2.775087	1.663889	3.183141
40	O	5.241979	2.301898	3.892892
41	O	3.889823	4.139831	4.078480
42	B	4.937723	3.552474	3.406085
43	C	8.564598	6.219057	4.022527
44	C	7.691920	7.465475	3.635922
45	O	8.061237	5.201825	3.098399
46	O	6.463142	6.838252	3.149043
47	B	6.775898	5.557997	2.750958
48	C	8.281034	5.693325	5.432077
49	H	8.773994	4.726755	5.549271
50	H	8.655737	6.374513	6.199309
51	H	7.211618	5.535821	5.577573
52	C	7.336676	8.389364	4.792712
53	H	8.241257	8.819885	5.230710
54	H	6.709012	9.205424	4.429273
55	H	6.787831	7.861834	5.571780
56	C	10.060934	6.383346	3.798323
57	H	10.288380	6.599167	2.754817
58	H	10.454780	7.193449	4.418135
59	H	10.574668	5.460235	4.073844
60	C	8.262993	8.266389	2.462963
61	H	8.514303	7.610031	1.627510
62	H	7.505585	8.973371	2.119880
63	H	9.155812	8.824108	2.754135

Cartesian coordinates of TS-1

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	5.682058	7.227392	-1.357207
2	C	5.945077	5.877429	-1.558872
3	C	5.494909	4.947636	-0.622639
4	C	4.572426	6.633413	0.680105
5	C	4.985128	7.611858	-0.215064
6	H	6.025455	7.964490	-2.073010
7	H	6.507948	5.556189	-2.424944
8	H	4.062721	6.879078	1.601668
9	H	4.767595	8.652458	-0.010751
10	C	5.731191	3.493469	-0.719156
11	C	6.242186	2.852149	-1.847267
12	C	6.403417	1.471688	-1.829115
13	H	6.496704	3.418119	-2.733268
14	C	5.533576	1.468441	0.401588
15	C	6.036690	0.766252	-0.685947
16	H	6.798484	0.956285	-2.696270
17	H	5.216035	0.973509	1.310621
18	H	6.134075	-0.310540	-0.632214
19	N	4.806643	5.324873	0.486168
20	N	5.393430	2.804227	0.399745
21	Ni	4.555818	3.887318	1.845363
22	C	2.074698	5.579902	4.757734
23	C	3.443209	6.303488	5.001159
24	C	1.089744	6.414634	3.931262
25	H	0.264745	5.771367	3.619022
26	H	0.683806	7.252708	4.503475
27	H	1.573513	6.801709	3.032097
28	C	1.392725	5.050367	6.013958
29	H	1.147834	5.869395	6.696533
30	H	0.465599	4.541658	5.740608
31	H	2.026897	4.336535	6.538456
32	C	3.361391	7.820655	5.118422
33	H	2.747799	8.111062	5.976267
34	H	4.364167	8.229640	5.261070
35	H	2.938205	8.269095	4.219441
36	C	4.236860	5.715955	6.173390
37	H	5.243152	6.139638	6.157234
38	H	3.774352	5.946404	7.136594
39	H	4.336114	4.636001	6.060422
40	O	4.177781	5.963573	3.795456
41	O	2.466976	4.454629	3.930186
42	B	3.672539	4.756994	3.290897
43	C	4.137668	0.828662	4.603208
44	C	5.428121	1.530303	5.147911
45	O	3.993106	1.445838	3.294972
46	O	5.372224	2.821266	4.491332
47	B	4.605168	2.704796	3.328505
48	C	2.877056	1.190177	5.395237

49	H	2.006160	0.825420	4.846876
50	H	2.877412	0.741594	6.391926
51	H	2.780684	2.273180	5.479381
52	C	5.457439	1.747312	6.656360
53	H	5.423317	0.791052	7.186516
54	H	6.380019	2.262019	6.934019
55	H	4.618356	2.359494	6.985085
56	C	4.246337	-0.680994	4.428381
57	H	5.047400	-0.946810	3.738398
58	H	4.435629	-1.169398	5.388794
59	H	3.308809	-1.070703	4.025564
60	C	6.723417	0.854401	4.683214
61	H	6.707702	0.694214	3.603185
62	H	7.561652	1.514824	4.912911
63	H	6.885398	-0.104734	5.181482
64	C	7.998671	4.565796	2.566816
65	H	8.073940	5.210110	3.443476
66	H	6.945300	4.359174	2.375914
67	H	8.442763	5.063280	1.702204
68	H	8.517904	3.625553	2.759246

Cartesian coordinates of INT-2

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	1.448399	3.473384	-1.328270
2	C	2.836062	3.511214	-1.406047
3	C	3.582040	3.517818	-0.228284
4	C	1.638839	3.449947	1.051731
5	C	0.834888	3.442509	-0.080183
6	H	0.854815	3.467530	-2.233949
7	H	3.323498	3.533300	-2.370405
8	H	1.215996	3.425579	2.048532
9	H	-0.241576	3.412296	0.021381
10	C	5.063367	3.556841	-0.180177
11	C	5.881216	3.612739	-1.307654
12	C	7.261256	3.644241	-1.142372
13	H	5.454148	3.633592	-2.300186
14	C	6.922378	3.565914	1.220354
15	C	7.795256	3.619364	0.141817
16	H	7.909851	3.688478	-2.008427
17	H	7.283631	3.547469	2.240941
18	H	8.863274	3.642546	0.311621
19	N	2.973220	3.486672	0.976795
20	N	5.595096	3.535713	1.061377
21	Ni	4.234517	3.490721	2.555174
22	H	4.234468	2.220970	3.255341
23	C	3.517615	6.782043	5.273526
24	C	5.033774	6.789184	5.140762
25	C	2.916344	8.033367	4.606998

26	H	1.850178	8.005952	4.693240
27	H	3.290956	8.910575	5.091841
28	H	3.190133	8.053002	3.572805
29	C	3.103574	6.815879	6.756437
30	H	3.276245	7.794680	7.152711
31	H	2.064697	6.574495	6.842279
32	H	3.682102	6.101973	7.304655
33	C	5.512106	8.099949	4.489076
34	H	5.197762	8.930479	5.085992
35	H	6.579818	8.094682	4.419335
36	H	5.091086	8.185413	3.509108
37	C	5.694285	6.706426	6.529458
38	H	6.751280	6.585712	6.415049
39	H	5.494845	7.605978	7.073453
40	H	5.295656	5.870088	7.064746
41	O	5.436110	5.592232	4.291045
42	O	2.994699	5.521355	4.600260
43	B	4.172478	4.819940	3.939272

Cartesian coordinates of TS-2

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	5.229033	7.282543	-1.480242
2	C	5.519961	5.941409	-1.701403
3	C	5.253381	5.011436	-0.697434
4	C	4.455617	6.680324	0.704473
5	C	4.688819	7.658507	-0.253530
6	H	5.431090	8.019893	-2.247764
7	H	5.964110	5.627782	-2.636565
8	H	4.071873	6.921413	1.686509
9	H	4.455954	8.692441	-0.032914
10	C	5.535006	3.566490	-0.808996
11	C	5.895982	2.924925	-1.993326
12	C	6.116925	1.552638	-1.982520
13	H	5.987782	3.484050	-2.914777
14	C	5.594196	1.557299	0.354302
15	C	5.957526	0.855434	-0.787787
16	H	6.397245	1.036886	-2.893041
17	H	5.433978	1.065566	1.305190
18	H	6.107103	-0.215432	-0.735527
19	N	4.718804	5.379922	0.495489
20	N	5.398308	2.886331	0.357849
21	Ni	4.713665	3.954326	1.889765
22	C	4.433297	0.820988	4.381416
23	C	4.920000	1.945981	5.357565
24	O	4.758893	1.390606	3.085039
25	O	4.750113	3.140647	4.553732
26	B	4.769492	2.786509	3.199692
27	C	2.913908	0.622005	4.401335
28	H	2.638725	-0.029763	3.569693

29	H	2.573887	0.164013	5.333695
30	H	2.404776	1.574623	4.252103
31	C	4.099464	2.092986	6.633722
32	H	4.141768	1.176715	7.229767
33	H	4.500105	2.912599	7.234512
34	H	3.056980	2.317172	6.410537
35	C	5.149172	-0.516361	4.526898
36	H	6.221405	-0.416502	4.357278
37	H	4.990416	-0.934513	5.525218
38	H	4.754581	-1.223119	3.793498
39	C	6.412375	1.847012	5.694212
40	H	7.006345	1.743687	4.783780
41	H	6.719886	2.767670	6.194106
42	H	6.626739	1.002697	6.354175
43	C	6.801733	3.762381	3.259094
44	H	6.920826	4.441438	4.077384
45	H	6.768907	5.101456	2.212289
46	H	7.590046	3.411906	2.626140
47	H	7.386014	3.172637	3.934163
48	H	4.242835	4.564402	2.861221

Cartesian coordinates of TS-3

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	1.756900	4.340483	-0.765337
2	C	3.019397	3.842411	-1.066683
3	C	4.028205	3.914468	-0.108418
4	C	2.584140	4.929784	1.405099
5	C	1.534741	4.883622	0.498019
6	H	0.959978	4.292421	-1.497368
7	H	3.211267	3.386083	-2.028674
8	H	2.464811	5.325143	2.404608
9	H	0.563262	5.266491	0.783677
10	C	5.389353	3.372491	-0.283448
11	C	5.914575	2.910984	-1.489212
12	C	7.211842	2.410375	-1.514692
13	H	5.327920	2.953692	-2.397260
14	C	7.364779	2.870272	0.829314
15	C	7.950610	2.387089	-0.334196
16	H	7.639500	2.049179	-2.442158
17	H	7.891188	2.884046	1.774183
18	H	8.963518	2.006042	-0.310765
19	N	3.817951	4.478552	1.113110
20	N	6.112445	3.348258	0.865087
21	Ni	5.292684	4.392993	2.340077
22	C	3.441899	6.619255	5.285295
23	C	4.826766	7.349471	5.216121
24	C	2.342912	7.352479	4.506516
25	H	1.474684	6.694645	4.420306
26	H	2.030509	8.270975	5.009210

27	H	2.685964	7.603360	3.500616	8	H	0.994547	4.667989	1.286890
28	C	2.954364	6.279635	6.689010	9	H	-0.463025	4.654705	-0.740261
29	H	2.823507	7.186983	7.286189	10	C	4.841918	4.799250	-0.941819
30	H	1.991013	5.767808	6.628095	11	C	5.659768	4.855148	-2.069296
31	H	3.653690	5.619430	7.200730	12	C	7.039807	4.886651	-1.904013
32	C	4.754858	8.869603	5.124197	13	H	5.232699	4.876001	-3.061827
33	H	4.254135	9.289638	6.001582	14	C	6.700929	4.808324	0.458713
34	H	5.765999	9.280192	5.078310	15	C	7.573808	4.861773	-0.619824
35	H	4.222479	9.188361	4.228409	16	H	7.688402	4.930888	-2.770068
36	C	5.778781	6.931057	6.343083	17	H	7.062182	4.789878	1.479299
37	H	6.778846	7.299677	6.107270	18	H	8.641825	4.884955	-0.450020
38	H	5.472277	7.340722	7.309089	19	N	2.751771	4.729082	0.215154
39	H	5.829482	5.843404	6.418337	20	N	5.373647	4.778122	0.299735
40	O	5.382511	6.830632	3.981009	21	Ni	4.013068	4.733130	1.793533
41	O	3.715009	5.383000	4.571929	22	H	3.961762	5.825917	2.745207
42	B	4.808799	5.587216	3.718937	23	H	3.887718	2.427449	1.804036
43	C	4.039982	0.331883	2.867809	24	H	3.782504	3.162266	0.835856
44	C	4.500676	0.577401	4.297459	25	C	3.989672	3.482119	2.603461
45	O	4.350519	1.580461	2.054985	26	H	5.056193	3.420444	2.663718
46	O	4.992714	2.014624	4.391695	27	H	2.937604	3.541377	2.789311
47	B	4.880004	2.641282	3.009110	28	H	4.052393	3.471632	3.671570
48	C	2.529245	0.034779	2.836149					
49	H	2.168106	0.129249	1.833376					
50	H	2.354204	-0.961166	3.185940					
51	H	2.015757	0.729825	3.467134					
52	C	3.344616	0.335937	5.285801					
53	H	2.999179	-0.672336	5.191156					
54	H	3.688964	0.502666	6.285063					
55	H	2.542467	1.009712	5.067888					
56	C	4.755133	-0.894659	2.271358					
57	H	5.360184	-0.587394	1.444073					
58	H	5.374734	-1.344631	3.018699					
59	H	4.027370	-1.604158	1.936886					
60	C	5.629298	-0.400803	4.672863					
61	H	6.167972	-0.679141	3.791240					
62	H	6.295785	0.071808	5.363756					
63	H	5.208310	-1.274737	5.124424					
64	H	7.062015	3.242547	3.899443					
65	H	7.009234	4.178612	3.658456					

Cartesian coordinates of TS-4

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	C	1.226951	4.715793	-2.089912
2	C	2.614614	4.753623	-2.167689
3	C	3.360591	4.760228	-0.989926
4	C	1.417390	4.692356	0.290089
5	C	0.613439	4.684918	-0.841824
6	H	0.633366	4.709940	-2.995590
7	H	3.102049	4.775709	-3.132046

6.9. XPS Analysis

All the binding energies were corrected with reference to the C1s peak at 284.8 eV. MULTIPAK software was used for peak analysis and de-convolution studies.

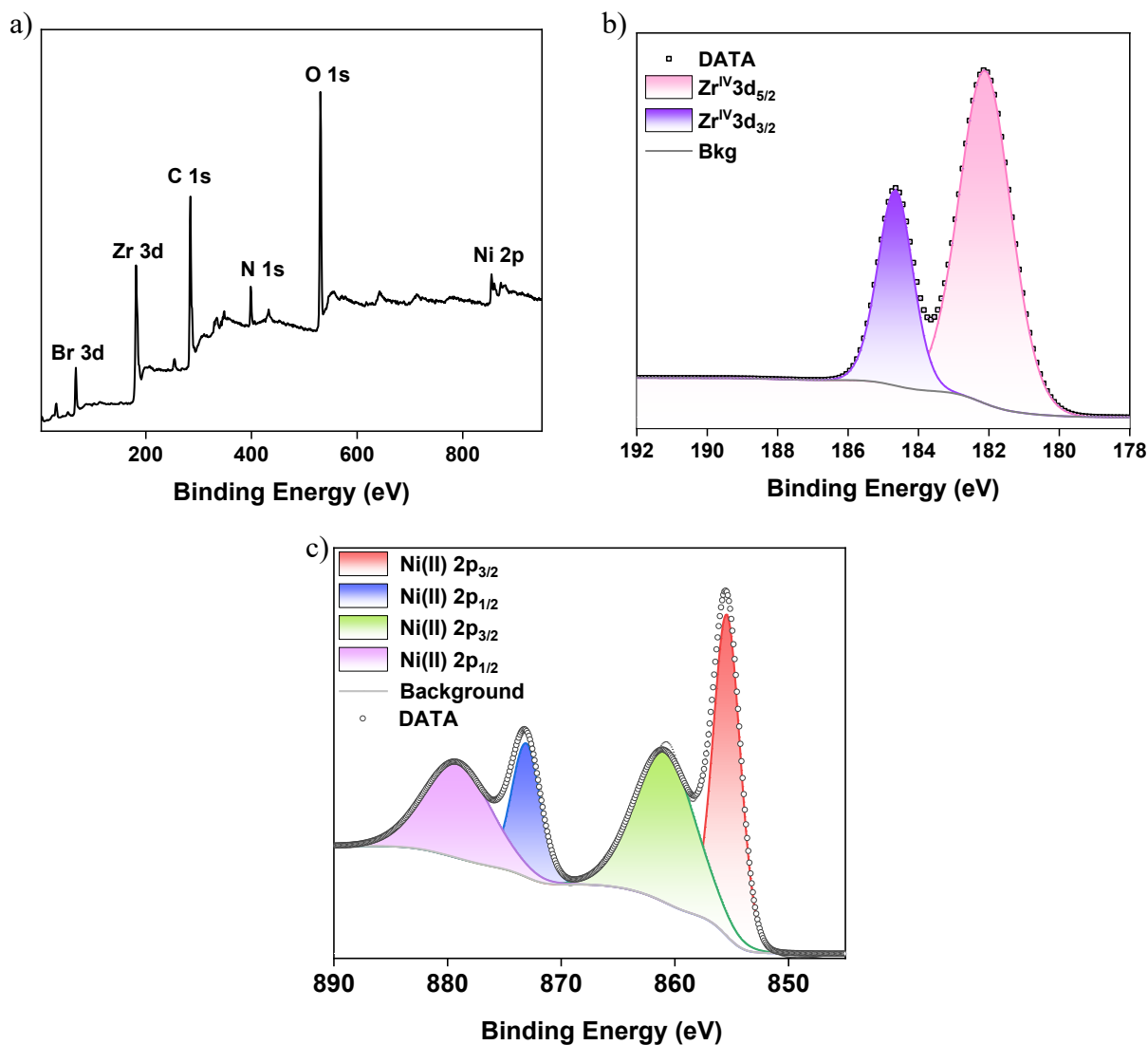
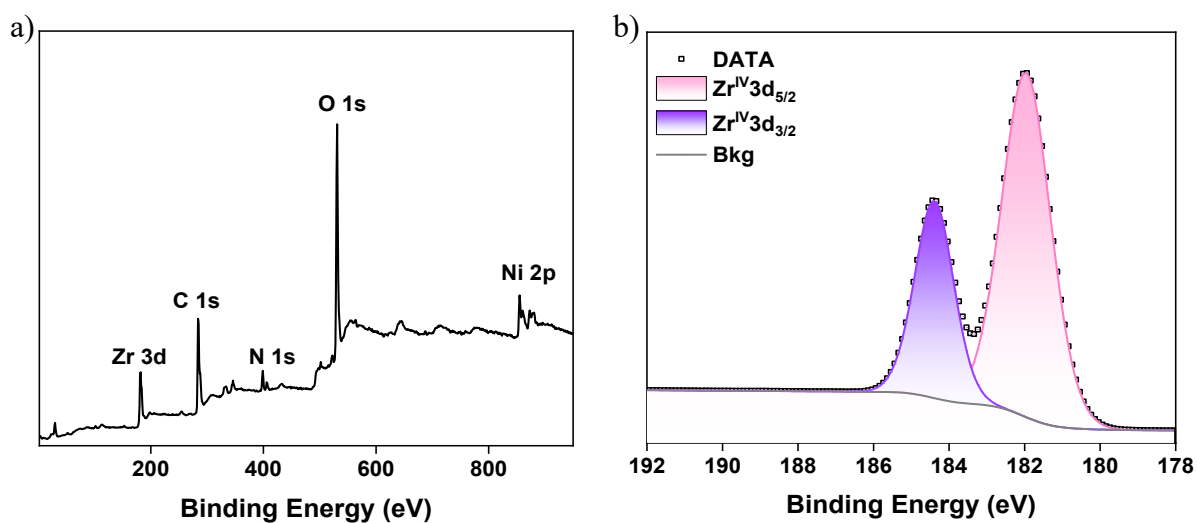


Figure 6.28. a) Raw XPS data of bpy-UiO-NiBr₂ b) Zr 3d XPS spectrum of bpy-UiO-NiBr₂ c) Ni 2p XPS spectrum of bpy-UiO-NiBr₂.



