engineering proceedings

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Cyclodextrin Metal–Organic Frameworks for Catalytic Applications: Current Research and Future Outlook †

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† Presented at the 3rd International Electronic Conference on Processes—Green and Sustainable Process Engineering and Process Systems Engineering (ECP 2024), 29–31 May 2024; Available online: https://sciforum.net/event/ECP2024.

Abstract: Catalysis is a fundamental process in chemistry and industry, driving the transformation of reactants into valuable products while minimizing energy input and waste generation. The quest for efficient and selective catalysts has led to the emergence of cyclodextrin metal–organic frameworks (CD-MOFs), a unique class of porous materials combining the advantages of cyclodextrins and metal–organic frameworks. CD-MOFs are gaining recognition for their distinctive capabilities in catalysis, offering benefits in terms of catalytic activity, selectivity, and sustainability. This paper presents an overview of current research on CD-MOFs in catalysis, emphasizing their application as hosts for catalytic materials and as catalysts themselves. The exploration includes studies on the confinement of redox-active monomers within CD-MOFs, resulting in controlled polymerization and enhanced electrical conductivity. Additionally, the paper discusses the encapsulation of photocatalysts in CD-MOFs, leading to stable and active hybrid materials for selective reduction processes. Further investigations focuses into the nanoconfined environment of CD-MOFs, showcasing their ability to influence the regio- and stereoselectivity of photodimerization reactions. The synthesis of bimetallic nanoparticles within CD-MOFs is also explored, highlighting their potential in catalytic applications with enhanced stability and recyclability. Despite significant progress, research gaps persist, urging a deeper understanding of the structure–function relationships within CD-MOFs. Mechanistic insights into catalytic processes, scalable synthesis methods, stability under catalytic conditions, recyclability, and diversification of catalytic functions are identified as critical areas for future exploration. The paper concludes by envisioning the future of CD-MOFs in catalysis, emphasizing tailored structures for specific reactions, multifunctionality, sustainability, industrial integration, and the exploration of novel catalytic frontiers in challenging environments. The catalytic prowess of CD-MOFs holds the promise of contributing to sustainable and efficient chemical processes, ushering in a new era of innovation at the intersection of materials science and catalysis.

Keywords: cyclodextrin metal–organic frameworks; catalysis

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Citation: Lopez, E.C.R. Cyclodextrin Metal–Organic Frameworks for Catalytic Applications: Current Research and Future Outlook. *Eng. Proc.* **2024**, *67*, 68. https://doi.org/10.3390/engproc2024067068

Academic Editor: Juan Francisco García Martín

Published: 21 October 2024

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1. Introduction

In recent years, the field of catalysis has witnessed a remarkable evolution with the emergence of new materials that promise to enhance reaction efficiency, selectivity, and sustainability. Among these innovative materials, coordination-driven metal–organic frameworks (CD-MOFs) have garnered significant attention due to their unique structural characteristics and versatile catalytic properties. CD-MOFs are a subclass of metal–organic frameworks (MOFs) distinguished by their ability to self-assemble through coordination bonds between metal ions and organic ligands, resulting in highly ordered and tunable

frameworks. This coordination-driven approach allows for the precise control of the framework's structure, pore size, and functionality, making CD-MOFs an attractive platform for various catalytic applications.

The catalytic potential of CD-MOFs stems from their highly porous nature, which provides a large surface area for the immobilization of catalytic sites. This high surface area not only facilitates the efficient diffusion of reactants and products but also ensures a high density of active sites, which can significantly enhance catalytic performance. Furthermore, the well-defined pore structures of CD-MOFs can be tailored to accommodate specific reactants or products, thereby improving selectivity and minimizing side reactions. The versatility of CD-MOFs is further exemplified by their ability to host a wide range of metal centers and organic ligands, allowing for the customization of catalytic properties to suit different reaction conditions and target molecules.

CD-MOFs represent a rapidly evolving area of research with significant potential for catalytic applications. Their unique structural characteristics, high surface area, and tunable properties make them a versatile platform for a wide range of catalytic reactions. While challenges related to stability and scalability remain, ongoing research is addressing these issues and paving the way for future advancements. As the field continues to progress, CD-MOFs are expected to play an increasingly important role in the development of efficient, selective, and sustainable catalytic processes. This paper will discuss the current research on CD-MOFs for catalysis. Current research gaps and future research outlooks are also highlighted.

