

TITLE: Engineering Earth-Abundant Metal Catalysts using Metal-Organic Frameworks (MOFs) for Selective Oxidation of Methane and other Hydrocarbons

ABSTRACT

The selective oxidation of methane into liquid oxygenates such as methanol and acetic acid represents one of the most compelling challenges in modern catalysis. Methane is abundant yet extremely inert because of its strong C–H bond, and under oxidative conditions it rapidly overoxidizes to CO₂. Developing catalysts that can activate methane at moderate temperatures while controlling product selectivity is therefore of great importance for both energy and chemical industries. This thesis addresses this challenge through the design of molecularly well-defined, single-site metal catalysts immobilized within metal-organic frameworks (MOFs), which provide a unique platform to isolate active centers, tune their coordination environments, and stabilize reactive intermediates that are difficult to control in conventional heterogeneous systems. MOFs offer high porosity, structural modularity, and the ability to anchor active sites with near-molecular precision. By integrating monomeric Cu or mono- and dinuclear Fe hydroxyl units into tailored MOF architectures such as MIL-53(Al), MOF-253(Al), and bipyridyl-functionalized UiO frameworks, this research demonstrates how active-site nuclearity, ligand environment, and pore confinement collectively govern oxygen activation pathways and reaction selectivity. Across the thesis, these catalysts enable the conversion of methane selectively into acetic acid or methanol using O₂ as the sole oxidant, operating under significantly milder conditions than traditional systems. Beyond methane, the work extends to the oxidation of benzene and styrene, where shape-selective pores and isolated Fe hydroxyl centers allow highly selective formation of phenol, benzaldehyde, or benzoic acid. Each chapter combines advanced synthetic strategies, comprehensive spectroscopic characterization (XPS, XAS, EPR, PXRD, BET), and DFT calculations to establish detailed structure-activity relationships. The findings demonstrate how the precise engineering of mono- versus dinuclear active sites inside MOFs enables control over radical and non-radical pathways, suppresses overoxidation, and enhances both activity and selectivity. Overall, this thesis highlights MOFs as powerful platforms for developing earth-abundant, recyclable, and selective oxidation catalysts, providing molecular-level insights that can guide future catalyst design for hydrocarbon functionalization.

Chapter 1: Introduction to Metal-Organic Frameworks and Single-Site Catalysts. This chapter provides an overview of metal–organic frameworks (MOFs) as crystalline, modular platforms for designing catalytically active sites with molecular precision. The tunable connectivity between metal nodes and organic linkers enables the construction of well-defined coordination environments that emulate enzymatic pockets while maintaining heterogeneous stability. Emphasis is placed on the role of linker functionality and postsynthetic metalation in tailoring the electronic and geometric structure of the active centers. The discussion traces the evolution of MOFs from inert porous hosts to redox-active catalytic materials, particularly those incorporating Fe and Cu sites capable of facilitating small-molecule activation and selective oxidation chemistry. By highlighting advances in framework engineering, site isolation, and cooperative multinuclear design, this chapter establishes the conceptual foundation for the Fe- and Cu-based catalytic systems discussed in the subsequent chapters.

Chapter 2: Materials and Methods. This chapter summarizes the experimental procedures and characterization methods used throughout this work. All starting materials, reagents, and

solvents were obtained from reliable commercial suppliers, with purification and drying performed when required. Glassware and reactors were cleaned using standardized solvent rinses and specialized treatments to ensure contamination-free synthesis. High-pressure methane and oxygen reactions were carried out in reinforced reactors under strict safety protocols, while air- and moisture-sensitive steps were conducted using Schlenk techniques or in an inert-atmosphere glovebox. A comprehensive suite of analytical tools was employed to characterize the structural, textural, and electronic properties of the MOF-based catalysts. PXRD, BET, FT-IR, TGA, SEMEDX, ICP-OES, XPS, EPR, and XAS provided detailed insight into crystallinity, porosity, functional groups, metal loading, oxidation states, and local coordination environments. Reaction mixtures were analyzed using NMR, GC, and HPLC for accurate product identification and quantification. Complementary density functional theory (DFT) calculations were performed to probe active-site structures, reaction energetics, and mechanistic pathways. Together, these methods establish a rigorous and reproducible foundation for the catalytic studies presented in this thesis.

Chapter 3: Copper Catalyzed Selective Methane Oxidation into Acetic Acid using O₂. The direct transformation of methane into C₂ oxygenates such as acetic acid selectively using molecular oxygen (O₂) is a significant challenge due to the chemical inertness of methane, the difficulty of methane C-H bond activation/C-C bond coupling and the thermodynamically favored over-oxidation. In this study, we have successfully developed a porous aluminium metal-organic framework (MOF)-supported single-site mono-copper(II) hydroxyl catalyst [MIL-53(Al)-Cu(OH)], which is efficient in directly oxidizing methane to acetic acid in water at 175 °C with a remarkable selectivity using only O₂. This heterogeneous catalyst achieved an exceptional acetic acid productivity of 11796 mmol_{CH₃CO₂H} mol_{Cu}⁻¹ h⁻¹ in 9.3% methane conversion with 95% selectivity in the liquid phase and can be reused at least 6 times. Our experiments, along with computational studies and spectroscopic analyses, suggest a catalytic cycle involving the formation of a methyl radical (\cdot CH₃). The confinement of Cu-active sites within the porous MIL-53(Al) MOF facilitates C-C bond coupling, resulting in the efficient formation of acetic acid with excellent selectivity due to the internal mass transfer limitations. This work advances the development of efficient and chemoselective earth-abundant metal catalysts using MOFs for the direct transformation of methane into value-added products under mild and eco-friendly conditions.