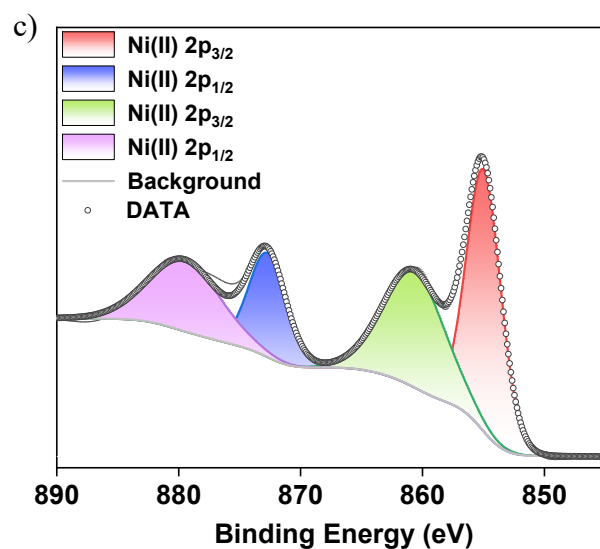


Figure 6.29. a) Raw XPS data of bpy-UiO-NiH₂ b) Zr 3d XPS spectrum of bpy-UiO-NiH₂ c) Ni 2p XPS spectrum of bpy-UiO-NiH₂.

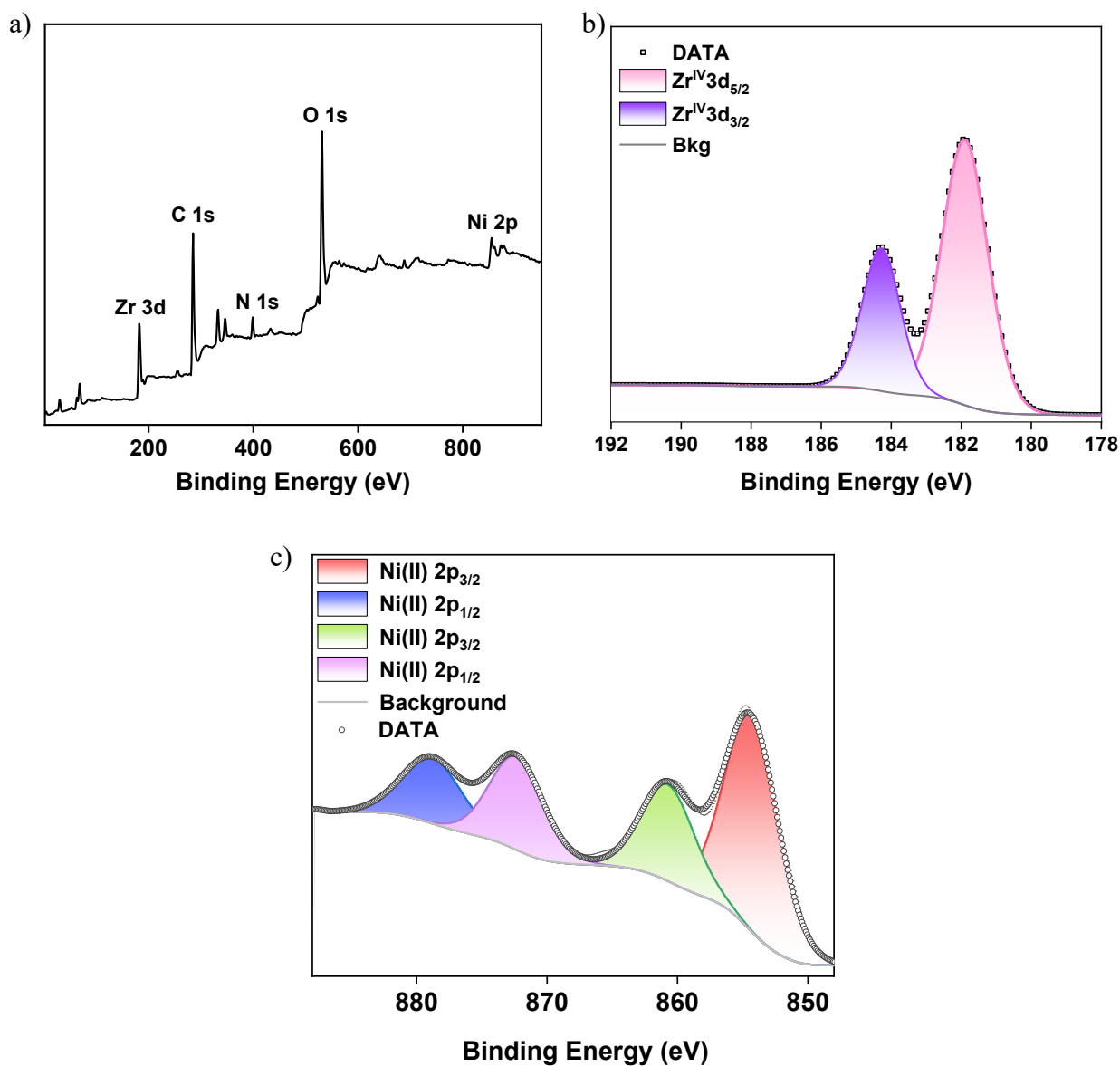


Figure 6.30. a) Raw XPS data of bpy-UiO-Ni after catalysis b) Zr 3d XPS spectrum of bpy-UiO-Ni after catalysis c) Ni 2p XPS spectrum of bpy-UiO-Ni after catalysis.

Table 6.13. Comparison of catalytic activity of bpy-UiO-NiH₂ with that of other reported catalysts in borylation of CH₄.

Reference	Catalysts	Metal Active site	CH ₄ pressure	Temp./ Reaction time	TON of CH ₃ Bpin
<i>Science</i> 2016 , 351 (6280), 1424-1427.	[Ir(COD)(μ-Cl)] ₂ + 2 equiv. dmpe	Ir	34.47 bar	150 °C (16 h)	104
<i>Science</i> 2016 , 351 (6280), 1421-1424.	(MesH)Ir(Bpin) ₃ + 3,4,7,8-tetramethylphenanthroline	Ir	35 bar	150 °C (14 h)	15
	[(Cp*)RuCl ₂] ₂	Ru	35 bar	150 °C (14 h)	22
	[Cp*Rh(η ⁴ -C ₆ Me ₆)]	Rh	35 bar	150 °C (14 h)	68
<i>ACS Catal.</i> 2018 , 8 (11), 10021-10031.	(dmpe)Ir(COD)Cl	Ir	34.47 bar	150 °C (16 h)	170
<i>Nat. Catal.</i> 2018 , 1 (5), 356-362.	UiO-67-Mix-Ir	Ir	34 bar	150 °C (14 h)	67
<i>J. Am. Chem. Soc.</i> 2019 , 141, 11196-11203.	Zr-P1-Ir	Ir	50 bar	110 °C (15 h)	127
<i>Angew. Chem. Int. Ed.</i> 2019 , 58, 10671--10676.	CAL-3-Ir	Ir	34 bar	150 °C (9 h)	126
<i>J. Am. Chem. Soc.</i> 2023 , 145, 7992–8000.	[(dmpe)Ir(cod)]-SiO ₂	Ir	34.47 bar	150 °C (16 h)	2031
This work	Bpy-UiO-NiH₂	Ni	20 bar	200 °C (10 h)	244

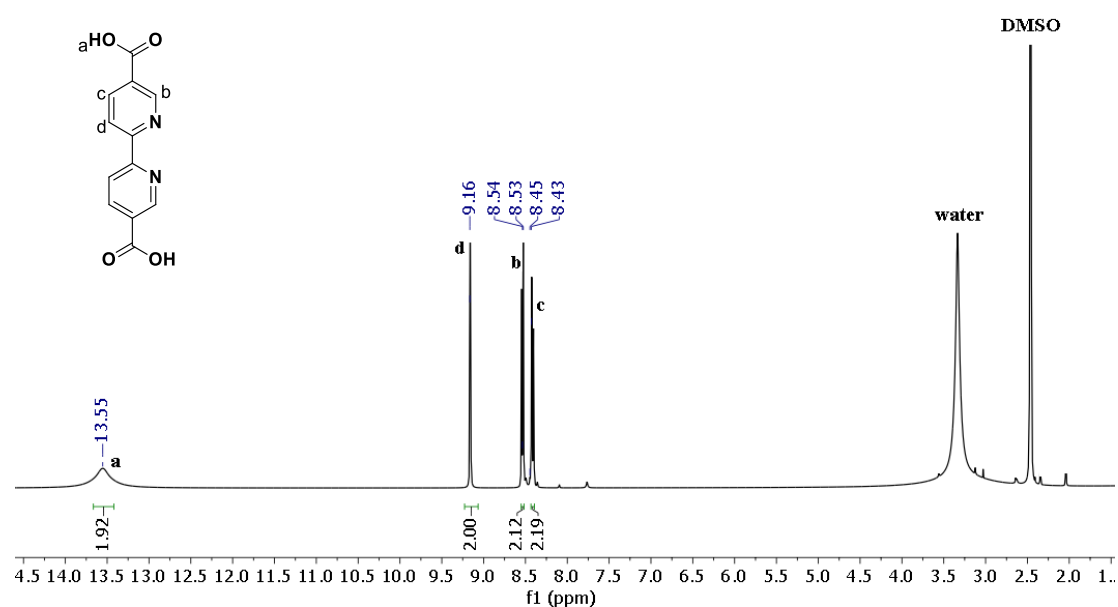


Figure 6.31. ¹H NMR spectrum (500 MHz, DMSO-*d*₆) of 2,2'-bipyridine-5,5'-dicarboxylic acid (H₂BPY).

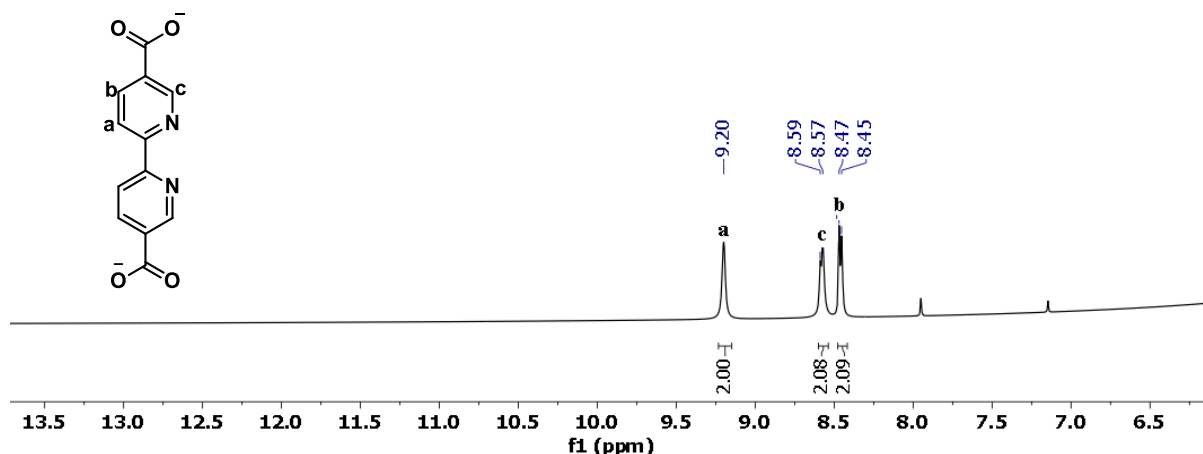


Figure 6.32. ^1H NMR spectrum (500 MHz, $\text{DMSO-}d_6$) of bpy-UiO-MOF digested in $\text{K}_3\text{PO}_4/\text{D}_2\text{O}/\text{DMSO-}d_6$.

6.10. Conclusion

In summary, we have developed a heterogeneous and recyclable catalyst using only earth-abundant elements for chemoselective methane C–H borylation. The active site isolation of mononuclear bipyridyl-nickel(II) dihydride species at the linkers of UiO-67 MOF affords a thermally robust and highly active single-site catalyst for methane activation by shutting the intermolecular degradation pathway. The molecular dimensions of the reactants and products with respect to MOF's pore sizes play a crucial role for selective formation of the mono-borylated product. The confinement of the nickel species within the uniform and rigid pores of the MOF facilitates the selective mono-borylation of methane through shape-selective catalysis, yielding CH_3Bpin in 98% selectivity. This high selectivity is attributed to the well-defined pore structure, where the narrower pore windows restrict the formation of the larger $\text{CH}_2(\text{Bpin})_2$, thereby improving overall catalytic performance. Bpy-UiO- NiH_2 is recyclable at least 6 catalytic runs affording a cumulative TON of 1388. In contrast to bpy-UiO- NiH_2 , the homogeneous controls undergo rapid detrimental intermolecular interaction, leading to the formation of catalytically inactive species. Our mechanistic investigation by experimental and computational studies suggests that the methane activation by σ -bond metathesis between the Ni–Bpin bond and methane C–H bond is the turnover limiting step. This work thus highlights the importance of MOFs in developing novel base-metal catalysts for efficient conversion of methane as the abundant carbon feedstocks into fine chemicals.

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

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Submitted

Abstract: 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 gcat⁻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.

7.1. Introduction

The catalytic hydrogenation of carbon dioxide (CO_2), an abundant and thermodynamically stable C_1 carbon source, represents a central challenge and opportunity in sustainable chemistry. Converting CO_2 into value-added chemicals enables both carbon neutrality and renewable energy storage by transforming a greenhouse gas into energy-dense molecules, particularly when coupled with hydrogen derived from renewable resources. Considerable advances have been achieved in the hydrogenation of CO_2 to C_1 products such as carbon monoxide,^{340–343} methane,^{344–347} and methanol^{348–353}. However, extending this transformation to selectively produce C_{2+} compounds, especially ethanol, remains highly challenging due to the intrinsic kinetic and thermodynamic barriers associated with C–C bond formation.^{354,355}

A wide range of catalytic systems have been explored for the direct hydrogenation of CO_2 to ethanol. These include noble-metal-based catalysts, such as Ir– In_2O_3 ,³⁵⁶ Rh,^{357,358} Ru– In_2O_3 ,³⁵⁹ and Pd-based materials,^{360–362} as well as catalysts derived from earth-abundant metals, including CoAlO_x ,³⁶³ Co–Ni– AlO_x mixed oxides,³⁶⁴ alkali-promoted transition-metal carbides,^{365,366} zeolite-supported copper systems,³⁶⁷ and iron-based sulfides.³⁶⁸ Although several of these catalysts exhibit promising activity, their ethanol productivity is typically constrained by the difficulty of controlling multi-electron and multi-proton transfer steps required for C–C coupling. Consequently, most reported systems exhibit a trade-off between CO_2 conversion and ethanol selectivity, often favoring kinetically preferred C_1 products or undergoing uncontrolled hydrocarbon chain growth. In many cases, high-temperature pretreatment, harsh reaction conditions, or poor catalyst stability further limit practical applicability.

Metal-organic frameworks (MOFs) have emerged as versatile platforms for heterogeneous catalysis owing to their crystalline order, tunable porosity, and well-defined metal–ligand environments that enable precise control over catalytic active sites.^{41,64,190,209,267} These features have facilitated mechanistic insights and catalytic design across a wide range of reactions, including CO_2 hydrogenation.^{369–382} Recent efforts toward MOF-based catalysts for CO_2 -to-ethanol conversion have employed strategies such as single-site metal grafting,^{380,383} MOF–nanoparticle hybridization,³⁸⁴ defect engineering,^{385,386} and linker functionalization³⁸⁷. Despite these advances, many MOF catalysts continue to suffer from limited turnover numbers, rapid deactivation, and insufficient selectivity or stability. A notable example involves a zirconium-based MOF containing Cs^+ -stabilized Cu(I) species at Zr_{12} -oxo nodes, which exhibited exceptionally high ethanol selectivity and CO_2 conversion.³⁸⁸ Nevertheless, the requirement for anaerobic conditions and organic solvents restricts its broader applicability. While catalysis within rigid porous frameworks has been extensively investigated, the role of conformational dynamics in flexible porous materials remains comparatively underexplored.

Increasing evidence suggests that structural adaptability arising from framework breathing, hemilabile coordination, photo-responsive linkers, or guest-induced transformations—can dynamically regulate active-site geometry, mass transport, and intermediate stabilization. Such adaptive behavior introduces an additional level of catalytic control that extends beyond static structure–activity relationships.^{389–395} We hypothesize that embedding atomically dispersed, earth-abundant metal active sites within a dynamically responsive MOF scaffold could synergistically couple precise CO₂ activation with framework-mediated regulation of reaction pathways, thereby facilitating selective C₁ homologation to ethanol.

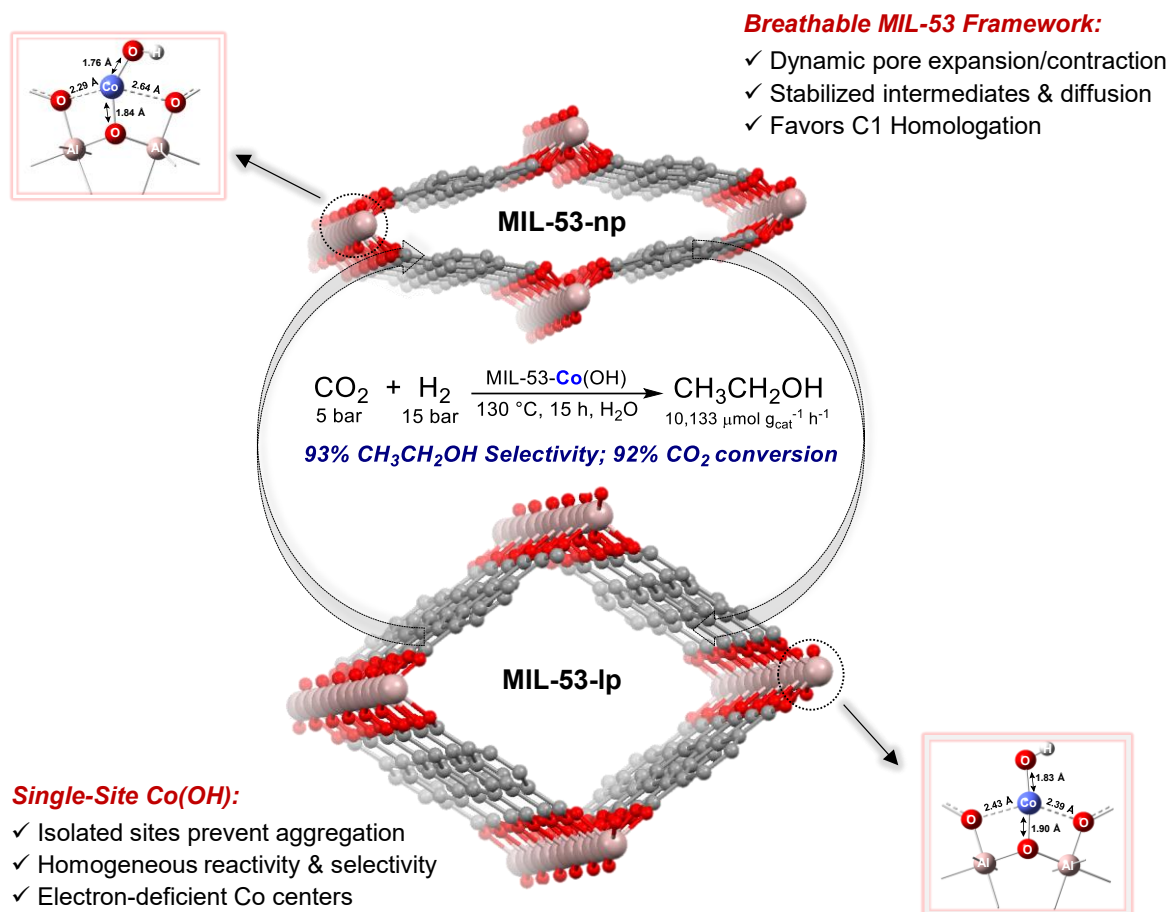


Figure 7.1. Dynamic pore breathing in MIL-53(Al) regulates Co(II)–OH active sites at the nodes, promoting selective CO₂ hydrogenation to ethanol.