2. CD-MOFs for Catalysis

2.1. CD-MOFs as Hosts of Catalytic Materials

CD-MOFs found their application in the field of catalysis due to their ability to host catalytic materials.

A study (Figure 1) explored the use of metal–organic frameworks (MOFs) as porous templates to control polymerization reactions. Specifically, Rb-CD-MOF was used to restrict the polymerization of pyrrole and capture highly reactive intermediates for a better understanding of the mechanism of polymerization reactions. The research involves immersing Rb-CD-MOF crystals in a pyrrole solution to load the monomer into the MOF's nanochannels. The confinement restricts the mobility and reactivity of pyrrole, allowing the formation and stabilization of terpyrrole (Tpy) cations. The results demonstrate the successful confinement of pyrrole within Rb-CD-MOF, leading to the formation of cationic terpyrrole complexes. The crystalline nature of Rb-CD-MOF allows for a direct visualization of the confined pyrrole reactivity and the resulting supramolecular interactions. The researchers further explore the use of iodine as an oxidizing agent to induce polymerization, leading to the formation of conductive terpyrrole complexes. The conductivity measurements reveal a million-fold enhancement in the electrical conductivity of Rb-CD-MOF loaded with terpyrrole compared to the pristine MOF. The conductivity results indicate a semiconductive behavior with an activation energy of 709 meV. The findings of this research contribute to the understanding of how MOFs, specifically cyclodextrin-based frameworks, can be employed as crystalline nanoreactors to control the polymerization of redox-active monomers. The direct visualization of the confined reactions and the subsequent enhancement in electrical conductivity provide valuable insights for the design and synthesis of functional materials with controlled properties [1].

In another study (Figure 2), a novel approach to creating a robust photocatalytic system by occluding the $[Ru(bpy)_3]Cl_2$ photocatalyst in a cyclodextrin metal–organic framework (MOF) was proposed. Unlike traditional methods involving covalent or coordination bonds, this approach relies on the physical confinement of the photocatalyst within the MOF's cavities. The resulting $[Ru(bpy)_3]Cl_2$/CD-MOF hybrid exhibits three key features: the MOF cavities are precisely sized to accommodate the photocatalyst without leaching, the tight confinement prevents photodegradation even under prolonged irradiation, and the CD MOF interior provides OH^- ions as electron donors, facilitating the catalytic cy-

cle. The synthesis involves co-crystallizing γ-cyclodextrin, RbOH, and varying amounts of $[Ru(bpy)_3]Cl_2$ to obtain millimeter-sized crystals. The crystals exhibit increased loading of $[Ru(bpy)_3]Cl_2$ with higher solution concentrations, up to approximately 40% of MOF cavities occupied at the highest loading. UV/Vis spectra confirm the occlusion of $[Ru(bpy)_3]Cl_2$ within the MOF without altering its framework structure. Importantly, the occluded $[Ru(bpy)_3]Cl_2$ shows minimal photodegradation even under prolonged light irradiation. In contrast, free $[Ru(bpy)_3]Cl_2$ in solution undergoes significant photodegradation with changes in the UV/Vis spectrum. This difference highlights the protective effect of the MOF environment. The $[Ru(bpy)_3]Cl_2$/CD-MOF hybrid is demonstrated to be catalytically active, photoreducing metal salts to nanoparticles. In one system, Pd nanoparticles are produced by immersing the MOF crystals in a $PdNO_3$ solution and irradiating with visible light. The resulting Pd nanotriangles exhibit a well-defined structure, indicating the effectiveness of the $[Ru(bpy)_3]Cl_2$/CD-MOF in facilitating the catalytic process. Furthermore, the hybrid system can selectively photoreduce metal salts, as demonstrated by the reduction of $AgNO_3$ in the presence of $PdNO_3$. The $[Ru(bpy)_3]Cl_2$/CD-MOF selectively produces Ag nanoparticles without forming Pd particles, showcasing the potential for controlled and selective reduction processes. In summary, the study demonstrates the synergistic effects of physical confinement and the chemical environment provided by the MOF scaffold in occluding $[Ru(bpy)_3]Cl_2$. This approach offers a technically straightforward alternative to covalent modifications of MOFs with catalytic units, opening possibilities for testing with other MOFs and occluded molecules. The $[Ru(bpy)_3]Cl_2$/CD-MOF system shows promise for various photocatalytic applications, including the reduction of metal salts to nanoparticles with enhanced stability and selectivity [2].

