


# Metal–Organic Frameworks for Precision Catalysis

Wenbin Lin\*

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By precisely controlling both active sites and their surrounding microenvironments, enzymes catalyze complex transformations with remarkable efficiency and selectivity. This intricate interplay of structure and function in natural enzymes has inspired the emerging field of precision catalysis, which seeks to similarly modify active site architecture and local environments to enhance catalytic activity and selectivity in nonenzymatic systems. Precision catalysis aims to enhance activity and selectivity, rivaling natural enzymes while achieving greater atom economy in catalyst design.

Among various material platforms, metal–organic frameworks (MOFs) are uniquely positioned to advance precision catalysis due to their modular construction, structural regularity, and synthetic tunability.<sup>1</sup> MOFs are porous crystalline molecular materials built from metal clusters and organic linkers. Their reticular nature enables the rational synthesis of hundreds of thousands of MOFs with diverse topologies and compositions.<sup>2</sup> Unlike conventional homogeneous or heterogeneous catalysts, MOFs allow for atomic-level spatial control over the placement of catalytic sites. In this commentary, we explore how MOFs have evolved as a foundational platform for precision chemistry by offering unprecedented control over active site structure, arrangement, and microenvironment in catalysis.

At its core, precision catalysis seeks to suppress side reactions and promote selective transformations by isolating and fine-tuning active sites. The modular nature of MOFs enables the precise incorporation of well-defined catalytic centers—at metal nodes, on linkers, or within pores—in a periodic and spatially controlled manner. While open metal sites in MOFs have been widely used as acid catalysts,<sup>3</sup> the integration of molecular catalysts within MOFs greatly expands their catalytic scope while maintaining uniformity, stability, and accessibility of active sites. This isolation of active sites shuts down many deactivation pathways (such as bimolecular decomposition) and facilitates mechanistic studies.<sup>4</sup> Linkers bearing diverse donor groups (e.g., phosphines, bipyridines, imidazoles) can coordinate to transition metals photosynthetically to generate catalytically active sites within the framework.<sup>5</sup> Furthermore, orthogonal incorporation of distinct catalytic functionalities enables the design of multifunctional MOF catalysts.

Enzymes derive much of their catalytic power not only from their active sites but also from the surrounding microenvironments. MOFs provide a unique opportunity to emulate this principle. By tuning pore size, geometry, surface polarity, and functional group identity, MOFs allow for the design of active site microenvironments that stabilize transition states, orient substrates, and modulate reaction energetics. For example,

hydrophobic MOF cavities can promote transformations of nonpolar substrates in aqueous media, while the chiral environments within MOF pores have enabled enantioselective catalysis via spatial confinement.<sup>6</sup> Moreover, MOFs facilitate cooperative catalysis through the precise spatial arrangement of multiple catalytic functionalities. By positioning acid/base, redox, or nucleophilic/electrophilic sites in proximity, MOFs efficiently carry out tandem and cascade reactions within a single crystalline host, which is particularly valuable for multistep processes that rely on the rapid transfer of reactive intermediates between active sites, minimizing deactivation. Such spatial precision is rarely achievable in other classes of porous materials.

Precision catalysis also entails the organization of complex reaction networks through synergistic functions of multiple active sites. MOFs are uniquely suited to this challenge as their frameworks can accommodate multiple chemically orthogonal active sites. For example, MOFs can incorporate both photoredox and catalytically active components to drive photocatalytic CO<sub>2</sub> reduction, water splitting, and methane oxidation.<sup>7,8</sup> These multifunctional MOF catalysts frequently outperform their homogeneous counterparts by stabilizing reactive intermediates and minimizing side reactions.<sup>9</sup> Recent advances have produced hierarchical MOF composites and defect-engineered structures, where catalysis occurs at precisely created defect sites. These innovations expand the scope and versatility of MOF-based catalysis and help achieve a balance among activity, selectivity, and stability.

Unlike conventional heterogeneous catalysts, MOFs can be characterized at atomic resolution using single-crystal X-ray diffraction, enabling direct visualization of host–guest interactions and even reaction intermediates within the framework. These structural insights are invaluable for elucidating reaction mechanisms, refining design strategies, and enabling predictive modeling of catalytic behaviors. In addition, a wide range of spectroscopic techniques, including X-ray absorption spectroscopy, diffuse reflectance IR spectroscopy, and solid-state NMR, are increasingly employed to probe the local environments and dynamics of catalytic sites within MOFs. These capabilities make MOFs a powerful platform for elucidating structure–

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function relationships, advancing the field from empirical discovery toward data-driven catalyst design.

Despite the promise of MOF-based precision catalysis, several challenges remain. First, many MOFs are unstable under harsh reaction conditions, especially in acidic, basic, or high-temperature environments. To address this, robust MOFs based on Zr-, Ti-, or rare-earth elements are under active development.<sup>10</sup> Second, the industrial translation of MOF catalysts requires scalable and cost-effective synthesis methods—an issue that remains largely unresolved. Third, the slow diffusion of substrates and products through MOF channels can limit catalytic performance. While mesoporous or hierarchically porous MOFs help alleviate these diffusional constraints, monolayered MOFs offer an ideal platform to overcome mass transport limitation.<sup>11</sup> Fourth, although MOFs are often regarded as rigid structures, their dynamic behaviors of breathing, flexing, and pore gating can significantly impact catalysis.<sup>12</sup> A deeper understanding of this framework flexibility may reveal new strategies for catalytic control.

Looking forward, we anticipate that the convergence of MOF chemistry with synthetic biology, machine learning,<sup>13</sup> and adaptive materials will yield a new generation of catalysts that are not only precise but also self-regulating and evolvable. Incorporating MOFs into flow reactors,<sup>14</sup> electrocatalytic systems,<sup>15</sup> and photochemical platforms<sup>16</sup> will further broaden their impact on sustainable chemical manufacturing and the synthesis of complex molecules.

In summary, MOFs offer a compelling platform for advancing precision catalysis. By enabling molecular-level control over structure, reactivity, and microenvironment, MOFs empower chemists to transcend the limitations of conventional catalytic systems. As our capabilities in atomic-scale synthesis, characterization, and design continue to progress, MOFs are well positioned to enable catalytic processes with the precision of natural enzymes and the scalability, tunability, and robustness of synthetic materials.

## AUTHOR INFORMATION

### Corresponding Author

Wenbin Lin – Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, United States; [orcid.org/0000-0001-7035-7759](https://orcid.org/0000-0001-7035-7759); Email: [wenbinlin@uchicago.edu](mailto:wenbinlin@uchicago.edu)

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/prechem.5c00052>

## Notes

The author declares no competing financial interest.

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