In this context, the present work introduces a “breathing” MIL-53(Al)-confined single-site cobalt(II) hydroxyl catalyst, denoted as MIL-53-Co(OH), for the selective hydrogenation of CO₂ to ethanol in aqueous media (Figure 7.1). MIL-53(Al) is well known for its pronounced structural flexibility, undergoing reversible transitions between narrow-pore and large-pore configurations in response to external stimuli such as temperature, pressure, and guest molecules including CO₂, H₂O, and H₂.^{396–398} We demonstrate that the dynamic modulation of the coordination environment at the MOF nodes under reaction conditions plays a critical role in facilitating C–C bond formation within the confined micropores, while simultaneously promoting local reactant enrichment and efficient product release. As a result, MIL-53-Co(OH)

achieves 92% CO₂ conversion in water with an ethanol productivity of 10,133 $\mu\text{mol gcat}^{-1} \text{ h}^{-1}$ and a selectivity of 93%, highlighting the potential of framework dynamics as a design principle for advanced MOF-based catalytic systems.

7.2. Results and Discussion

7.2.1. Synthesis and Characterization of MIL-53–Co(OH) and Related Derivatives

MIL-53(Al) and its two functionalized derivatives, MIL-53-NO₂ and MIL-53-NH₂, were synthesized using a general solvothermal protocol involving the reaction of Al(NO₃)₃·9H₂O with the corresponding dicarboxylate linkers in water or DMF/H₂O mixtures at 150–220 °C.^{396,399} Powder X-ray diffraction (PXRD) confirmed that all three pristine frameworks adopt the characteristic MIL-53 sql topology, consisting of Al(OH) secondary building units (SBUs) linked by pristine or functionalized terephthalate ligands to form one-dimensional rhombic channels.⁴⁰⁰ Post-synthetic modification of the μ_2 -OH groups at the SBUs was achieved through sequential treatment with *n*-BuLi, CoCl₂, NaEt₃BH, and H₂O, yielding uniformly dispersed Co(OH) moieties anchored at the metal nodes. PXRD patterns of the cobalt-functionalized materials revealed that MIL-53-Co(OH) predominantly exists in the large-pore (lp) phase, whereas MIL-53-NO₂-Co(OH) and MIL-53-NH₂-Co(OH) exhibit the coexistence of lp and narrow-pore (np) phases (Figures 7.2a–b). Inductively coupled plasma–optical emission spectroscopy (ICP-OES) of digested samples indicated Co loadings of 38%, 36%, and 42% relative to the μ_2 -OH sites for MIL-53-Co(OH), MIL-53-NO₂-Co(OH), and MIL-53-NH₂-Co(OH), respectively. Brunauer–Emmett–Teller (BET) surface area analysis showed specific surface areas of 900, 534, and 348 m² g^{−1} for the corresponding Co-functionalized frameworks (Figure 7.2c). Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) mapping confirmed the homogeneous distribution of Al and Co throughout the MIL-53-Co(OH) crystallites (Figure 7.2d). X-ray photoelectron spectroscopy (XPS) established the +2 oxidation state of the grafted cobalt centers in all three materials (Figure 7.2e). This assignment was further corroborated by X-ray absorption near-edge structure (XANES) analysis, where the Co K-edge position of MIL-53-Co(OH) (7119.7 eV) closely matches that of CoO, confirming the presence of Co(II) species (Figure 7.2f).

Extended X-ray absorption fine structure (EXAFS) analysis of MIL-53-Co(OH), fitted using a DFT-optimized structural model of the cobalt active site, confirms that cobalt is incorporated within the large-pore (lp) phase of the MIL-53 framework. The fitting results reveal a tetrahedral coordination environment around the cobalt center, consisting of one terminal hydroxyl ligand (Co–OH, 1.80 Å), one μ_2 -oxo bridge to the Al node (Co–O μ_2 , 1.91

Å), and two carboxylate oxygen atoms from the linker (Co–Ocarboxylate, 2.30 Å) (Figure 7.3a).

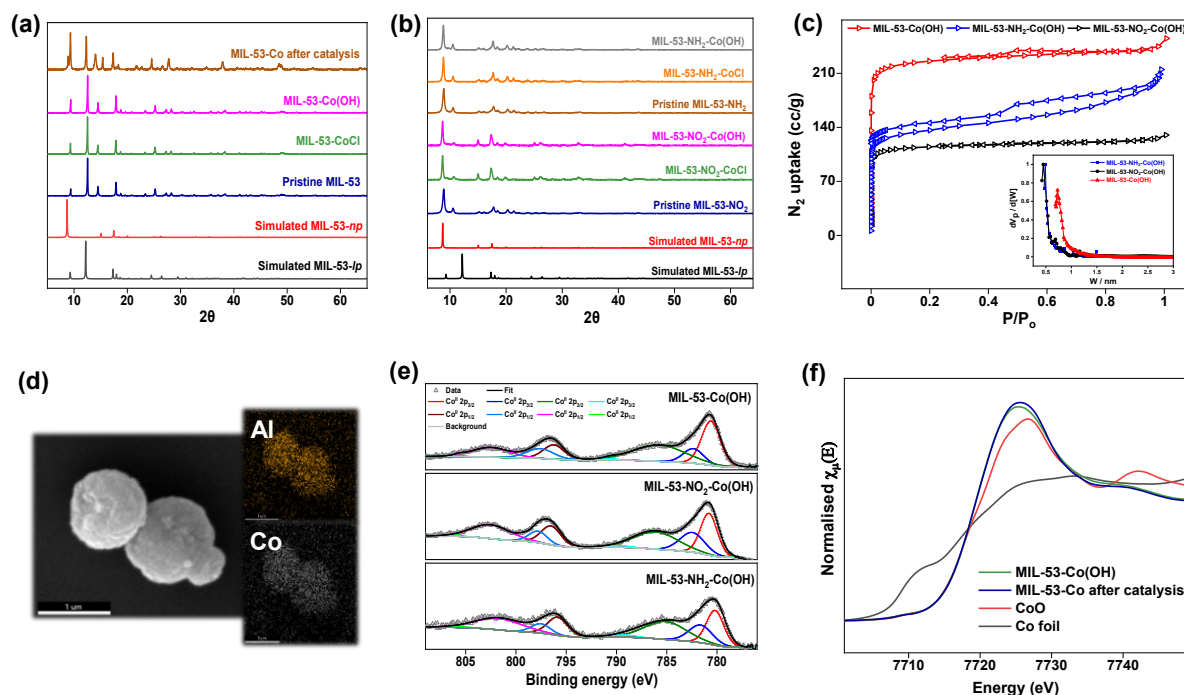


Figure 7.2. (a) PXRD patterns of simulated MIL-53-*lp* (black), simulated MIL-53-*np* (red), pristine MIL-53 (blue), MIL-53-CoCl (green), MIL-53-Co(OH) (magenta), and MIL-53-Co(OH) after catalysis (brown). (b) PXRD patterns of simulated MIL-53-*lp* (black), simulated MIL-53-*np* (red), pristine MIL-53-NO₂ (blue), MIL-53-NO₂-CoCl (green), MIL-53-NO₂-Co(OH) (magenta), pristine MIL-53-NH₂ (brown), MIL-53-NH₂-CoCl (orange) and MIL-53-NH₂-Co(OH) (gray). (c) N₂ sorption isotherm of MIL-53-Co(OH) (red), MIL-53-NH₂-Co(OH) (blue) and MIL-53-NO₂-Co(OH) (black) measured at 77 K. (d) SEM-EDX mapping of MIL-53-Co(OH) particles. (e) Co 2p XPS spectra of MIL-53-Co(OH), MIL-53-NO₂-Co(OH), and MIL-53-NH₂-Co(OH). (f) Co K-edge XANES spectra of MIL-53-Co(OH) (green), MIL-53-Co after catalysis (blue), CoO (red) and Co foil (black).

The phase-uncorrected k^2 -weighted EXAFS spectrum of MIL-53-Co(OH) exhibits a dominant Co–O scattering contribution at ~ 1.53 Å, consistent with Co(II)–O bonding distances observed in CoO (Figure 7.3c). Importantly, no discernible Co–Co or Co–O–Co multiple-scattering features are observed. Only weak features at ~ 2.2 Å and ~ 2.7 Å are present, effectively ruling out the formation of metallic cobalt clusters or CoO nanoparticles within the framework. This conclusion is further supported by quantitative EXAFS fitting, which shows poor agreement when structural models incorporating 5–50% contributions from metallic cobalt or cobalt oxide species are introduced (Figure 7.15). Wavelet transform (WT) analysis further corroborates these findings, displaying a single intensity maximum at $k \approx 4.3$ Å^{−1}, characteristic of Co–O coordination, with no high- k intensity features around $k \approx 6.5$ Å^{−1} that would indicate Co–Co interactions (Figure 7.3d). Collectively, these spectroscopic results unequivocally confirm the presence of atomically dispersed Co(II) sites anchored at the MIL-53 nodes.

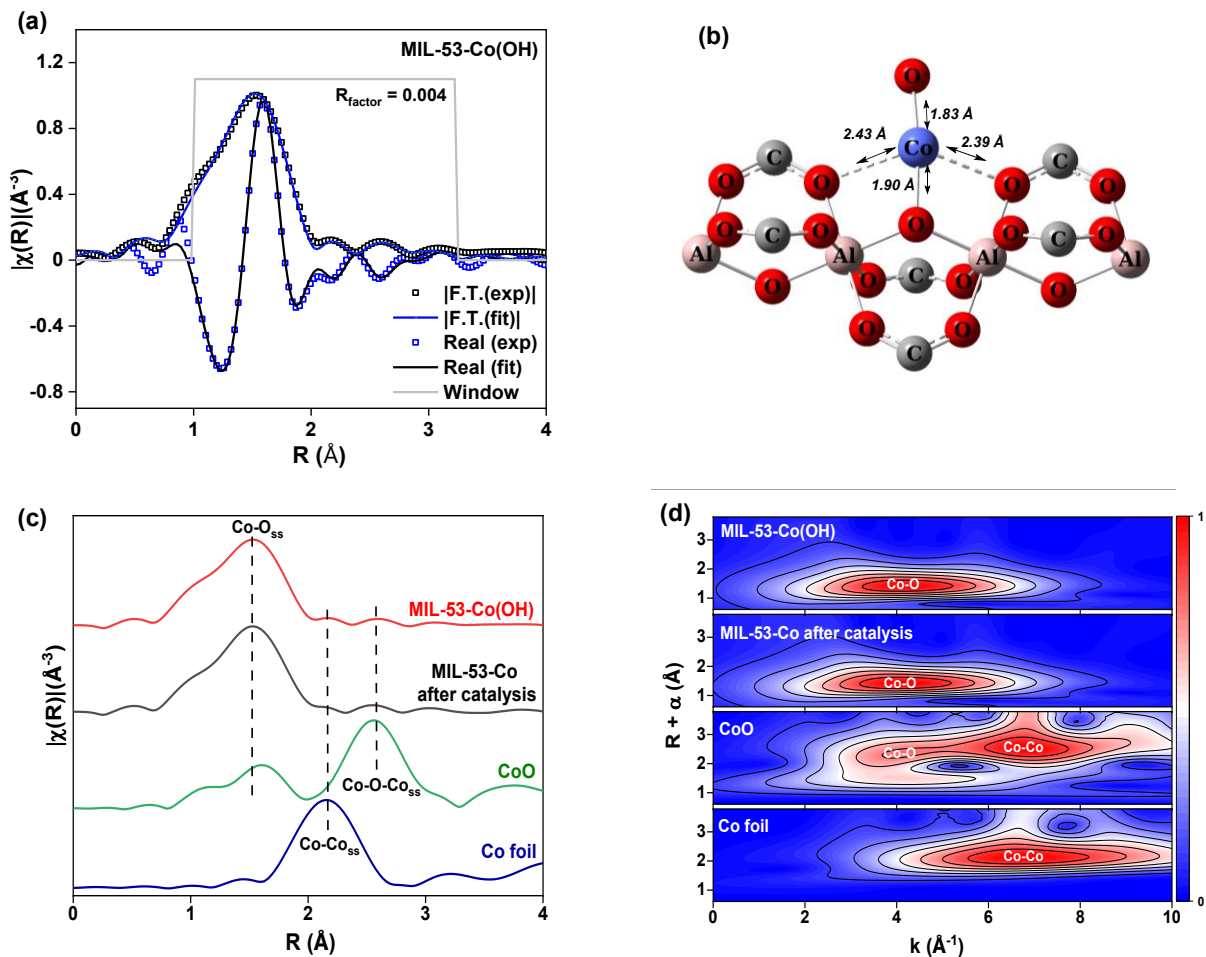


Figure 7.3. (a) EXAFS spectra (black and blue squares) and fits (black and blue lines) of MIL-53-Co(OH) in the R space from 1-3.25 Å. (b) DFT-optimized structure of the cobalt active-center in MIL-53 (*lp*). Hydrogen atoms are omitted for clarity. (c) k^2 -weighted Co-EXAFS $\chi(R)$ spectra of MIL-53-Co(OH) (red), MIL-53-Co after catalysis (black), CoO (green), and Co foil (blue). (d) Wavelet transform for the k^2 -weighted EXAFS signal at the Co K-edge.

7.2.2. MIL-53-Co(OH) Catalyzed Hydrogenation of CO₂

Catalytic evaluations were conducted in a high-pressure stainless-steel batch reactor (total free volume: 65 mL) using H₂O (15 mL) as the solvent and MIL-53-Co(OH) (5 mg, 8 μmol Co) as the catalyst. After reaction, liquid products were identified and quantified by gas chromatography coupled with mass spectrometry and a flame-ionization detector (GC-MS/FID), while gaseous products were analyzed by GC equipped with a thermal-conductivity detector (GC-TCD). Under a total pressure of 20 bar ($P_{H_2}/P_{CO_2} = 3$) at 130 °C for 15 h, MIL-53-Co(OH) produced 0.58 mmol of ethanol with an exceptional selectivity of 98.3%, corresponding to a productivity of 7733 μmol g cat⁻¹ h⁻¹ (Entry 1, Table 7.1). No C₂⁺ hydrocarbons, methanol, or other oxygenated products were detected; methane was the sole byproduct, formed only in trace amounts (0.01 mmol). Time-resolved studies showed a monotonic increase in ethanol formation from 0.49 mmol at 12 h to 0.72 mmol at 21 h; however, prolonged reaction times resulted in a gradual decrease in selectivity from 98% to

90%, attributable to increased methane formation (0.06 mmol) and minor methanol production (Entries 8-10, Table 7.3).

Increasing the total pressure to 32 bar further enhanced ethanol yield to 0.77 mmol but led to a decrease in selectivity and CO₂ conversion, reaching 87% and 8%, respectively (Entry 3, Table 7.1). Adjusting the P_{H₂}/P_{CO₂} ratio from 3 to 4 increased CO₂ conversion to 12.7%; however, ethanol yield decreased to 0.31 mmol, and acetic acid became the dominant product (0.64 mmol), indicating a shift in reaction pathway under hydrogen-rich conditions (Entry 4, Table 7.1). Temperature-dependent studies revealed a 3.5-fold increase in CO₂ conversion between 100 and 150 °C; nevertheless, higher temperatures favored acetic acid formation and reduced ethanol selectivity to 74%, identifying 130 °C as the optimal temperature for maximizing ethanol productivity (Entries 5-7, Table 7.3).

To further improve catalytic performance, a compact stainless-steel batch reactor with a reduced free volume of 17 mL was employed, and the catalyst loading was doubled to 10 mg (16 μmol Co). These modifications are supported by thermodynamic and kinetic considerations in multiphase catalysis. According to Henry's law, gas solubility in the liquid phase scales with partial pressure; therefore, reducing the reactor headspace at constant total pressure (30 bar) effectively increases gas dissolution and mass transfer, particularly important for CO₂, which exhibits low solubility in aqueous media.⁴⁰¹ Simultaneously, increasing catalyst loading raises the density of accessible Co(OH) active sites, reducing turnover times. In confined reactor volumes, enhanced collision frequencies between dissolved reactants and catalytic sites further promote reaction kinetics, especially under diffusion-limited conditions. As a result of these combined effects, the optimized system achieved a markedly enhanced ethanol yield of 1.52 mmol with 92% CO₂ conversion under 20 bar at 130 °C for 15 h (Entry 6, Table 7.1). Ethanol selectivity remained high at 93%, with only trace quantities of methanol (0.03 mmol) and methane (0.09 mmol) detected. Overall, MIL-53-Co(OH) delivered a high productivity of 10,133 μmol g cat⁻¹ h⁻¹, achieving performance comparable to state-of-the-art systems while operating under aqueous, mild, and pre-activation-free conditions, thereby overcoming the conventional trade-off between ethanol selectivity and CO₂ conversion efficiency.

MIL-53-Co(OH) achieved a CO₂ conversion of 92% with an ethanol selectivity of 93% at 130 °C in the aqueous phase, outperforming the majority of previously reported base-metal thermocatalysts despite operating under relatively mild conditions (Table 7.9). The formation of ethanol was unequivocally confirmed by both ¹H NMR spectroscopy (D₂O) and GC-MS analysis of the crude reaction mixture. No ethanol was detected in control experiments conducted either in the absence of MIL-53-Co(OH) or when CO₂ was replaced with N₂, confirming that CO₂ serves as the sole carbon source (Entry 2, Table 7.3). Post-catalytic characterization confirmed the excellent structural and chemical stability of both the

framework and the active sites. PXRD patterns indicated full retention of crystallinity, while XPS and XAS analyses suggest that the $[(\mu_2\text{-O})(\text{carboxylate-O})_2\text{Co}^{\text{II}}(\text{OH})]$ coordination motif remains intact after catalysis (Figures 7.2a, 7.4a and 7.21). The absence of metallic Co(0) or CoO species in the recovered catalyst was further verified by combinatorial EXAFS fitting, which showed poor agreement when 5-50% contributions from these phases were introduced (Figure 7.15). Importantly, MIL-53-Co(OH) exhibited excellent recyclability, maintaining high catalytic activity over at least eight consecutive cycles with a cumulative turnover number (TON) of 504. Only a marginal decrease in productivity was observed, while ethanol selectivity consistently remained above 96% (Table 7.6).

Table 7.1. Optimization of reaction conditions for MIL-53-Co(OH) catalysed CO₂ hydrogenation.

Entry	Catalyst	P (Bar)	Temp. (°C)	n (mmol) ^[a]			EtOH Selectivity (%)	CO ₂ Conv. (%)
				EtOH	MeOH	CH ₄		
1	MIL-53-Co(OH)	20	130	0.58	0	0.01	98.3	8.9
2	No catalyst	20	130	0	0	-	-	-
3	MIL-53-Co(OH)	32	130	0.77	0.01	0.11	86.5	7.9
4	MIL-53-Co(OH)	30 ^[b]	130	0.31	0.08	<0.01	20.1	12.6 ^[c]
5	MIL-53-Co(OH)	20	100	0.48	0.09	<0.01	83.1	4.07
6	MIL-53-Co(OH) ^[d]	20	130	1.52	0.03	0.09	92.6	92.1

Standard reaction conditions: 5 mg MIL-53-Co(OH) (8 μmol of Co), H₂/CO₂=3, P=20 bar, time=15 h, 15 mL H₂O, 130 °C in 100 mL high pressure batch reactor (free volume=65 mL). [a] The liquid product yields were quantified by GC-FID using ethylene glycol as an internal standard, whereas gaseous products were analyzed by GC-TCD. [b] H₂/CO₂=4. [c] 0.64 mmol of CH₃CO₂H was obtained as a product. [d] 10 mg of MIL-53-Co(OH) (16 μmol of Co) was used in 50 mL batch reactor (free volume=17 mL).