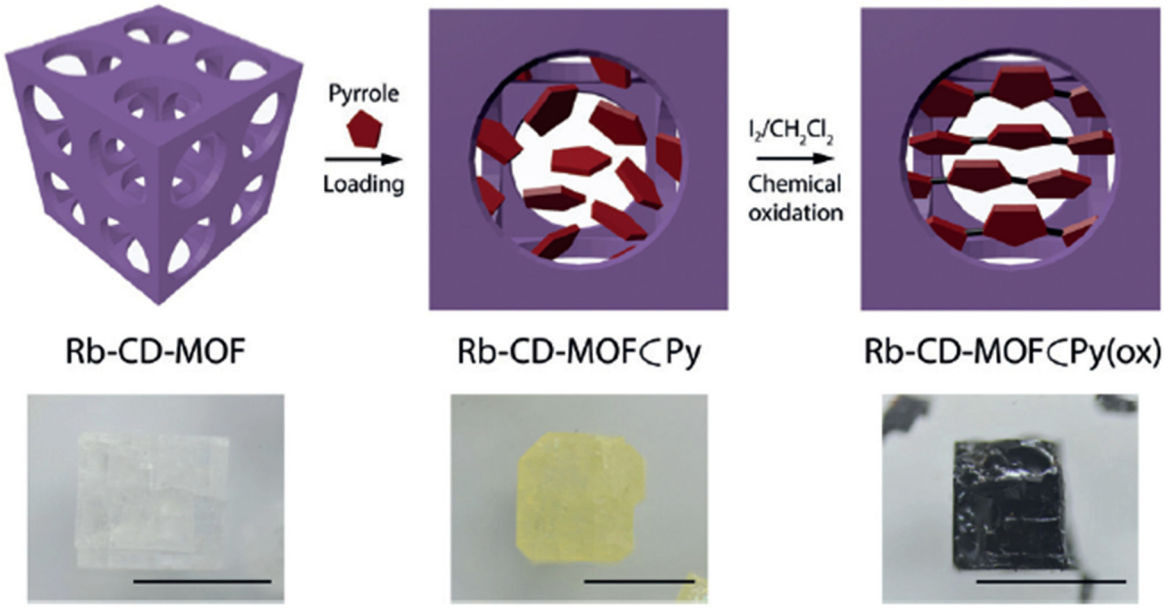


Figure 1. Schematic representation of the loading and chemical oxidation of pyrrole monomers within Rb-CD-MOF mesopores. Reproduced with permission from [1]. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA.

Another study (Figure 3) discusses the photodimerization of anthracenes, specifically 1-anthracenecarboxylate (1-AC^-), in both solution and within the nanoconfined space of a cyclodextrin-based metal–organic framework (CD-MOF-1). The study aims to understand the regio- and stereoselective behavior of the photodimerization process and explores the role of the CD-MOF-1 structure in influencing the outcomes. In solution, 1-AC^- undergoes non-selective photodimerization, producing all four possible regioisomers. The study investigates the impact of various solvents and the presence of cyclodextrin (γ-CD) on the selectivity of the reaction. The results show that solution-based photodimerization