Chapter 4: Dinuclear Iron(II)-Hydroxyl Active Sites for Selective Methane Oxidation to Acetic Acid Using O₂. The selective oxidation of methane to liquid oxygenates using molecular oxygen under mild conditions remains a major challenge due to the inertness of methane and the competing overoxidation reactions. This chapter describes the development of a dinuclear bipyridyl Fe(II) hydroxyl catalyst confined within the porous MOF-253(Al) framework, denoted as MOF-253-Fe₂, featuring a [(bpy)FeII(μ₂-OH)(OH)]₂ active site. The catalyst exhibits 100% liquid selectivity toward acetic acid with a productivity of 2,757 mmol_{CH₃CO₂H} mol_{Fe}⁻¹ h⁻¹ at 160 °C. Detailed spectroscopic studies reveal that the confinement of the dinuclear Fe centers within the MOF facilitates redox cooperativity and multi-electron transfer, enabling efficient O₂ activation and methane C-H bond activation followed by C-C coupling with in situ generated CO to yield acetic acid. The formation of a [(bpy)FeIII(μ₂-OH)(OH)]₂ intermediate is proposed as the key step in the catalytic cycle. These findings highlight the crucial role of binuclear site design in achieving selective methane-to-acetic acid conversion.

Chapter 5: Mononuclear Iron(II)-Hydroxyl Active Sites for Selective Methane Oxidation to Methanol Using O₂ Direct oxidation of methane to methanol using O₂ under mild conditions is highly desirable yet challenging due to methane's chemical inertness and the tendency of methanol to overoxidize. This chapter presents a mononuclear bipyridyl Fe(II) hydroxyl catalyst supported on MOF-253(Al), designated as MOF-253-Fe, containing a (bpy)FeII(OH)₂ active site. The catalyst achieves a methanol productivity of 6,060 mmol_{CH₃OH} mol_{Fe}⁻¹ h⁻¹ with 96% selectivity in the aqueous phase at 95 °C. Spectroscopic investigations suggest that the isolated Fe(II)-OH centers promote selective C-H hydroxylation through a radical-mediated pathway, efficiently activating O₂ and methane without further oxidation of methanol. In contrast to the dinuclear analogue, MOF-253-Fe operates via single-site redox chemistry, emphasizing the importance of active site nuclearity in dictating product selectivity. This work provides mechanistic insight into the design of MOF-supported Fe catalysts for selective methane-to-methanol conversion.

Chapter 6: Bipyridyl based Metal-Organic Framework for Selective Hydroxylation of Benzene into Phenol Direct hydroxylation of benzene to phenol is more appealing in the industry for the economic and environmentally friendly phenol synthesis than the conventional cumene process. We have developed a UiO-metal-organic framework (MOF)-supported mono bipyridyl-Iron(II) hydroxyl catalyst [bpy-UiO-Fe(OH)₂] for the selective benzene hydroxylation into phenol using H₂O₂ as the oxidant. The heterogeneous bpy-UiO-Fe(OH)₂ catalyst showed high activity and remarkable phenol selectivity of 99%, giving the phenol mass-specific activity up to 1261 mmol_{PhOH} g_{Fe}⁻¹ h⁻¹ at 60 °C. Bpy-UiO-Fe(OH)₂ is significantly more active and selective than its homogeneous counterpart, bipyridine-Fe(OH)₂. This enhanced catalytic activity of bpy-UiO-Fe(OH)₂ over its homogeneous control is attributed to the active site isolation of the bpy-Fe(OH)₂ moiety by the solid MOF that prevents intermolecular decomposition. Moreover, the exceptional selectivity of bpy-UiO-Fe(OH)₂ in benzene to phenol conversion is originated via shape-selective catalysis, where the confined reaction space within the porous UiO-MOF prevents the formation of larger overoxidized products such as hydroquinone or benzoquinone, leading to the formation of only smaller-sized phenol after monohydroxylation of benzene. Spectroscopic and controlled experiments and theoretical calculations elucidated the reaction pathway, in which the in situ generated ·OH radical mediated by bpy-UiO-Fe^{II}(OH)₂ is the key species for benzene hydroxylation. This work underscores the significance of MOF-supported earth-abundant metal catalysts for sustainable production of fine chemicals.

Chapter 7: Mononuclear Bipyridyl-Iron(III) Hydroxide in Metal-Organic Framework for Selective Alkene Oxidation The selective oxidation of styrene to value-added products such as benzaldehyde and benzoic acid is of significant industrial importance. We report the design of a single-site iron catalyst supported on a bipyridine-functionalized metal-organic framework, bpy-UiOFe(OH)₃, which enables selective oxidation of styrene into benzaldehyde or benzoic acid using H₂O₂ as the oxidant. Systematic optimization of solvent composition, temperature, and reaction time revealed that benzaldehyde can be obtained with 100% selectivity at 80 °C in 8 h, while prolonged reactions furnish benzoic acid in high yields. Control experiments confirmed the heterogeneous, single-site nature of the catalyst, which remained structurally robust and can be recycled at least three times with negligible Fe leaching. Mechanistic studies suggest a non-radical pathway involving epoxide and diol intermediates prior to carbon-carbon

bond cleavage. This work demonstrates the potential of MOF-supported abundant-metal catalysts for sustainable oxidation of alkenes under environmentally benign conditions.