7.3. Control Experiments and Mechanistic Investigation

Having established the stability and catalytic competence of MIL-53-Co(OH), we next sought to elucidate the mechanistic role of the atomically dispersed Co(OH) moieties. Control experiments employing the pristine, non-metallated MIL-53 framework or metallic Co(0) resulted in only trace methanol formation and no detectable ethanol, underscoring the necessity of site-isolated Co(OH) species anchored at the MOF nodes for effective catalysis (Figure 7.4c). Notably, Co(0)@MIL-53 produced only trace amounts of ethanol, with methanol as the predominant product. Likewise, bulk Co(OH)₂, CoCl₂, and Co supported on Al₂O₃ were catalytically inactive, highlighting the unique reactivity conferred by atomically dispersed Co(OH) centers within the MIL-53 framework. To delineate the operative pathway for ethanol formation, a series of targeted mechanistic control experiments were performed. Under

standard reaction conditions, a $\text{CO}_2 + \text{H}_2$ feed delivered the highest ethanol yield, establishing direct CO_2 hydrogenation as the dominant and most efficient reaction pathway (Figure 7.4d). In contrast, feeding 0.6 mmol of CH_3OH under identical conditions resulted in zero ethanol formation, demonstrating that free methanol in the bulk phase is not a competent intermediate for C–C coupling and may instead passivate the active sites (Entry 12, Table 7.4).

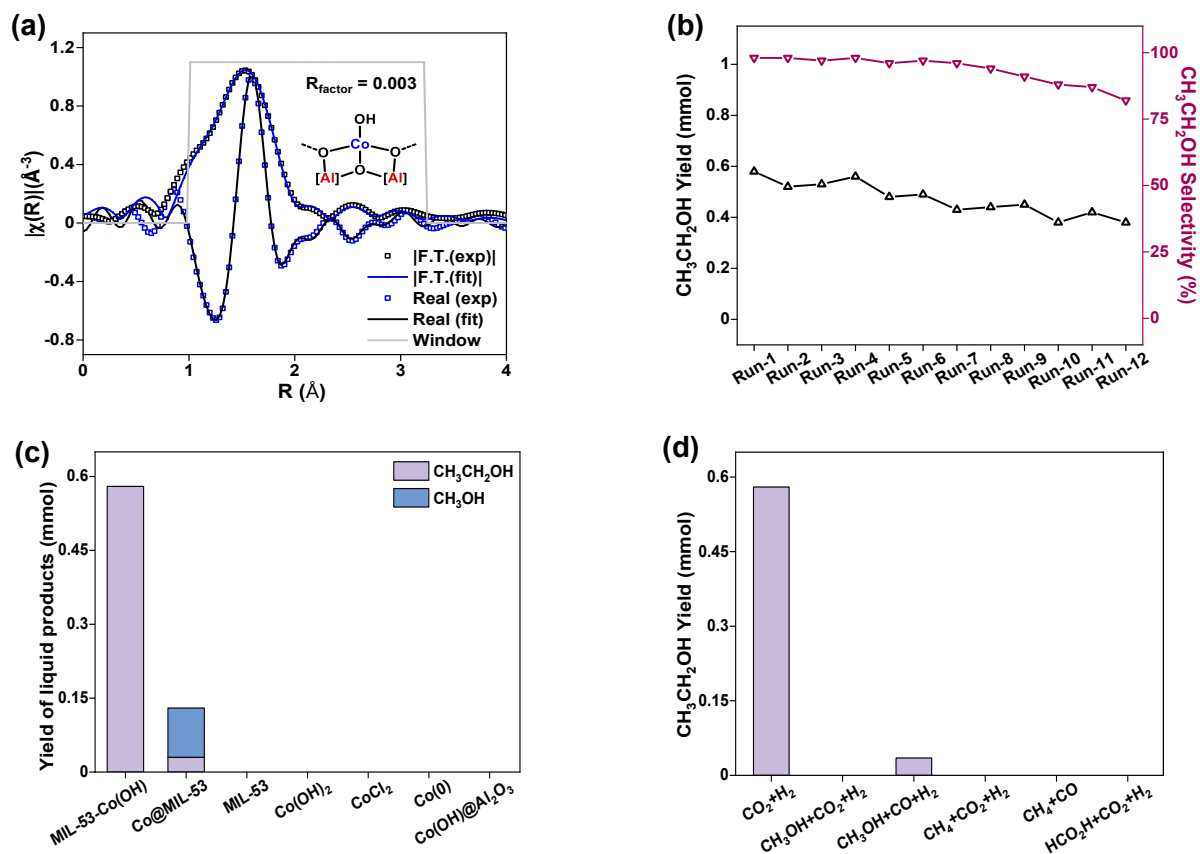


Figure 7.4. (a) EXAFS spectra and fits of MIL-53-Co after catalysis in R-space (1.0–3.25 Å). (b) Recyclability of MIL-53-Co(OH) for CO_2 hydrogenation over multiple catalytic cycles. (c) Comparative catalytic activity of MIL-53-Co(OH) and control materials for CO_2 hydrogenation. (d) Control experiments probing reaction intermediates and mechanistic pathways in MIL-53-Co(OH)-catalyzed CO_2 hydrogenation to ethanol.

A critical mechanistic insight emerged from experiments using a $\text{CH}_3\text{OH} + \text{CO} + \text{H}_2$ feed, which produced only 0.035 mmol of ethanol—an order of magnitude lower than that obtained under $\text{CO}_2 + \text{H}_2$ conditions. This result indicates that while methanol-derived methyl species can participate in C–C bond formation when co-activated with CO under hydrogenation conditions, their dominant effect remains site passivation. These findings emphasize the essential role of confinement within the MOF framework in enabling selective C–C coupling (Figure 7.4d). Importantly, whereas the $\text{CH}_3\text{OH} + \text{CO} + \text{H}_2$ mixture yielded ethanol, a $\text{CH}_3\text{OH} + \text{CO}_2 + \text{H}_2$ feed was completely inactive, unequivocally identifying CO, rather than CO_2 , as the requisite C_1 coupling partner for surface-bound methyl intermediates. Finally, the complete lack of ethanol formation from alternative C_1 feeds—including $\text{CH}_4 + \text{CO}_2 + \text{H}_2$, $\text{CH}_4 + \text{CO}$, and $\text{HCOOH} + \text{CO} + \text{H}_2$ —rules out methane homologation and formic acid derived pathways as viable routes for ethanol production under these conditions (Figure 7.4d).

7.3.1. Proposed Catalytic Pathway for CO₂ Hydrogenation to Ethanol

Based on the experimental observations, we propose a plausible mechanistic sequence for ethanol formation over MIL-53-Co(OH). The overall transformation can be rationalized as three interconnected catalytic subcycles occurring at the well-defined Co(OH) nodes of the MIL framework: (i) CO generation, (ii) methanol formation, and (iii) C–C coupling to ethanol. Catalysis is initiated by heterolytic activation of H₂ at the Co–OH sites, producing a cobalt hydride intermediate (INT-1) accompanied by the release of a water molecule. The resulting Co–H species subsequently transfers a hydride to CO₂, forming a cobalt formate intermediate (Co–OCHO, INT-2). From this point, the catalytic network diverges into two interlinked reduction pathways. In the first pathway, partial decarboxylation of the formate intermediate liberates CO, thereby establishing an in situ CO reservoir (Figure 7.5a).⁴⁰² In the competing parallel pathway, INT-2 undergoes a sequence of stepwise reduction processes (INT-2 → INT-3 → INT-4), progressively reducing the carbon center to generate a cobalt methoxy species (Co–O–CH₃; Figure 7.5b).⁴⁰³ Subsequent hydrolysis of this methoxy intermediate releases methanol and regenerates the Co–OH active site.

Ethanol formation arises from the convergence of these two pathways (Figure 7.5c). Specifically, methanol reacts with the Co–H species via σ -bond metathesis to generate a cobalt methyl intermediate (INT-5). Coordination of the in situ generated CO to the Co²⁺ center, followed by migratory insertion into the Co–CH₃ bond, yields an acyl species (Co–COCH₃, INT-6).⁴⁰⁴ Subsequent hydrogenation affords INT-7, which upon hydrolysis releases ethanol and regenerates the MIL-53-Co-OH catalytic site. Notably, the overall stoichiometry of the reaction ($2\text{ CO}_2 + 6\text{ H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{ H}_2\text{O}$) intrinsically requires a 3:1 H₂/CO₂ molar ratio. Accordingly, the applied pressure ratio of 15 bar H₂ to 5 bar CO₂ not only satisfies this stoichiometric requirement but also provides a kinetic driving force that accelerates hydrogenation steps, suppresses excessive CO accumulation, and sustains an optimal pool of CO₂-derived intermediates necessary for efficient C–C coupling. This synergy between reaction stoichiometry and optimized pressure conditions highlights the bifunctional nature of the Co–OH motifs, which simultaneously facilitate CO₂ activation, H₂ dissociation, and selective C–C bond formation leading to ethanol.

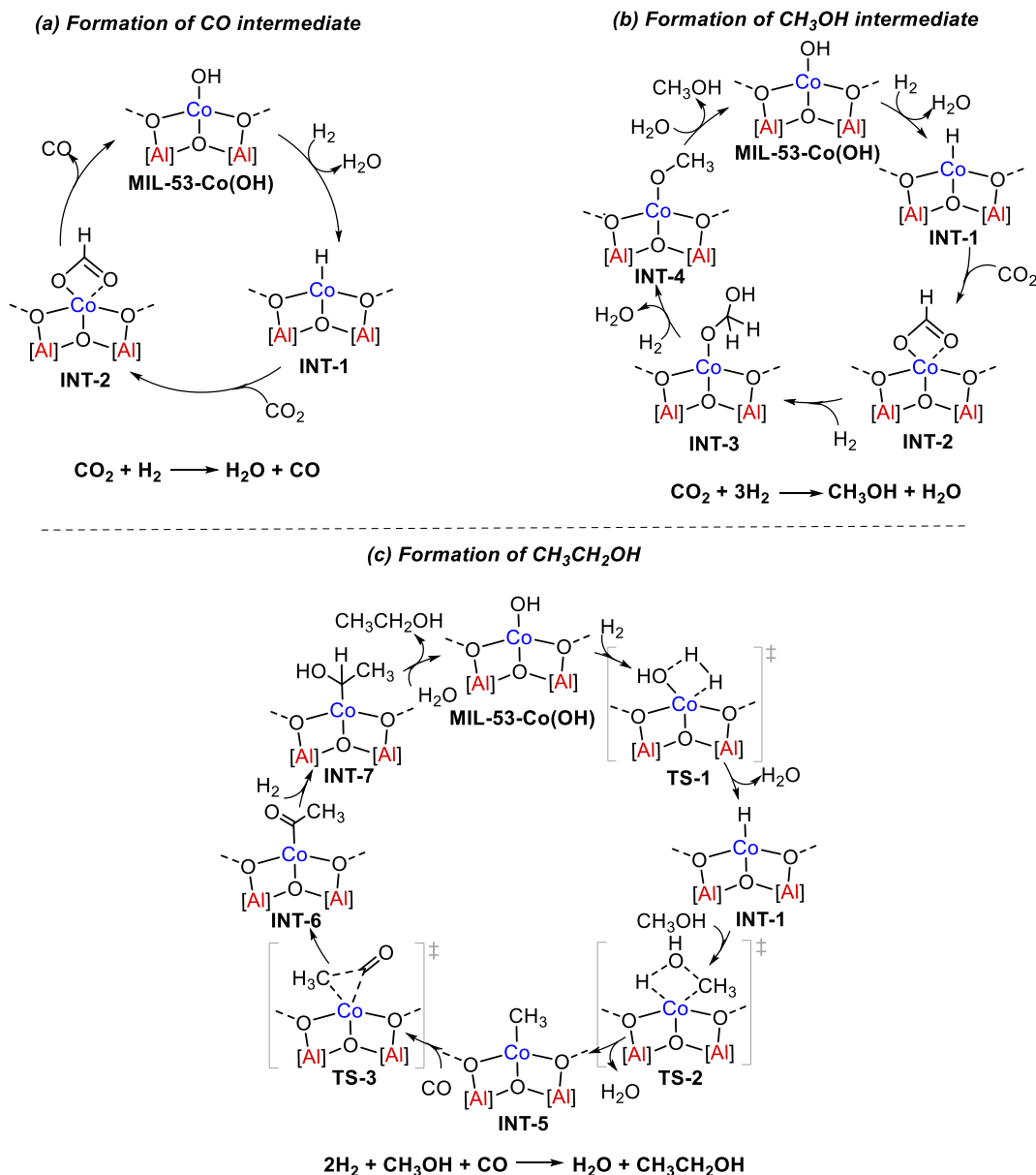


Figure 7.5. (a-c) Proposed reaction pathways for MIL-53-Co(OH) catalyzed CO₂ hydrogenation to ethanol.

7.4. Influence of Framework Dynamics on Active-Site Structure

To elucidate the role of framework dynamics in governing catalytic performance, we systematically compared a series of Co(OH)-functionalized MIL-53 derivatives. Introduction of –NH₂ and –NO₂ substituents on the BDC linker is known to progressively suppress the intrinsic flexibility (“breathing”) of the MIL-53 framework, following the order MIL-53 > MIL-53-NO₂ > MIL-53-NH₂, as established in prior studies.^{399,405} Notably, despite comparable cobalt loadings and nearly identical local coordination environments around the Co centers, as confirmed by EXAFS, pronounced differences in catalytic activity and selectivity were observed as a function of framework flexibility.

Catalytic evaluations under identical conditions (5 bar CO₂, 15 bar H₂, 15 mL H₂O, 130 °C, 15 h) revealed a clear correlation between ethanol productivity and framework dynamics.

Specifically, MIL-53-NO₂-Co(OH) and MIL-53-NH₂-Co(OH) delivered ethanol selectivities of 83% and 67%, respectively, in contrast to the markedly higher selectivity of 98% achieved with the parent MIL-53-Co(OH) catalyst (Figure 7.6a). Concurrently, methanol selectivity increased systematically with decreasing breathing capacity (0% → 14% → 30%), indicating that restricted lattice dynamics impede the C–C coupling step required for C₁ homologation to ethanol. To further isolate the effect of framework rigidity, MIL-68-Co(OH), a rigid, non-breathable polymorph of MIL-53(Al), was synthesized via post-synthetic modification of pristine MIL-68 (Section 7.5.1.7).⁴⁰⁶

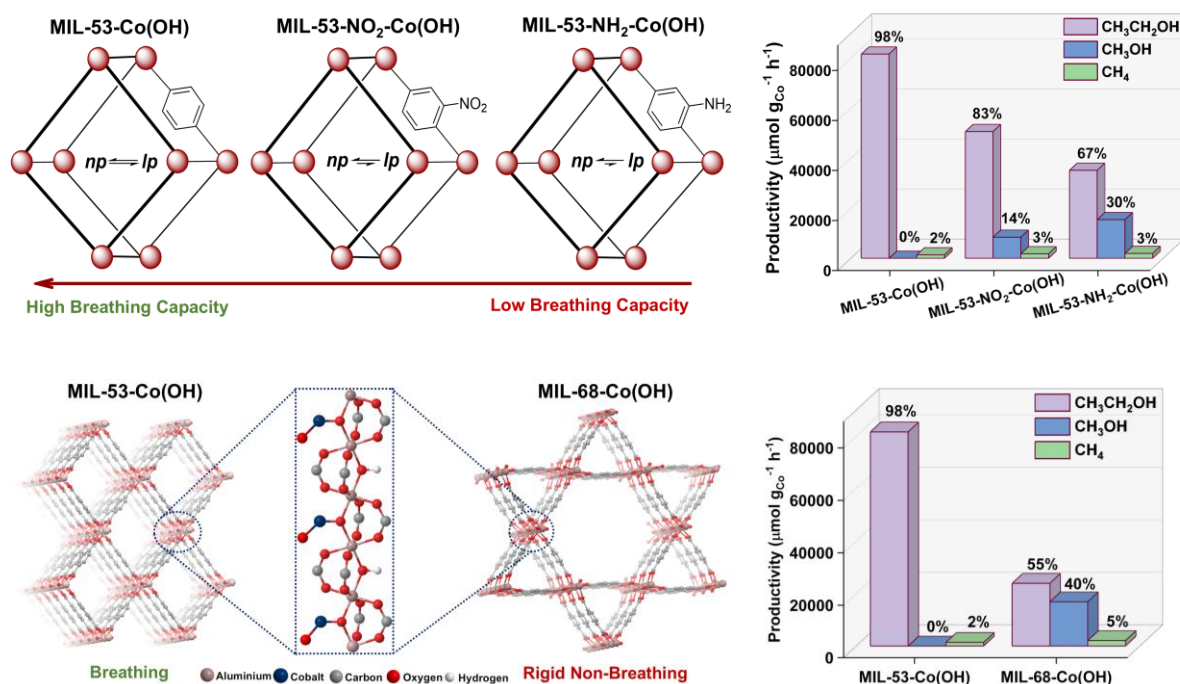


Figure 7.6. (a) Influence of linker functionalization on the breathing behavior of MIL-53-Co(OH), comparing highly flexible MIL-53-Co(OH) with the less flexible MIL-53-NO₂-Co(OH) and MIL-53-NH₂-Co(OH) derivatives. The associated product selectivities demonstrate a positive correlation between framework breathing capacity and ethanol formation. (b) Structural comparison between the flexible, breathing MIL-53-Co(OH) framework and the rigid, non-breathing MIL-68-Co(OH) framework, highlighting differences in pore dynamics and coordination environments at the Co(OH) active sites. The corresponding bar chart shows product distributions for CO₂ hydrogenation, illustrating the superior ethanol productivity of MIL-53-Co(OH).

Under identical cobalt loadings and optimized reaction conditions (5 bar CO₂, 15 bar H₂, 15 mL H₂O, 130 °C), MIL-68-Co(OH) exhibited approximately 3.5-fold lower activity than MIL-53-Co(OH), accompanied by a dramatic decrease in ethanol selectivity to 55% (Figure 7.6b). Simultaneously, methanol selectivity increased to 40%, compared to its absence in the flexible MIL-53-Co(OH) system, highlighting a pronounced framework-induced shift in product distribution. Collectively, these results demonstrate that the dynamic flexibility of the MIL-53 framework is a critical determinant of catalytic performance. The breathing behavior of MIL-53-Co(OH) likely enables dynamic restructuring of the cobalt active sites under reaction

conditions, thereby facilitating efficient C–C coupling and driving selective ethanol formation during CO₂ hydrogenation.

7.5. Experimental Section

7.5.1. Synthesis and Characterization of Different MIL-(Al)-Co(OH) Metal-Organic Frameworks

7.5.1.1. Synthesis of MIL-53(Al)

MIL-53(Al) was synthesized following a previously reported method.³⁹⁶ In a 5 mL aqueous solution of aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O) (1.30 g, 3.47 mmol), terephthalic acid (BDC) (0.29 g, 1.73 mmol) was added. The mixture was heated to 220 °C for 3 days. After cooling, the resulting white powder was collected by centrifugation and washed with water (H₂O) and dimethylformamide (DMF). To exchange the BDC trapped in the pores, DMF was introduced at 150 °C for 15 h. The DMF molecules were subsequently removed by heating the material at 280 °C in air for 12 h in a muffle furnace. Finally, the resulting white crystalline solid of MIL-53(Al) was washed and stored in tetrahydrofuran (THF).