lacks regioselectivity, with the anti-head-to-tail regioisomer being the most abundant. The researchers then shift their focus to the nanoconfined environment of CD-MOF-1. Anion exchange protocols are used to encapsulate 1-AC$^-$ within the CD-MOF-1 structure, leading to the creation of 1-AC$^-$⊂CD-MOF-1. Interestingly, the nanoconfined environment of CD-MOF-1 exhibits remarkable regio- and stereoselectivity during the photodimerization of 1-AC$^-$. Experimental results reveal that CD-MOF-1 serves as a highly efficient and enantioselective platform for delivering the anti-head-to-head regioisomer (anti-HH/2) with good yields and enantioselectivities. The study compares different conditions of anion exchange and reaction temperatures, showing that CD-MOF-1 prepared in specific conditions leads to optimal regio- and stereoselectivity. The researchers then used theoretical calculations to gain insights into the thermodynamic favorability of different relative orientations of 1-AC− pairs within the (γ-CD)2 tunnels of CD-MOF-1. The results indicate that the anti-HH orientation is more favorable, supported by multiple non-covalent interactions such as electrostatic, hydrogen-bonding, and hydrophobic interactions. Additionally, the study presents a solid-state superstructure analysis of 1-AC−⊂CD-MOF-1, highlighting the role of the (γ-CD)2 tunnels in aligning substrate pairs and influencing the photodimerization outcomes. The flexible nature of the CD-MOF-1 framework, along with the specific interactions between the substrates and the CD-MOF-1 structure, contributes to the observed regio- and stereoselectivity. In conclusion, the study demonstrates the importance of nanoconfined environments, such as those provided by CD-MOFs, in influencing the regio- and stereoselectivity of photodimerization reactions. The unique structural features of CD-MOF-1 contribute to the observed selectivity, showcasing the potential of tailored frameworks in controlling chemical reactions. The research suggests that this approach could inspire the design of enzyme analogs with distributed active sites for enhanced selectivity in various chemical transformations [3].

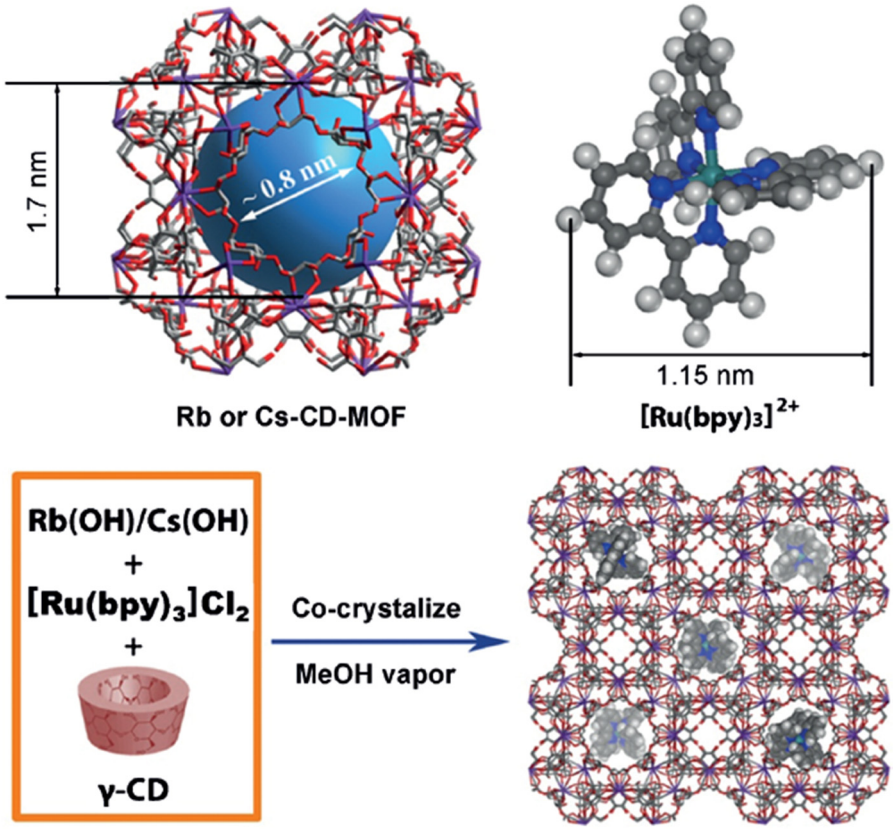


Figure 2. Scheme illustrating the physical incorporation of $[Ru(bpy)_3]Cl_2$ into the CD-MOF matrix by co-crystallization. Reproduced with permission from [2]. Copyright 2013, Wiley-VCH Verlag GmbH & Co. KGaA.