7.5.1.2. Synthesis of MIL-53(Al)-Co(OH)

n-BuLi (50 μL, 1.65 M in cyclohexane) was added to the slurry of MIL-53(Al) (0.015 g, 0.072 mmol) in 1 mL of THF in a vial, and the mixture was stirred for 1.5 h at room temperature inside the glovebox. The solid was washed with THF several times to remove the excess *n*-BuLi. A THF solution of CoCl₂·6H₂O (0.074 g, 0.312 mmol) was added to the brown solid of MIL-53(Al)-Li, and the mixture was stirred overnight at room temperature. MIL-53(Al)-CoCl was obtained as a crystalline blue solid and washed with THF several times. Inside the glovebox, NaEt₃BH (40 μL, 1 M in THF) was added dropwise to the vial containing a slurry of MIL-53(Al)-CoCl (0.016 g) in 3 mL of THF and was kept at room temperature for one hour. The resultant dark purple solid of putative MIL-53(Al)-CoH was separated via centrifugation and washed several times with THF to remove excess NaEt₃BH. MIL-53(Al)-CoH was taken out of the glovebox and kept in water for 30 minutes to afford MIL-53(Al)-Co(OH). ICP-OES analysis of the digested MOF sample revealed a cobalt loading of 38% with respect to the μ₂-OH sites in MIL-53(Al)-Co(OH). TGA analysis showed that MIL-53(Al)-Co(OH) had 30% solvent weight.

7.5.1.3. Synthesis of MIL-53-NH₂

MIL-53(Al)-NH₂ was synthesized with some modifications based on previous articles.³⁹⁹ Al(NO₃)₃·9H₂O, (0.1086 g, 0.29 mmol) was dissolved in 1 mL of deionized water, while 2-

aminoterephthalic acid, $\text{NH}_2\text{-BDC}$ (0.08 g, 0.44 mmol) was dissolved in 3 mL of DMF. The two solutions were combined, stirred for 1 h, then transferred to a stainless-steel autoclave and heated at 150 °C for 24 h. The resulting solid was collected by centrifugation, washed three times with DMF, and refluxed in DMF for 5 h. Subsequently, it was washed four times with acetone and dried under vacuum at 30 °C for 12 h.

7.5.1.4. Synthesis of MIL-53- $\text{NH}_2\text{-Co(OH)}$

$n\text{-BuLi}$ (50 μL , 1.65 M in cyclohexane) was added to the slurry of MIL-53(Al)- NH_2 (0.016 g, 0.072 mmol) in 1 mL THF in a vial, and the mixture was stirred for 1.5 h at room temperature inside the glovebox. The solid was washed with THF several times to remove the excess $n\text{-BuLi}$. A THF solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.074 g, 0.312 mmol) was added to the brown solid of MIL-53(Al)- $\text{NH}_2\text{-Li}$, and the mixture was stirred overnight at room temperature. The MIL-53(Al)- $\text{NH}_2\text{-CoCl}$ was obtained as a crystalline blue solid and washed with THF several times. Inside the glovebox, NaEt_3BH (40 μL , 1 M in THF) was added dropwise to the vial containing a slurry of MIL-53- $\text{NH}_2\text{-CoCl}$ (0.016 g) in 3 mL THF and was kept at room temperature for one hour. The resultant dark purple solid of putative MIL-53- $\text{NH}_2\text{-CoH}$ was separated via centrifugation and washed several times with THF to remove excess NaEt_3BH . MIL-53- $\text{NH}_2\text{-CoH}$ was taken out of the glovebox and kept in water for 30 min to afford MIL-53- $\text{NH}_2\text{-Co(OH)}$. MIL-53- $\text{NH}_2\text{-Co(OH)}$ has 42% cobalt loading with respect to $\mu_2\text{-OH}$ as analyzed by ICP-OES of the digested MOF.

7.5.1.5. Synthesis of MIL-53- NO_2

MIL-53(Al)- NO_2 was synthesized with some modifications based on previous articles.³⁹⁹ A mixture of $\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.298 g, 0.794 mmol), $\text{H}_2\text{BDC-NO}_2$ (0.184 g, 0.874 mmol) and water (10 mL) was placed in a stainless-steel autoclave, and the resulting mixture was heated in a conventional oven at 170 °C for 12 h and cooled to room temperature. The white microcrystalline product of MIL-53- NO_2 was obtained by filtration.

7.5.1.6. Synthesis of MIL-53- $\text{NO}_2\text{-Co(OH)}$

$n\text{-BuLi}$ (50 μL , 1.65 M in cyclohexane) was added to the slurry of MIL-53(Al)- NO_2 (0.018 g, 0.072 mmol) in 1 mL THF in a vial, and the mixture was stirred for 1.5 h at room temperature inside the glovebox. The solid was washed with THF several times to remove the excess $n\text{-BuLi}$. A THF solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.074 g, 0.312 mmol) was added to the brown solid of MIL-53(Al)- $\text{NO}_2\text{-Li}$, and the mixture was stirred overnight at room temperature. MIL-53(Al)-

NO₂-CoCl was obtained as a crystalline blue solid and washed with THF several times. Inside the glovebox, NaEt₃BH (40 μ L, 1 M in THF) was added dropwise to the vial containing a slurry of MIL-53-NO₂-CoCl (0.016 g) in 3 mL THF and was kept at room temperature for one hour. The resultant dark purple solid of putative MIL-53-NO₂-CoH was separated via centrifugation and washed several times with THF to remove excess NaEt₃BH. MIL-53-NO₂-CoH was taken out of the glovebox and kept in water for 30 min to afford MIL-53-NO₂-Co(OH). MIL-53-NO₂-Co(OH) has 36% cobalt loading with respect to μ_2 -OH as analyzed by ICP-OES of the digested MOF.

7.5.1.7. Synthesis of MIL-68

MIL-68(Al) was synthesized according to previous articles with some modifications.⁴⁰⁶ Accordingly, AlCl₃·6H₂O (241 mg, 1 mmol) and terephthalic acid (249 mg, 1.5 mmol) were mixed into 15 mL of DMF under stirring for 20 min. In order to completely dissolve the mixture, it was subjected to ultrasonication for 20 min, and subsequently, the resulting solution was transferred into a 250 mL round-bottom flask and refluxed at 135 °C for 20 h with continuous stirring under air. The white precipitate was filtered and washed several times with fresh DMF and methanol to remove unreacted linkers, respectively. Then, the mixture was stirred in 10 mL of methanol overnight at ambient temperature. After drying the white powder at 80 °C for 2 h, it was placed in the oven at 155 °C for 8 h to be activated and to completely remove the DMF guest molecules from the MOF cavities.

7.5.1.8. Synthesis of MIL-68-Co(OH)

n-BuLi (50 μ L, 1.65 M in cyclohexane) was added to the slurry of MIL-68 (0.015 g, 0.072 mmol) in 1 mL THF in a vial, and the mixture was stirred for 1.5 h at room temperature inside the glovebox. The solid was washed with THF several times to remove the excess *n*-BuLi. A THF solution of CoCl₂·6H₂O (0.074 g, 0.312 mmol) was added to the solid of MIL-68-Li, and the mixture was stirred overnight at room temperature. MIL-68(Al)-CoCl was obtained as a crystalline blue solid and washed with THF several times. Inside the glovebox, NaEt₃BH (40 μ L, 1 M in THF) was added dropwise to the vial containing a slurry of MIL-68-CoCl (0.016 g) in 3 mL THF and was kept at room temperature for one hour. The resultant dark purple solid of putative MIL-68-CoH was separated via centrifugation and washed several times with THF to remove excess NaEt₃BH. MIL-68-CoH was taken out of the glovebox and kept in water for 30 min to afford MIL-68-Co(OH). MIL-68-Co(OH) has 30% cobalt loading with respect to μ_2 -OH as analyzed by ICP-OES of the digested MOF.

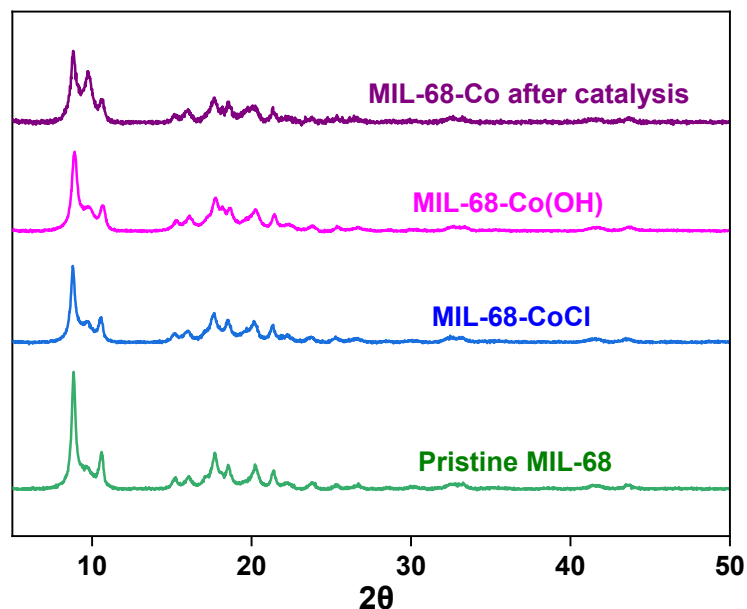


Figure 7.7. PXRD patterns of simulated MIL-68 (black), pristine MIL-68 (green), MIL-68-CoCl (blue), MIL-68-Co(OH) (magenta), and MIL-68-Co after catalysis (purple).

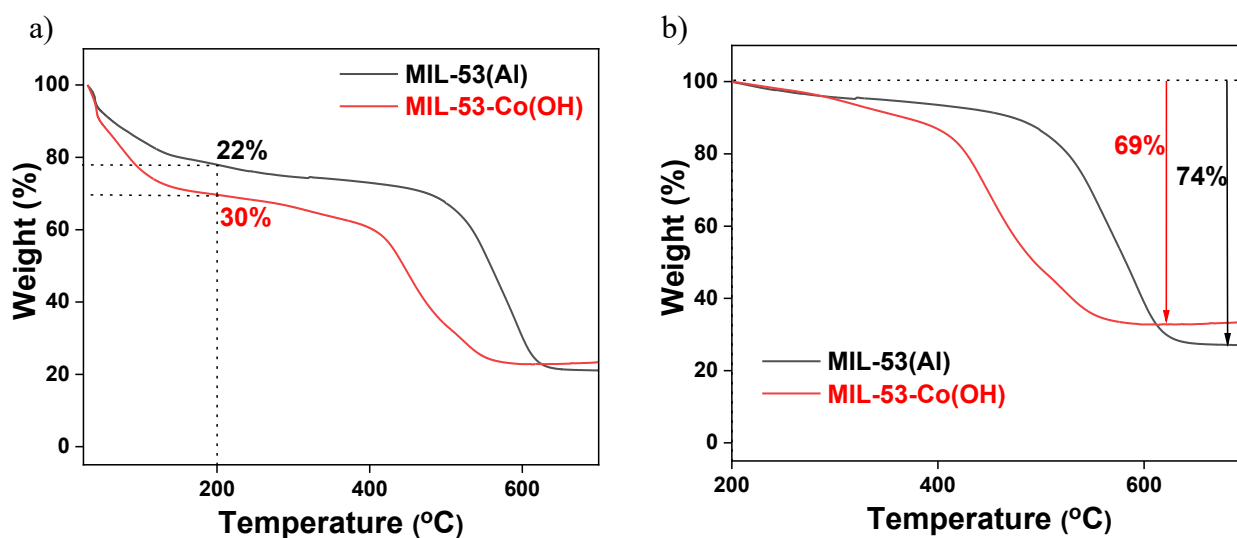


Figure 7.8. (a) TGA curve of freshly prepared MIL-53(Al) (black) and MIL-53(Al)-Co(OH) (red). A solvent weight loss of 22% in MIL-53(Al) (black) and 30% in MIL-53(Al)-Co(OH) (red) was observed from 40 °C to 200 °C. (b) TGA curve of freshly prepared MIL-53(Al) (black) and MIL-53(Al)-Co(OH) (red) from 200-700 °C. The increased weight of MIL-53(Al)-Co(OH) is due to the presence of Co within the MOF framework.

Table 7.2. Determination of defect sites in MIL-53(Al) and MIL-53(Al)-Co(OH) MOF by TGA analysis.

		% Solvent	% Linker	% Residue
MIL-53(Al)	Calculated	-	75.5	24.5
	TGA	22	57	21
	Corrected	-	74	26
MIL-53(Al)-Co(OH) (38% Co-loading)	Calculated	-	70.8	29.9
	TGA	30	47	23
	Corrected	-	69	31

Theoretical calculation:

(a) 1 mole of $\text{Al(OH)(BDC)} = 0.5$ moles Al_2O_3

208.1 g of $\text{Al(OH)(BDC)} = 50.98$ g Al_2O_3

% Residue = $(50.98/208.1) \times 100 = 24.5\%$

% Linker = $100 - 24.5 = 75.5\%$

(b) 1 mole $\text{Al(OH)}_{0.62}(\text{BDC})[\text{OCo(OH)}]_{0.38} = 0.5$ moles Al_2O_3 and 0.24 moles CoO

236.46 g of $\text{Al(OH)}_{0.62}(\text{BDC})[\text{OCo(OH)}]_{0.38} = 50.98$ g Al_2O_3 and 17.98 g CoO

% Residue = $[(50.98 + 17.98)/236.46] \times 100 = 29.16\%$

% Linker = $100 - 29.16 = 70.84\%$

The %linker calculated theoretically matches well with that of %ligand observed experimentally for MIL-53(Al) and MIL-53(Al)-Co(OH) MOFs. This indicates the absence of any missing-linker defects within MIL-53(Al) and MIL-53(Al)-Co(OH) MOFs.

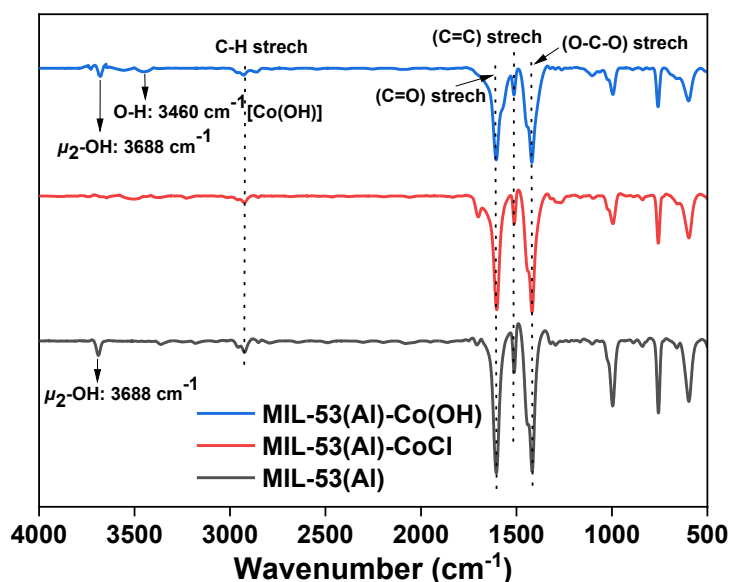


Figure 7.9. IR spectra of freshly prepared MIL-53(Al) (gray), MIL-53(Al)-CoCl (red), and MIL-53(Al)-Co(OH) (blue). In the IR spectra, μ_2 -OH stretching frequency peak of MIL-53(Al) at 3688 cm^{-1} disappeared upon metalation, however, a small peak of μ_2 -OH reappeared for MIL-53(Al)-Co(OH) due to protonation of unreacted μ_2 -OLi with water. The peak intensity of μ_2 -OH stretching frequency of MIL-53(Al)-Co(OH) at 3688 cm^{-1} was smaller compared to that of pristine MIL-53(Al) MOF due to the partial metalation of the μ_2 -OH of the SBUs.

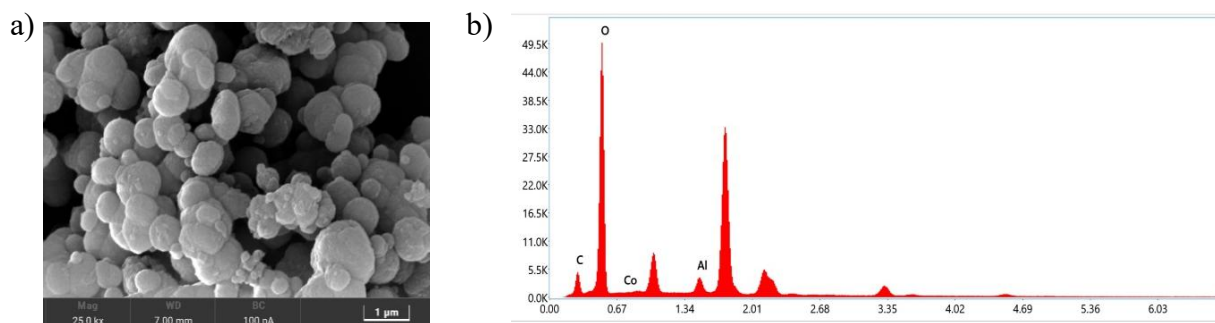


Figure 7.10. a) SEM image and (b) SEM-EDX analysis of MIL-53(Al)-Co(OH). SEM image displayed spherical particles of MIL-53(Al)-Co(OH) with an average size of 200 nm.

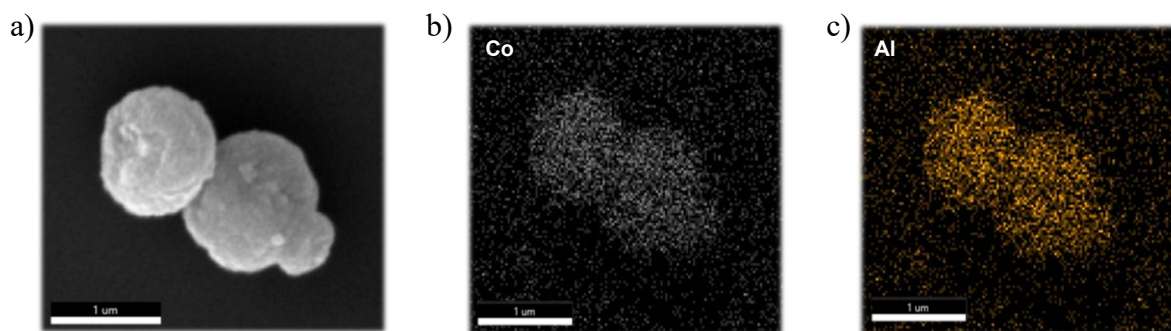
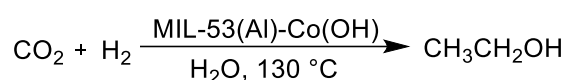


Figure 7.11. (a) SEM image of MIL-53(Al)-Co(OH) particles along with EDX mapping of (b) Co and (c) Al of the respective particles. Uniform distribution of Co and Al throughout the MIL-53(Al)-Co(OH) particles is observed.

7.5.2. MIL-53(Al)-Co(OH) Catalysed Hydrogenation of CO₂

7.5.2.1. Standard procedure for MIL-53(Al)-Co(OH) catalysed hydrogenation of CO₂



A 1 mL slurry of MIL-53(Al)-Co(OH) (5 mg, 8 μmol of Co) in water was transferred to a glass liner containing 14 mL of water. Then the glass liner was fitted into a high-pressure reactor. The high-pressure reactor was sealed and then purged with CO₂ two times. The reactor was pressurized with 5 bar CO₂ followed by 15 bar H₂ and then heated at 130 °C for 15 h without any mechanical stirring. After the reaction, the reactor was cooled to room temperature, and the gas was analysed directly by gas chromatography equipped with a thermal conductivity detector (GC-TCD). A 1 mL of the aqueous solution was transferred to a centrifuge tube, which was centrifuged for 1 min. Then, 1 mL of the clear solution was quickly transferred to a GC vial and 5 μL of ethylene glycol (internal standard) was added. The sample was then identified and quantified by gas chromatography coupled with mass spectrometry and flame ionization detector (GC-MS/FID) in the liquid phase. 1 μL sample was injected in GC and standard calibration curves were used for the quantification of ethanol.

7.5.2.2. Detection and quantification of liquid oxygenates

GC-MS conditions: The column used was the Agilent DB-WAX column with 30 m length, 0.320 mm internal diameter, and 0.25 μm film. The chromatographic conditions were: flow rate of helium at 1 mL min⁻¹, injection volume: 1 μL, column oven temperature was initially 45.0 °C and then increased up to 230 °C with the rate of 5 °C per minute, and detector temperature was 250 °C.

GC-FID conditions: The column used was the Agilent DB-WAX column with 30 m length, 0.320 mm internal diameter, and 0.25 μm film. The chromatographic conditions were: flow rate of nitrogen at 1 mL min^{-1} , injection volume of $1\text{ }\mu\text{L}$, column oven temperature at $40.0\text{ }^{\circ}\text{C}$ for 4 minutes followed by $5\text{ }^{\circ}\text{C/min}$ ramp to $70\text{ }^{\circ}\text{C}$ and then followed by $35\text{ }^{\circ}\text{C/min}$ ramp to $200\text{ }^{\circ}\text{C}$ and finally a hold time of 5 minutes, and 19 min for total run time. The detector temperature was $250\text{ }^{\circ}\text{C}$. Products were quantified using a calibration plot of ethylene glycol as the internal standard.

7.5.2.3. Detection and quantification of CO_2 and gaseous products

GC-TCD conditions: The gas after catalysis was analysed by an Agilent GC (8890) equipped with a PoraPlot Q column in sequence with a molecular sieves column and a Thermal conductivity detector (TCD). The chromatographic conditions are as follows; Carrier gas: helium, Column: $45\text{ }^{\circ}\text{C}$, TCD: $250\text{ }^{\circ}\text{C}$, and Injection temperature: $100\text{ }^{\circ}\text{C}$. Retention time for CO_2 , CH_4 and CO were 4 minutes, 9.3 minutes and 10.75 minutes, respectively.

CO_2 conversion was calculated by determining the mmol of CO_2 before and after the catalysis using a GC-TCD response factor-based calculation. For this calculation, a high-pressure reactor containing a glass liner (free volume inside the reactor with liner: 17 mL) was filled with 15 mL mixture of water and MIL-53(Al)-Co(OH) catalyst, and then purged it with CO_2 two times. Then pressurized it with 5 bar CO_2 followed by 15 bar H_2 . The gas was analysed with GC-TCD at room temperature ($35\text{ }^{\circ}\text{C}$) before catalysis to quantify the amount of CO_2 in the feed. The gas of the same high-pressure reactor was analysed after the reaction at room temperature ($35\text{ }^{\circ}\text{C}$) to quantify the amount of unreacted CO_2 after the catalysis and the other gaseous products. At the optimized reaction condition (entry 6, Table 7.1), the amount of CO_2 was calculated as 3.43 mmol before catalysis and 0.26 mmol after catalysis. Therefore, the loss of CO_2 during the reaction is 3.17 mmol and a CO_2 conversion of $\sim 92\%$.

Procedure for taking gas sample: First, the gas from the Parr reactor was filled in an evacuated tedlar bag via making an air-tight fitting connection of Parr reactor outlet with the bag using a hose pipe. Then 2.5 mL from the bag was taken in an air-tight syringe and injected into GC for analysis. Then, the mmol of CO_2 was calculated. Separately, 2.5 mL of a known sample of a standard gas containing a specific composition of CO_2 was also injected, which was used to calculate the individual gas (x) response factor (R_f) following the given formula. The detailed calculation to quantify the initial CO_2 amount in the feed is as follows:

$$\text{Step 1: } R_f (\text{carbon dioxide}) = \frac{\text{Fraction of carbon dioxide (g)}}{\text{Area of peak of carbon dioxide in chromatogram (GC-TCD)}}$$

Fraction of carbon dioxide = (Volume injected (mL)) *

(Composition of CO₂ in standard) Fraction of carbon dioxide = 2.5 (mL) * $\frac{10^{-4} \text{ g}}{\text{mL}}$

Rf (carbon dioxide) = 2.5*10⁻⁴g/5482

Rf (carbon dioxide) = 4.56*10⁻⁸ g

Step 2: The volume of CO₂ in the unknown sample taken from the high-pressure reactor was measured. The injected volume of the unknown sample was also same as of standard 2.5 mL.

Amount of CO₂ in unknown sample: Rf (CO₂)*area of the peak of CO₂ in the chromatogram

Amount of CO₂ = 4.56*10⁻⁸ *98,600

Amount of CO₂ = 4.5*10⁻³ g

Step 3: Molar mass of CO₂ = 44.01 g/mol

Moles of CO₂ = 4.5*10⁻³/44.01 mol

Moles of CO₂ = 102.2 μmol

So, the initial moles of CO₂ in 2.5 mL of an unknown sample of gas was measured. This measurement is at atmospheric pressure and 308 K.

Step 4: Using eq. $P_1V_1/T_1n_1 = P_2V_2/T_2n_2$; the mmol of CO₂ present in high-pressure reactor was calculated.

n_1 = mol of CO₂ in 2.5 mL measured in step 3

P_1 = atm pressure; V_1 = 2.5 mL; T_1 = 308 K

n_2 = mol of CO₂ in Parr reactor; P_2 = pressure of CO₂ in Parr reactor (5 bar)

V_2 = free volume of Parr reactor (17 mL); T_2 = 308 K

1.01325 bar*2.5 mL/102.2 μmol = 5 bar*17 mL/ n_2 ;

n_2 = 5 bar*17 mL*102.2 μmol/1.01325 bar*2.5 mL;

n_2 (amount of initial CO₂ in the reactor before catalysis) = 3.43 mmol

Using the similar method described above, the CO₂ and other gaseous products were quantified after the catalysis.

Table 7.3. Optimization of catalytic conditions for MIL-53(Al)-Co(OH) catalyzed hydrogenation of CO₂.^[a]

Entr y	Temp. (°C)	P[CO ₂] (bar)	P[H ₂] (bar)	%CO ₂ Conv.	EtOH (mmol) ^[b]	CH ₃ OH (mmol) ^[b]	CH ₄ (mmol) ^[c]	%EtOH Selectivity
1	130	5	15	8.9	0.58	0	0.01	98.3
2 ^[d]	130	5	15	-	0	0	-	-
3	130	8	24	7.9	0.77	0.01	0.11	86.5
4	130	6	24	12.6 ^[e]	0.31	0.08	<0.01	20.1

5	100	5	15	4.07	0.48	0.09	<0.01	83.1
6	110	5	15	6.17	0.5	0.06	0.01	87.7
7	150	5	15	9.2	0.43	0	0.15	74.1
8 ^[f]	130	5	15	7.2	0.34	0	0.01	97
9 ^[g]	130	5	15	8.2	0.49	0	0.01	98
10 ^[h]	130	5	15	9.8	0.72	0.02	0.06	90
11	130	5	0	-	0	0	-	-
12 ^[i]	130	5	15	92.1	1.52	0.03	0.09	92.6
13 ^[j]	130	5	15	8.8	0.56	0	0.01	98.2

^[a] Standard conditions: 5 mg of MIL-53(Al)-Co(OH) (8 μ mol of Co), 15 mL H₂O, 15 h; in 100 mL high pressure batch reactor (free volume = 65 mL); N₂ balance was applied to optimize partial pressures of CO₂ and H₂ (entry 11) maintaining total reaction pressure at 20 bar; nd: not determined. ^[b] Analysed by GC-FID using ethylene glycol as the internal standard. ^[c] Analysed by GC-TCD. ^[d] No catalyst was used. ^[e] 0.64 mmol of CH₃CO₂H was obtained as a product. ^[f] Reaction time was 5 h. ^[g] Reaction time was 12 h. ^[h] Reaction time was 21 h. ^[i] 10 mg of MIL-53-Co(OH) (16 μ mol of Co) was used in 50 mL batch reactor (free volume=17 mL). ^[j] Catalyst was performed in the presence of a drop of Hg.

Table 7.4. Control experiments for MIL-53(Al)-Co(OH) catalyzed hydrogenation of CO₂ to ethanol.^[a]

Entry No.	Catalyst	P[CO ₂] (bar)	P[H ₂] (bar)	CH ₃ CH ₂ OH (mmol) ^[b]	CH ₃ OH (mmol) ^[b]	%EtOH Selectivity
1	MIL-53(Al)-Co(OH)	5	15	0.58	0	98.3
2	MIL-53(Al)	5	15	0	trace	-
3	Co(OH) ₂	5	15	0	0	-
4	CoCl ₂	5	15	0	0	-
5	Co@MIL-53	5	15	0.03	0.13	18.8
6	Co(0) nanoparticulates	5	15	0	trace	-
7	Co(OH)@Al ₂ O ₃	5	15	0	0	-
8	MIL-53-NO ₂ -Co(OH)	5	15	0.36	0.06	83
10	MIL-53-NH ₂ -Co(OH)	5	15	0.25	0.11	67
11	MIL-68-Co(OH)	5	15	0.17	0.12	55
12 ^[c]	MIL-53(Al)-Co(OH)	5	15	0	0.6	-
13 ^[c]	MIL-53(Al)-Co(OH)	5 ^[d]	15	0.035	0.565	5.8
14 ^[e]	MIL-53(Al)-Co(OH)	5	15	0	0	-
15 ^[f]	MIL-53(Al)-Co(OH)	5	15	0	0	-

^[a] Standard conditions: Catalyst (8 μ mol of Co), 15 mL H₂O, 130 °C, 15 h; in 100 mL high pressure batch reactor (free volume=65 mL); N₂ balance was applied to keep constant pressure of 20 bar if needed; nd: not determined. ^[b] Analysed by GC-FID using ethylene glycol as the internal standard. ^[c] CH₃OH (0.6 mmol) was added to the reaction mixture. ^[d] CO (5 bar) was used instead of CO₂. ^[e] CH₄ (5 bar) was added. ^[f] HCOOH (10 μ L) was added to the reaction mixture.

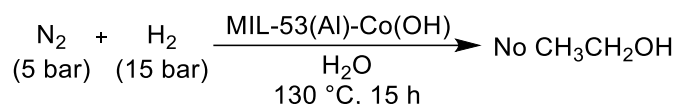
Table 7.5. Carbon balance in MIL-53-Co(OH) catalysed hydrogenation of CO₂ to ethanol.^[a]

Initial CO ₂ (mmol)	Post-reaction CO ₂ (mmol)	CO ₂ Consumed (mmol)	Oxygenates and other products (mmol)			Total Carbon Yield (mmol)	Carbon Balance (%)
			CH ₃ CH ₂ OH (mmol)	CH ₃ OH (mmol)	CH ₄ (mmol)		
3.43	0.26	3.17	1.52	0.03	0.09	3.16	99.6

Optimized reaction conditions: 10 mg MIL-53-Co(OH) (16 μmol of Co), 5 bar CO₂, 15 bar H₂, 130 °C, 15 h.

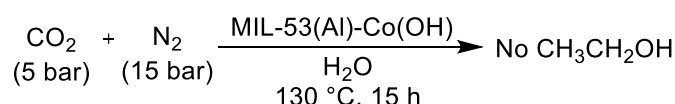
7.5.3. Control Experiments for MIL-53(Al)-Co(OH) Catalyzed Hydrogenation of CO₂

7.5.3.1. Blank reaction with H₂ under N₂ without CO₂



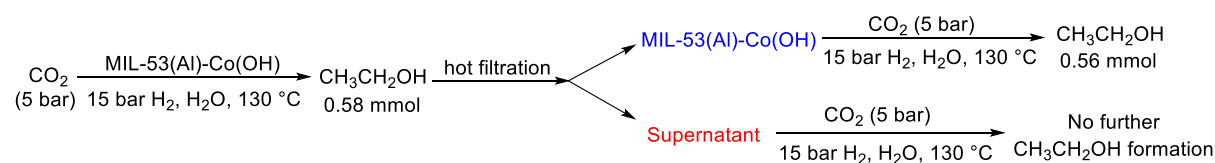
Reaction conditions: 5 mg of MIL-53(Al)-Co(OH) (8 μmol of Co), 15 mL H₂O, 5 bar N₂, 15 bar H₂, 130 °C, 15 h. General procedure mentioned in Section 7.5.2.1. was followed replacing CO₂ with nitrogen. No liquid products were detected, suggesting CO₂ as the sole carbon source for CH₃CH₂OH production in the MIL-53(Al)-Co(OH) catalyzed CO₂ hydrogenation.

7.5.3.2. Blank reaction with CO₂ under N₂ without H₂



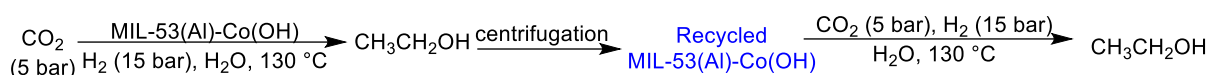
Reaction conditions: 5 mg of MIL-53(Al)-Co(OH) (8 μmol of Co), 15 mL H₂O, 5 bar CO₂, 15 bar N₂, 130 °C, 15 h. General procedure mentioned in Section 7.5.2.1. was followed replacing H₂ with nitrogen. No liquid products were detected (Entry 11, Table 7.4), suggesting H₂ as the only reductant for CH₃CH₂OH production in the MIL-53(Al)-Co(OH) catalyzed CO₂ hydrogenation.

7.5.3.3. Test for “heterogeneity of MIL-53(Al)-Co(OH) in CO₂ hydrogenation to ethanol

**Figure 7.12.** Hot filtration test of MIL-53(Al)-Co(OH) in the CO₂ hydrogenation to ethanol.

General procedure mentioned in [Section 7.5.2.1.](#) was followed. After 15 h of reaction, the solid was filtered out of the hot suspension. Two reactions were set up separately in two different high-pressure reactors with solid and supernatant. The extracted solid and supernatant were added into two separate glass liners. Then added 15 mL of water to the glass liner containing solid MOF. Then both the glass liners were fitted into two separate reactors. The reactors were sealed and purged them with CO₂. The reactors were pressurized with 5 bar CO₂ and 15 bar H₂ and then heated at 130 °C for 15 h without any mechanical stirring. The reactor was cooled to room temperature, and gas was analysed directly with GC-TCD. The liquid phase of reactions was analysed with GC-FID. No further ethanol was produced in the reaction involving just the supernatant. While the other reaction containing the solid MOF yielded 0.56 mmol of ethanol. This experiment excludes the potential of any leached Co-species responsible for catalysis and confirms that solid MIL-53(Al)-Co(OH) was the actual catalyst for the hydrogenation of CO₂.

7.5.3.4. Recycling of MIL-53(Al)-Co(OH) for CO₂ hydrogenation to ethanol



The recycle and reuse experiment was conducted to check the stability of the MOF-catalyst. General procedure mentioned in [Section 7.5.2.1.](#) was followed, except the recovered MOF-catalyst was washed several times with water. It was added to the glass liner along with 15 mL H₂O. The glass liner was fitted into a high-pressure reactor which was then sealed and purged with CO₂ twice. The reactor was pressurized with 5 bar CO₂ followed by 15 bar H₂ and then heated at 130 °C. The procedure was repeated for 8 runs with very minimal % leaching of cobalt and aluminium ([Table 7.6](#)). The MOF retains its crystallinity and stability as can be seen by the PXRD patterns of the recycling experiments ([Figure 7.2a](#)). The MOF could be recycled and reused at least 8 times without a significant drop-in activity giving a cumulative TON of 504.

Table 7.6. mmol of ethanol formed and the leaching of Co and Al in various runs of the recycling of MIL-53(Al)-Co(OH) for the CO₂ hydrogenation to ethanol.

No. of Run	Time	CH ₃ CH ₂ OH	% Leaching (Al, Co)
Run-1	15	0.58	0.01, 0.012
Run-2	15	0.52	
Run-3	15	0.53	0.018, 0.03
Run-4	15	0.56	
Run-5	15	0.48	0.06, 0.04
Run-6	15	0.49	

Run-7	15	0.43	0.07, 0.06
Run-8	15	0.44	

7.5.3.5. Comparison of catalytical activity between MIL-53(Al)-Co(OH) and other materials for CO₂ hydrogenation to ethanol

7.5.3.5.1. Co(OH)/Al₂O₃ catalyzed CO₂ hydrogenation

Al₂O₃ was activated at 150 °C under vacuum for 24 h. Then inside the glove box, n-BuLi (130 µL, 1.65 M in cyclohexane) was added to activated alumina (30.0 mg) in 1 mL THF in a 5 mL glass vial and kept for stirring at room temperature for overnight. The solid was washed with THF several times. The lithiated Al₂O₃ was treated with CoCl₂·6H₂O (192 mg, 0.808 mmol) and stirred overnight. The excess of CoCl₂·6H₂O was washed away with the multiple washing using THF. The metalated Al₂O₃ was dried, and cobalt loading was measured as 18% with respect to aluminium as determined by ICP-OES. NaEt₃BH (21 µL, 1 M in toluene) was added dropwise into the vial containing Al₂O₃-CoCl (0.025 mmol Co) as a slurry in 3 mL THF and the mixture was stirred gently at room temperature for 1 h. The light grey solid was washed with THF several times and then it was taken outside from the glovebox and added water to afford alumina-supported Co-hydroxide [Al₂O₃-Co(OH)], which was directly used for catalysis.

General procedure mentioned in [Section 7.5.2.1.](#) was followed, using Co(OH)/Al₂O₃ (8.0 µmol Co) instead of MIL-53(Al)-Co(OH). Reaction conditions: Co(OH)/Al₂O₃ (8.0 µmol Co), 15 mL water, 5 bar CO₂, 15 bar H₂, 130 °C, 15 h. Results are summarized in [entry 7, Table 7.4.](#)

7.5.3.5.2. Co@MIL-53(Al) catalyzed CO₂ hydrogenation

In a 5 mL round bottom flask, CoCl₂·6H₂O (49 mg, 0.18 mmol) was dissolved in ethyl acetate (2 mL), followed by the addition of the MIL-53(Al) (100 mg). The mixture was heated for 48 h at a temperature of 50 °C. After that the solid was collected by centrifugation and washed thoroughly and dried to give MIL-53(Al)-CoCl₂. NaBH₄ (10 mg) was added to 6 mL of deionized water in a round-bottom flask, after which 80 mg of MIL-53(Al)-CoCl₂ was added. The pH was controlled in the range of 6-8 throughout the addition of NaBH₄. The obtained mixture was stirred for 30 min, then was subject to filtration. The collected solid was washed thoroughly with deionized water to give black powder of Co@MIL-53(Al).⁴⁰⁷

General procedure mentioned in [Section 7.5.2.1.](#) was followed, using Co@MIL-53(Al) (8.0 µmol of Co) instead of MIL-53(Al)-Co(OH). Reaction conditions: Co@MIL-53(Al) (8.0 µmol of Co), 15 mL water, 5 bar CO₂, 15 bar H₂, 130 °C, 15 h. CH₃OH was observed as major product ([Entry 5, Table 7.4](#)) with trace amount of ethanol (0.03 mmol) was observed.

7.5.3.5.3. Co(0) catalyzed CO₂ hydrogenation⁴⁰⁸

CoCl₂·6H₂O (0.002 g, 0.0084 mmol) was first charged into a glass vial containing 2 mL of THF inside the glovebox. This was followed by the addition of NaEt₃BH (10 μL, 1M in toluene) to the glass vial and was stirred gently for an hour to get black colored Co(0) nanoparticulates. The resultant black solid was washed with THF multiple times and then finally dried.