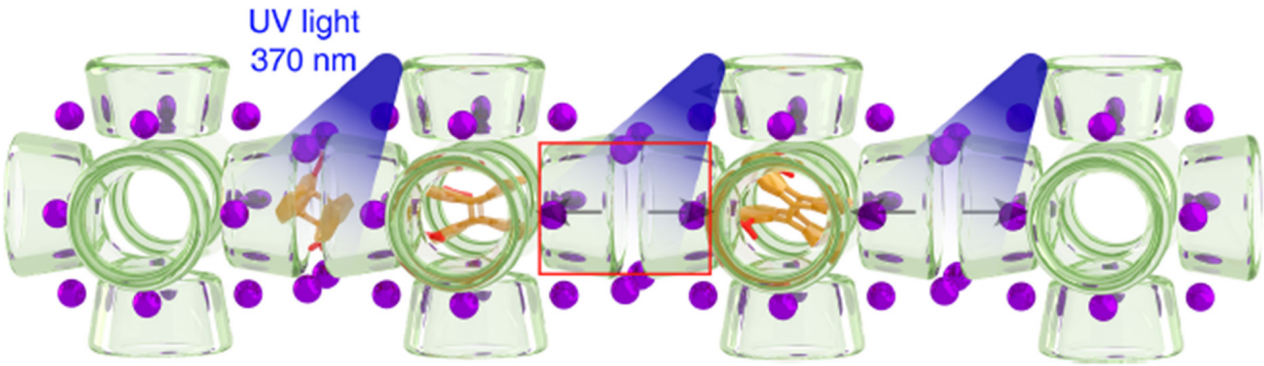


Figure 3. Schematic representation of the photodimerization of 1-AC$^-$ in CD-MOF-1. Reproduced with permission from [3]. Copyright 2021, American Chemical Society.

Another study (Figure 4) demonstrates a novel method for synthesizing bimetallic nanoparticles within cesium-based cyclodextrin metal–organic frameworks (CD-MOFs) and their subsequent transfer to various supports for potential catalytic applications. The CD-MOFs, composed of γ-cyclodextrin and CsOH, were synthesized by reacting γ-CD with CsOH in aqueous solution, followed by vapor diffusion of methanol. These CD-MOF crystals, characterized by large pores of approximately 1.2 nm in diameter, possess the unique ability to reduce metal salts into metal nanoparticles due to the hydrophilic nature of their nanosized pores. The primary challenge addressed in the study was the synthesis of binary metallic alloy nanoparticles within the CD-MOF, which was achieved through the diffusion of two kinds of metallic ions into CD-MOF crystals. In this process, hydroxide counterions played a crucial role in reducing the metal salts in situ, forming bimetallic nanoparticles within the CD-MOF. The specific example of Cu_xAu_y alloy nanoparticles was detailed, where the CD-MOF crystals were immersed in acetonitrile, and a precursor solution containing a 3:1 molar ratio of $HAuCl_4{\cdot}3H_2O$ to $Cu(NO_3)_2$ was added. The resulting Cu_xAu_y alloy nanoparticles were confirmed by analyzing the atomic ratio using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and high-resolution transmission electron microscopy (HRTEM). The study emphasized the importance of reaction time in controlling nanoparticle size and crystallinity, noting that prolonged reactions could lead to nanoparticle aggregation, affecting CD-MOF crystallinity. A significant feature of the CD-MOF crystals is their ability to dissolve in water, releasing the nanoparticles. Cyclodextrin molecules weakly bound to the nanoparticle surfaces during the dissolution process prevent coalescence between nanoparticles. This property allows the simultaneous deposition of nanoparticles onto various supports in aqueous media, forming composite materials of bimetallic nanoparticles and the desired supports, such as ceria nanorods, mesoporous silica, and carbon. The resulting bimetallic nanoparticle/metal oxide support composites were demonstrated to exhibit enhanced colloidal stability and catalytic activity in liquid-phase reactions. The catalytic performance was evaluated in CO oxidation and the reduction of 4-nitrophenol with $NaBH_4$. The composites showed superior catalytic activity compared to individual metallic nanoparticles under ambient conditions. Additionally, the study highlighted the recyclability and stability of the catalytic system over multiple reaction cycles. In conclusion, the research introduces a versatile approach for synthesizing and transferring bimetallic nanoparticles using CD-MOFs as sacrificial templates. The resulting composites exhibit promising catalytic properties, making them potential candidates for various applications in catalysis [4].