General procedure mentioned in [Section 7.5.2.1](#) was followed, using Co(0) nanoparticulates (8.0 μmol of Co) instead of MIL-53(Al)-Co(OH). Reaction conditions: Co nanoparticles (8.0 μmol of Co), 15 mL water, 5 bar CO₂, 15 bar H₂, 130 °C, 15 h. Negligible quantities of ethanol was observed ([Entry 6, Table 7.4](#)).

7.6. X-ray Absorption Spectroscopic Analysis

X-ray Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) measurements have been carried out at the Energy-Scanning EXAFS beamline (BL-9) at the Indus-2 Synchrotron Source at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.²²⁰ All the measurements were performed at room temperature. This beamline operates in the energy range of 4 keV to 25 keV. The beamline optics consist of a Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si (111) based double crystal monochromator (DCM). The second crystal of the DCM is a sagittal cylindrical crystal which is used for horizontal focusing of the beam while another Rh/Pt coated bendable post mirror facing downward is used for vertical focusing of the beam at the sample position. Two ionization chambers (300 mm length each) have been used for data collection in the transmission mode; one ionization chamber for measuring incident flux, the second one for measuring transmitted flux. For energy calibration, standard metal foils were used. Appropriate gas pressure and gas mixture have been chosen to achieve 10-20% absorption in the first ionization chamber and 70-90% absorption in the second ionization chamber to obtain a better signal-to-noise ratio. Pellets were made from powder samples for recording absorption spectra. Sample powder was mixed homogeneously with cellulose powder in appropriate proportion and pressed (2 Ton) into a 15 mm diameter disc. The amount of the sample was estimated such that to get a reasonable edge jump at a particular absorption edge of the element to be probed. Spectra were collected at the cobalt K-edge in transmission mode and were calibrated against the reference spectrum of metallic cobalt (7709 eV). Data were processed using Demeter software.²²¹ A metallic cobalt foil standard was used as a reference for energy calibration and was measured simultaneously with experimental samples.

7.6.1. XANES Analysis

The oxidation states of the Co species within MIL-53(Al)-Co(OH) and MIL-53(Al)-Co after hydrogenation of CO₂ were determined by the comparison of the energy of its K-edge positions to that of CoO. The positions of the Co K-edge of MIL-53(Al)-Co(OH), MIL-53(Al)-Co after hydrogenation of CO₂ aligned well with that of CoO (7719.7 eV). We, therefore, concluded that Co ion in MIL-53(Al)-Co(OH) and MIL-53(Al)-Co after hydrogenation of CO₂ has +2 oxidation state.

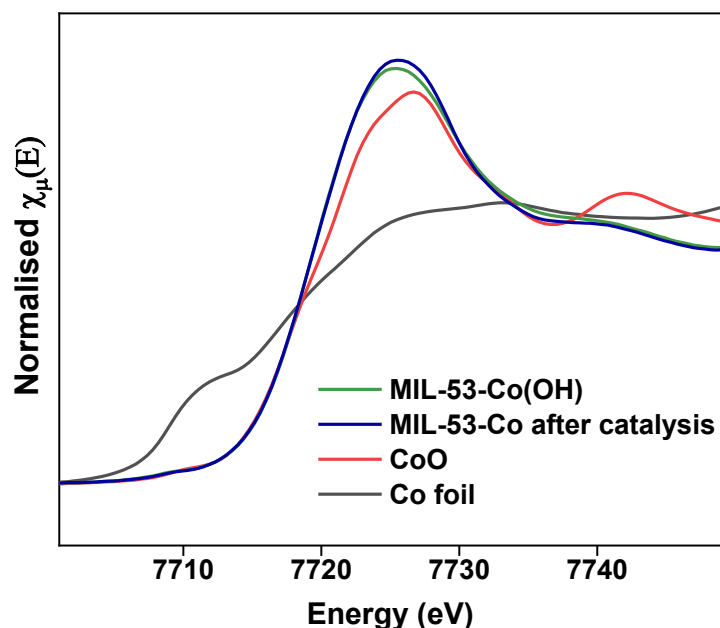


Figure 7.13. Co K-edge XANES spectra of MIL-53-Co(OH) (green), MIL-53-Co after catalysis (blue), CoO (red) and Co foil (black).

7.6.2. EXAFS Fitting using DFT Optimized Structures

The spectra were calibrated against the reference spectra and aligned to the first peak in the smoothed first derivative of the absorption spectrum, the background noise was removed, and the spectra were processed to obtain a normalized unit edge step.

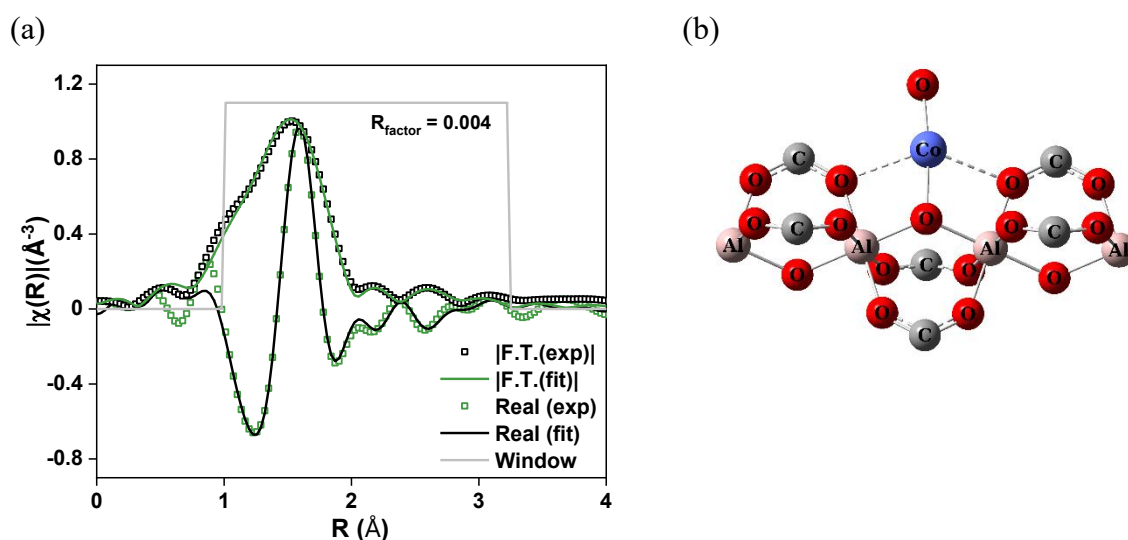


Figure 7.14. (a) EXAFS spectra (black and green squares) and fits (black and green lines) of MIL-53-Co(OH) in the R space from 1-3.25 Å. (b) DFT-optimized structure of MIL-53(Al)-Co(OH). Hydrogen atoms are omitted for clarity.

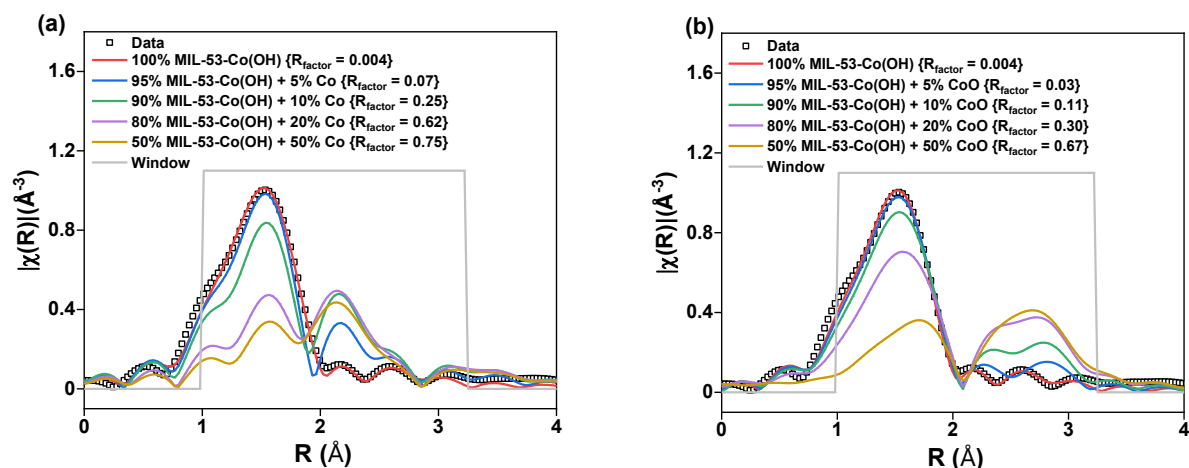


Figure 7.15. (a) EXAFS spectra of MIL-53(Al)-Co(OH) fitted with combined models of Co(0) and MIL-53(Al)-Co(OH). (b) EXAFS spectra of MIL-53(Al)-Co(OH) fitted with combined models of CoO and MIL-53(Al)-Co(OH). The significant misfits indicate that MIL-53(Al)-Co(OH) does not contain any Co nanoparticles or CoO.

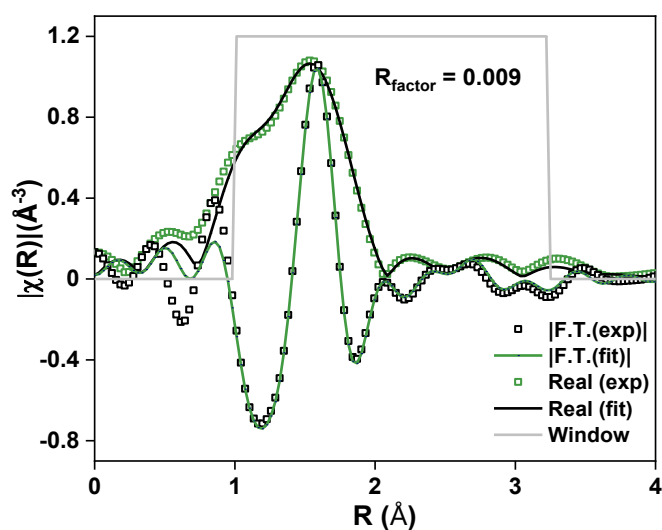


Figure 7.16. (a) EXAFS spectra (black and green squares) and fits (black and green lines) of MIL-53-NH₂-Co(OH) in the R space from 1-3.25 Å.

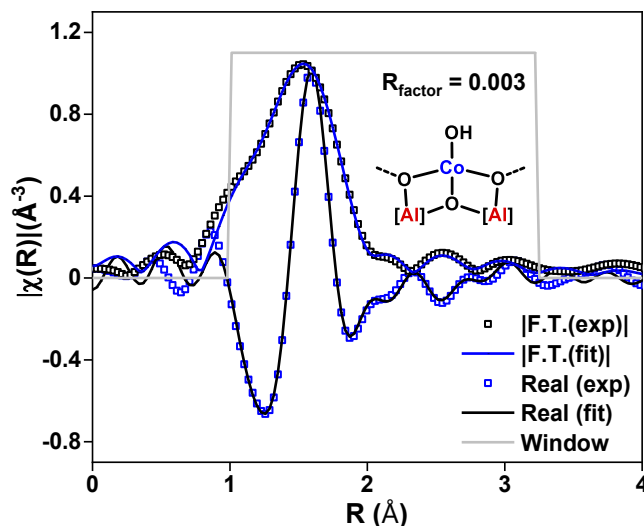


Figure 7.17. (a) EXAFS spectra (black and blue squares) and fits (black and blue lines) of MIL-53-Co after hydrogenation of CO₂ in the R space from 1-3.25 Å.

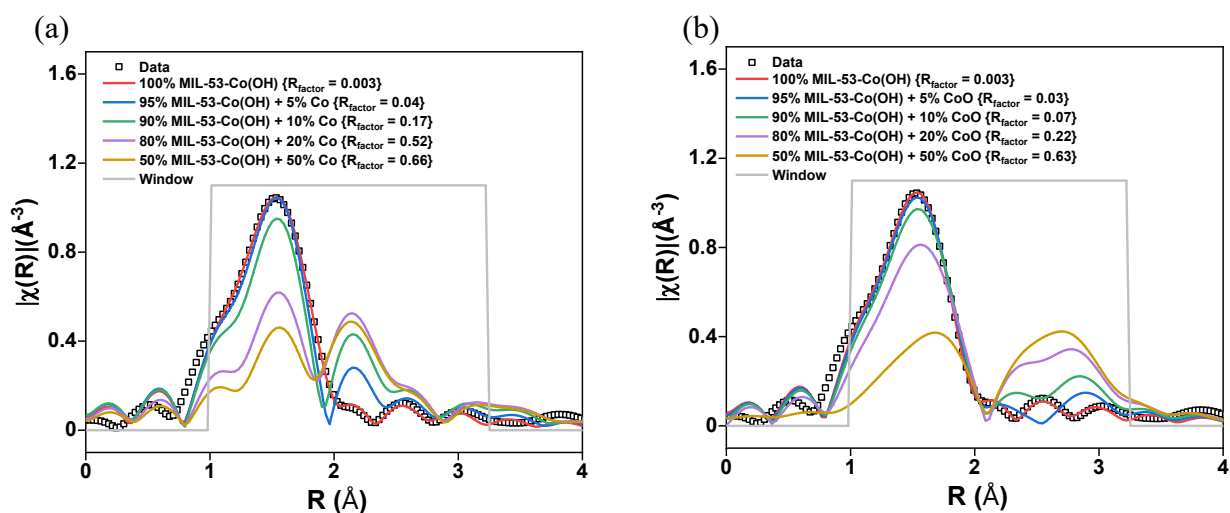


Figure 7.18. (a) EXAFS spectra of MIL-53(Al)-Co recovered after catalysis fitted with combined models of Co(0) and MIL-53(Al)-Co(OH). (b) EXAFS spectra of MIL-53(Al)-Co after catalysis fitted with combined models of CoO and MIL-53(Al)-Co(OH). The significant misfits indicate that MIL-53(Al)-Co(OH) after catalysis does not contain any Co nanoparticles or CoO.

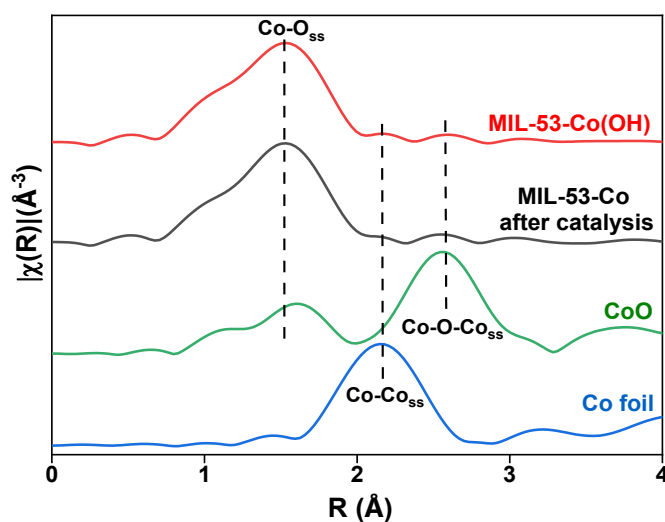


Figure 7.19. k^2 -weighted Co-EXAFS $\chi(R)$ spectra of MIL-53-Co(OH) (red), MIL-53-Co after catalysis (black), CoO (green), and Co foil (blue).

7.7. XPS Analysis

All the binding energies were corrected with reference to the C1s peak at 284.8 eV. CASA XPS software was used for peak analysis and de-convolution studies.

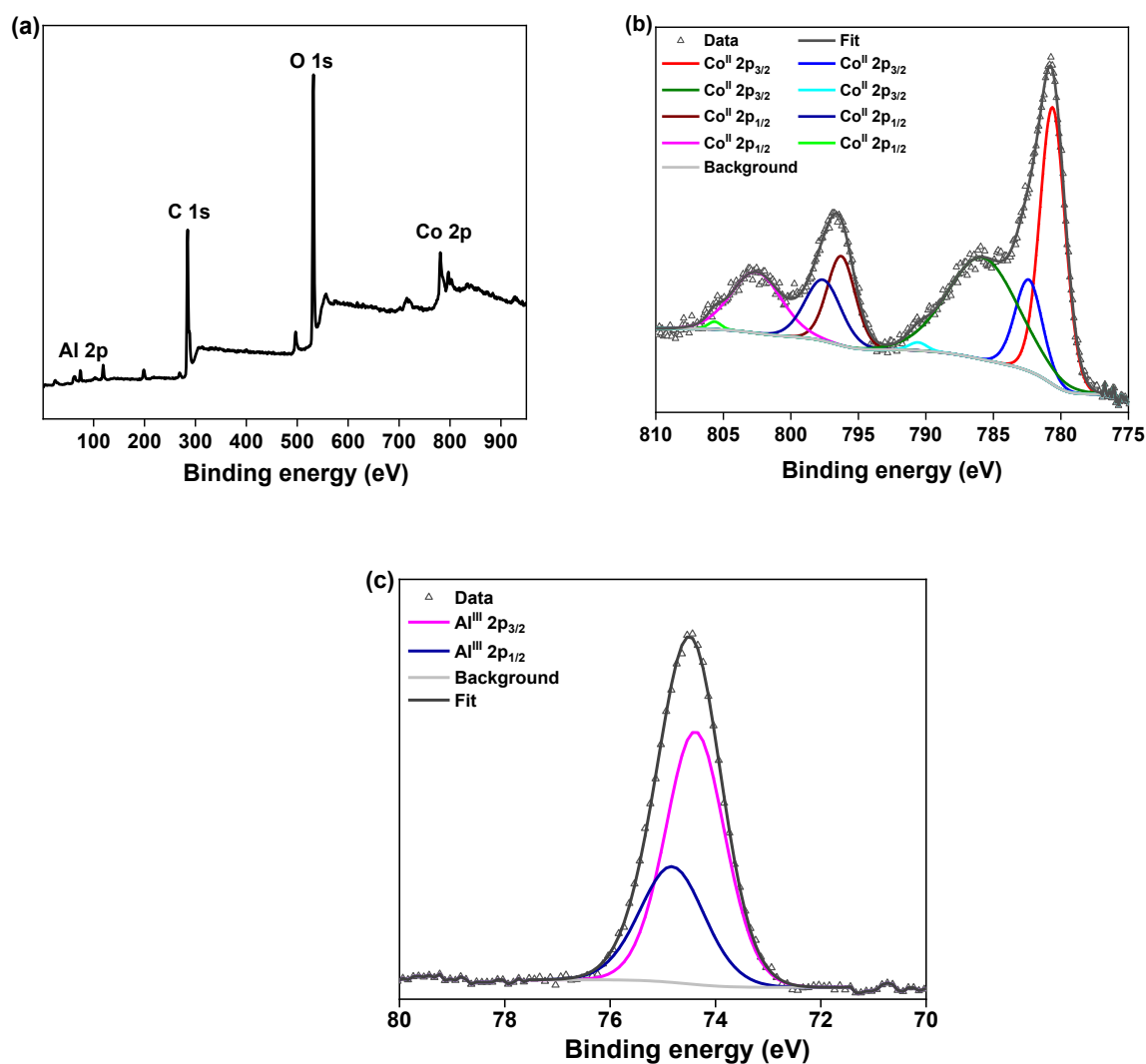


Figure 7.20. (a) Raw XPS data of MIL-53(Al)-Co(OH). (b) XPS fitting of cobalt in MIL-53(Al)-Co(OH). (c) XPS fitting of aluminium in MIL-53(Al)-Co(OH).

Table 7.7. XPS fitting parameters for Co(II) in MIL-53(Al)-Co(OH).

Component	Binding Energy	FWHM (eV)	Area %	Line shape
Co ^{II} 2p _{3/2}	780.62	2.05	28.40	GL(30)
Co ^{II} 2p _{3/2}	782.19	2.3	10.13	GL(30)
Co ^{II} 2p _{3/2}	785.78	5.1	29.05	GL(30)
Co ^{II} 2p _{3/2}	790.58	1.5	0.59	GL(30)
Co ^{II} 2p _{3/2}	796.27	2.4	13.18	GL(30)
Co ^{II} 2p _{3/2}	797.63	2.7	5.88	GL(30)
Co ^{II} 2p _{3/2}	802.57	4.3	12.14	GL(30)
Co ^{II} 2p _{3/2}	805.65	1.1	0.59	GL(30)

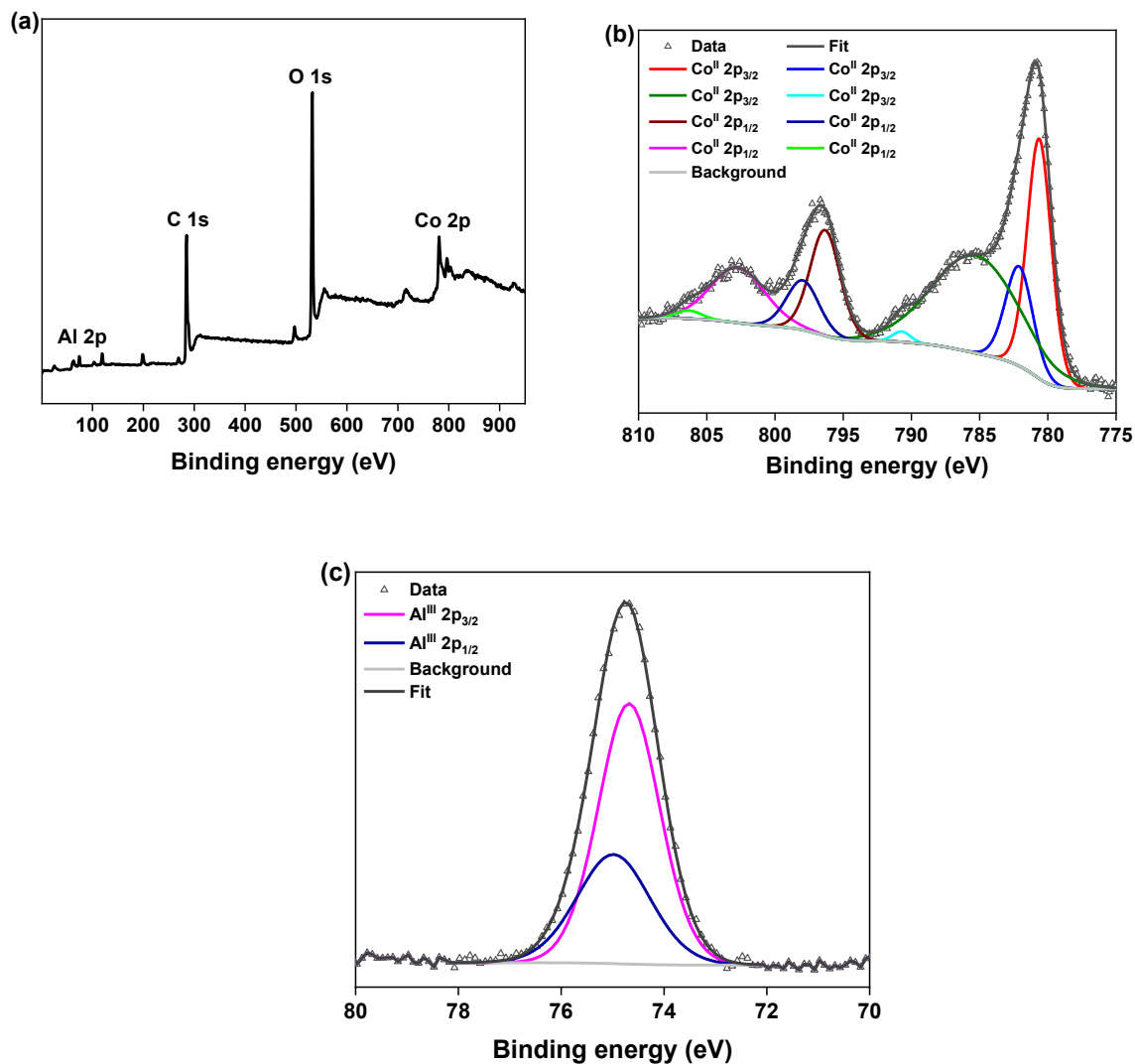


Figure 7.21. (a) Raw XPS data of MIL-53(Al)-Co recovered after catalysis. (b) XPS fitting of cobalt in MIL-53(Al)-Co recovered after catalysis. (c) XPS fitting of aluminium in MIL-53(Al)-Co recovered after catalysis.

Table 7.8. XPS fitting parameters for Co(II) in MIL-53(Al)-Co MOF recovered after catalysis.

Component	Binding energy	FWHM (eV)	Area %	Line shape
Co ^{II} 2p _{3/2}	780.63	2.02	23.07	GL(30)
Co ^{II} 2p _{3/2}	782.11	2.3	10.85	GL(30)
Co ^{II} 2p _{3/2}	785.30	4.3	33.55	GL(30)
Co ^{II} 2p _{3/2}	790.52	1.5	0.75	GL(30)
Co ^{II} 2p _{3/2}	796.33	2.6	13.66	GL(30)
Co ^{II} 2p _{3/2}	797.96	2.5	5.39	GL(30)
Co ^{II} 2p _{3/2}	802.74	4.7	11.92	GL(30)
Co ^{II} 2p _{3/2}	806.32	2.1	0.81	GL(30)

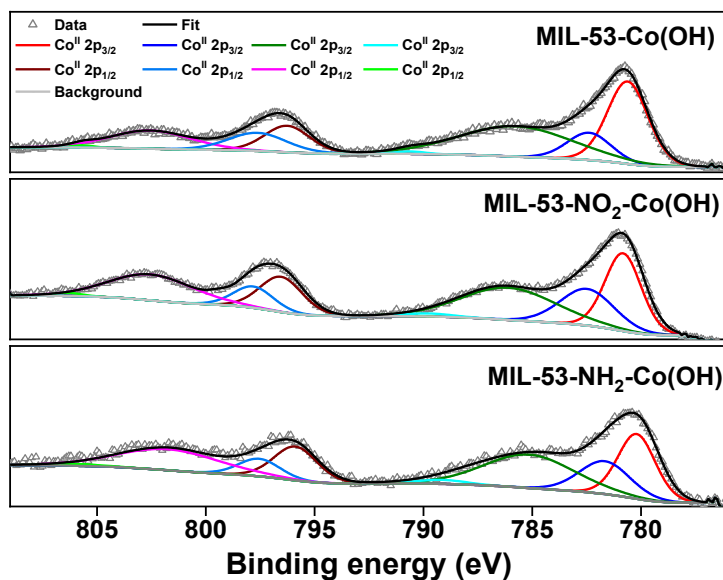


Figure 7.22. XPS fitting of cobalt in MIL-53(Al)-Co(OH), MIL-53-NO₂-Co(OH) and MIL-53-NH₂-Co(OH).

Table 7.9. Comparison of the catalytic performance of MIL-53-Co(OH) in CO₂ hydrogenation to ethanol with other reported catalysts.

Reference	Catalyst	Condition	Catalyst stability	Pressure (bar)	%Co nv. of CO ₂	Temp. (°C)	Selectivity EtOH (%)	Productivity (mmol.g _{cat} ⁻¹ .h ⁻¹)
<i>Catal. Commun.</i> 2011 , 14, 111–113.	CuMoS	Flow	Stable; requires pre-activation	104	32	340	5.5	0.8
<i>J. Catal.</i> 2016 , 343, 147–156.	Cu/Mo ₂ C	Batch	Stable; requires pre-activation at 450 °C	40	90	200	14	2.1
<i>Angew. Chem., Int. Ed.</i> 2018 , 57, 6104–6108.	CoAlO _x -600	Batch	Stable; requires pre-activation at 600 °C	40	-	140	92.1	0.444
<i>ACS Catal.</i> 2019 , 9, 11335–11340.	Co _{0.52} Ni _{0.48} AlO _x	Batch	Stable; requires pre-activation at 600 °C	40	-	200	85.7	1.316
<i>Nat. Catal.</i> 2019 , 2, 709–717.	Zr ₁₂ -bpdc-CuCs	Batch	Unstable; requires anaerobic conditions; THF is used as solvent	20	96	100	99	87.9
<i>ACS Catal.</i> 2020 , 10, 14516–14526.	4.6K-CMZ	Flow	Stable; requires pre-activation at 350 °C	50	36.6	330	19.8	1.58
<i>Chem</i> 2020 , 6, 2673–2689.	Cu/Na-Beta	Flow	Stable; requires pre-activation at 350 °C	13	7.9	300	76.9	5.6

<i>Appl. Catal., B</i> 2021 , 293, 120207.	Na-Co ₂ C	Flow	Stable; requires pre-activation at 350 °C	50	53.2	310	17.5	1.1
<i>ChemCatChem</i> 2021 , 13, 3333– 3339.	CoMoC _x - 800	Batch	Stable; requires pre-activation at high temp.	20	-	180	97.4	0.528
<i>Appl. Catal., B</i> 2021 , 298, 120556.	FeNaS-0.6	Flow	Stable; requires pre-activation at 350 °C	30	32	320	12.8	1.7
<i>ACS Sustain. Chem. Eng.</i> 2022 , 10, 14972–14979.	sp- CuNaFe	Flow	Stable; requires pre-activation at 350-550 °C	30	32.3	310	10	3.32
<i>J. Environ. Sci.</i> 2025 , 149, 598– 615.	Co/MgO- MgAl ₂ O ₄	Flow	Stable; requires pre-activation at 400 °C	40	25	300	17.9	104.1
<i>Catal. Today</i> 2025 , 444, 115014.	Cu/UiO- 67	Flow	Stable; requires pre-activation at 150 °C	1.013	4	280	12	0.015
This work	MIL-53- Co(OH)	Batch	Stable, requires no pre activation	20	92.1	130	92.6	10.13

7.8. Conclusion

This study introduces a novel catalytic system featuring atomically dispersed Co(OH) groups attached to the Al-OH sites of MIL-53(Al), combining single-site precision with the framework's dynamic properties to enable highly efficient and selective conversion of CO₂ to ethanol. Under aqueous conditions at 130°C and 20 bar, the catalyst achieves 92% CO₂ conversion, 93% selectivity toward ethanol, and a productivity rate of 10,133 $\mu\text{mol gcat}^{-1} \text{h}^{-1}$. Insights from structural, mechanistic, and DFT analyses show that a reversible np $\leftrightarrow$ lp transition actively adjusts the Al-[$\mu_3\text{-O-Co(OH)}$]-Al hinge, selectively reducing the energy barrier for σ -bond metathesis. This process forms the key Co-CH₃ intermediate within the flexible MIL-53 structure, facilitating selective ethanol production through homologation. In comparison, the rigid MIL-68(Al) framework and modified MIL-53 variants with limited lattice flexibility display significantly lower ethanol yields and higher methanol selectivity, directly linking framework adaptability to effective C-C bond formation. Characterization after catalysis confirms the preservation of crystallinity, cobalt oxidation state, and local coordination around the active sites, while recyclability tests demonstrate consistent performance across at least eight cycles. Overall, these results offer a mechanistic foundation for integrating framework dynamics with single-site design, presenting a versatile approach to developing recyclable, water-based MOF catalysts for transforming CO₂ into C₂₊ compounds.

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- Bajali College, Gauhati University, India, **2016-2019**
Graduation in Chemistry (Honours), Score: 8.8 CGPA
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Class 12th; AHSEC-Board; Score: 86%
- Sarupeta High School, Sarupeta, India, **2010-2014**
Class 10th; SEBA-Board; Score: 88%

List of Publications:

1. **Kalita, R.**; Chauhan, M.; Gupta, P.; Begum, W.; Manna, K. Selective Monoborylation of Methane by a Mono Bipyridyl-Nickel(II) Hydride Catalyst. *Angew. Chem. Int. Ed.* **2025**, *64*, e202413402. [{link}](#)
2. **Kalita, R.**; Chauhan, M.; Gupta, P.; Begum, W.; Thadhani, C.; Ghosh, B.; Balendra; Bisht, H.; Manna, K. Selective monoborylation of methane by metal–organic framework confined mononuclear pyridylimine-iridium(i) hydride. *Chem. Commun.* **2024**, *60*, 6504-6507. [{link}](#)
3. **Kalita, R.**; Thadhani, C.; Manna, K. Architecting Metal–Organic Framework-Based/Derived Catalysts for Methane Functionalization. *ACS Catal.* **2026**, *16*, 882-909. [{link}](#)
4. Thadhani, C.[†]; **Kalita, R.**[†]; Rana, B.; Akhtar, N.; Chauhan, M.; Gupta, P.; Ghosh, B.; Manna, K. Cobalt-Catalyzed Selective Monoborylation of Methane. *ACS Catal.* **2025**, *15*, 13958. ([†] co-first author). [{link}](#)
5. **Kalita, R.**; Aditya, M.; Gupta, P.; Rana, B.; Sardar, B.; Chauhan, M.; Ghosh, B.; Monga, Y.; Manna, K. Regioselective Oxidative Bromination of Arenes by a Metal–Organic Framework-Confined Mono-Bipyridyl Iron(III) Catalyst. *Dalton Trans.* **2025**, *54*, 6812-6821. [{link}](#)
6. **Kalita, R.**; Monga, Y.; Manna, K. N-Alkylation of Aniline Derivatives by a Bipyridyl Metal–Organic Framework-Supported Cobalt Catalyst. *New J. Chem.* **2025**, *49*, 2071. [{link}](#)
7. **Kalita, R.**; Begum, W.; Gupta, P.; Chauhan, M.; Akhtar, N.; Newar, R.; Manna, K. Chemoselective Oxidation of Alkenes by a Metal–Organic Framework-Supported Copper Catalyst. *Eur. J. Inorg. Chem.* **2023**, *26*, e202300215. [{link}](#)
8. Kumar, A.;[†] **Kalita, R.**[†]; Gupta, P.; Rana, B.; Chauhan, M.; Manna, K. Regioselective Hydroboration of Alkenes by Metal–Organic Framework Confined Mononuclear Bipyridyl-Iron Hydride Catalyst. *Inorganica Chimica Acta*, **2026**, *10.1016/j.ica.2026.123082*. ([†] co-first author) [{link}](#)
9. Begum, W.;[†] Chauhan, M.;[†] **Kalita, R.**; Gupta, P.; Akhtar, N.; Antil, N.; Newar, R.; Manna, K. Synergetic Ni–Ce Active Sites in Mixed Cerium/Zirconium Metal–Organic

Framework Nodes for Selective Methane Oxidation into Ethanol. *ACS Catal.* **2024**, *14*, 10427-10436. [{link}](#)

10. Gupta, P.; Chauhan, M.; Rana, B.; **Kalita, R.**; Maurya, R.; Manna, K. Engineering Mono- vs Dinuclear Iron(II) Active Sites to Steer Liquid Oxygenate Selectivity in Methane Oxidation Pathways Using O₂. *J. Am. Chem. Soc.* **2025**, *147*, 25372-25384. [{link}](#)

11. Chauhan, M.; Rana, B.; Gupta, P.; **Kalita, R.**; Thadhani, C.; Manna, K. Tailored pore-confined single-site iron(III) catalyst for selective CH₄ oxidation to CH₃OH or CH₃CO₂H using O₂. *Nat. Commun.* **2024**, *15*, 9798. [{link}](#)

12. Antil, N.;[†] Chauhan, M.;[†] Akhtar, N.; **Kalita, R.**; Manna, K. Selective Methane Oxidation to Acetic Acid Using Molecular Oxygen over a Mono-Copper Hydroxyl Catalyst. *J. Am. Chem. Soc.* **2023**, *145*, 6156-6165. [{link}](#)

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15. Gupta, P.; Rana, B.; Maurya, R.; **Kalita, R.**; Chauhan, M.; Manna, K. Copper Catalyzed Selective Methane Oxidation into Acetic Acid using O₂. *Chem. Sci.* **2025**, *16*, 2785-2795. [{link}](#)

16. Balendra,* **Kalita, R.**; Ali, M.; Sanyukta; Murugavel, S.; Manna, K. Multifunctional Manganese Coordination Polymer with Polar Solvent-Responsive Tunable Dielectric Properties and Selective Catalysis. *J. Mater. Chem. C* **2025**, *13*, 21122-21131. [{link}](#)

17. Gupta, P.; Akhtar, N.; Begum, W.; Rana, B.; **Kalita, R.**; Chauhan, M.; Thadhani, C.; Manna, K. Metal–Organic Framework-Supported Mono Bipyridyl–Iron Hydroxyl Catalyst for Selective Benzene Hydroxylation into Phenol. *Inorg. Chem.* **2024**, *63*, 11907-11916. [{link}](#)

18. Akhtar, N.; Chauhan, M.; Rana, B.; Thadhani, C.; **Kalita, R.**; Begum, W.; Ghosh, B.; Manna, K., Selective Reduction of Nitro Compounds by Organosilanes Catalyzed by a Zirconium Metal-Organic Framework Supported Salicylaldimine-Cobalt(II) Complex. *ChemPlusChem* **2024**, 89, e202300520. [{link}](#)

19. Raveena; **Kalita, R.**; Moronshing, M.; Kumari, P.; Manna, K.; Kakkar, R. * Quercetin–Copper Complexation-Based Porous Polymer for Chromium, Mercury, and Cadmium Metal Ion Adsorption: Experimental and Computational Study. *Ind. Eng. Chem. Res.* **2025**, 64, 5818–5829. [{link}](#)

20. Gupta, P.†; Sarmah, S.†; **Kalita, R.**; Rana, B.; Manna, K. * Mononuclear Bipyridyl–Iron(III) Hydroxide in a Metal–Organic Framework for Selective Alkene Oxidation. *J. Mol. Chem.* **2025**, 5 (3), 1225-1225. [{link}](#)

21. Newar, R.; **Kalita, R.**; Akhtar, N.; Antil, N.; Chauhan, M.; Manna, K. N-Formylation of amines utilizing CO₂ by a heterogeneous metal–organic framework supported single-site cobalt catalyst. *Catal. Sci. Technol.* **2022**, 12, 6795-6804. [{link}](#)

Awaiting:

22. Chauhan, M;† **Kalita, R.**;† Kumar, A.; Rana, B.; Sarmah, S.; Manna, K. Leveraging Conformational Dynamics of MOFs to Overcome Conversion-Selectivity Trade-off in CO₂ Hydrogenation to Ethanol. *Submitted*. († co-first author)

Patents:

1. Isorecticular metal-organic framework catalysts and process of synthesizing the said MOF catalysts for shape-selective hydrogenolysis of polymers” Kuntal Manna, Manav Chauhan, **Rahul Kalita**, Application no: 202311064737, patent filed on 27-September-2023.

Conferences:

1. Poster Presentation at “IUPAC Chains-2023”; 20-25th August 2023, The Hague, Netherlands.

2. Poster Presentation at “17th International conference on materials chemistry (MC17)”;
7-10th July, 2025, Edinburgh, United Kingdom.

3. Poster presentation at “Modern Trends in Inorganic Chemistry (MTIC)-XXII”; 18-21st
December, 2025, Delhi, India.

4. Poster presentation at “GITAM CHEMISTRY RESEARCH CONFERENCE 2023”; 7-
9th December, 2023, Visakhapatnam, India.

5. Oral Presentation at Graduate Student Seminar (GSS) at IIT Delhi on the topic entitled
“Catalytic Monoborylation of Methane,” 1st January, 2025.