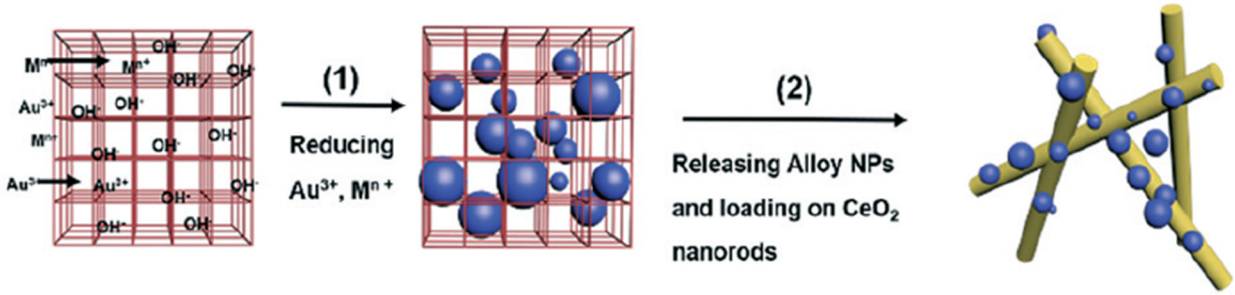


Figure 4. Experimental schematic diagram of the catalyst synthesis in a CD-MOF. Reproduced with permission from [4]. Copyright 2019, The Royal Society of Chemistry.

Another study (Figure 5) outlines the synthesis and characterization of Fe/N/C catalysts for the oxygen reduction reaction (ORR). The catalysts are prepared through the encapsulation of FePc (iron phthalocyanine) molecules within the internal cavities of γ-CD-MOF (gamma-cyclodextrin metal–organic framework) molecules. This encapsulation process helps prevent the aggregation of Fe atoms during pyrolysis, resulting in atomically dispersed Fe on a carbon carrier. The obtained FePc@CD/M (1:20)-1000 catalyst exhibits an interconnected cavity structure with no observed metal aggregation, indicating successful encapsulation. The porous characteristics of the carbon sheets are maintained, and the study explores the effects of different annealing temperatures and doping ratios on the internal and surface morphologies of the catalysts. Various imaging techniques, including transmission electron microscopy (TEM), scanning electron microscopy (SEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), confirm the atomically dispersed nature of Fe on the carbon nanosheets. The catalyst's hierarchical porous structure is evident from nitrogen adsorption–desorption curves, revealing a large specific surface area. X-ray diffraction (XRD) and Raman spectroscopy analyses indicate the absence of crystalline metal or metal compounds in the catalysts. The Raman spectra further reveal a low graphitization degree, with defects introduced by additional nitrogen doping. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements provide insights into the chemical state and coordination environment of Fe in the catalyst. The Fe atoms are well dispersed on the carbon nanosheets, with no noticeable metal aggregation. X-ray photoelectron spectroscopy (XPS) analysis reveals the presence of carbon, nitrogen, iron, and oxygen in the catalysts. Different nitrogen species are identified, and the Fe-N_x species are found to be uniformly dispersed on the carbon nanosheets. The catalyst's oxygen reduction reaction (ORR) activity is studied through cyclic voltammetry (CV) and linear sweep voltammetry (LSV) in alkaline solution. FePc@CD/M (1:20)-1000 exhibits excellent ORR activity with a significant cathodic peak in O2-saturated solution. The catalyst follows a four-electron transfer pathway and shows superior performance compared to a commercial 20% Pt/C catalyst. The study also explores the catalyst's tolerance to methanol crossover, demonstrating a rapid recovery after methanol addition. Additionally, the stability evaluation indicates that FePc@CD/M (1:20)-1000 maintains a slightly larger original current than the 20% Pt/C catalyst after continuous operation. In summary, the encapsulation of FePc within γ-CD-MOF, followed by pyrolysis and melamine doping, results in an Fe/N/C catalyst with atomically dispersed Fe, hierarchical porous structure, and excellent ORR performance. This work contributes to the design of non-noble metal catalysts with high atom utilization and performance [5].

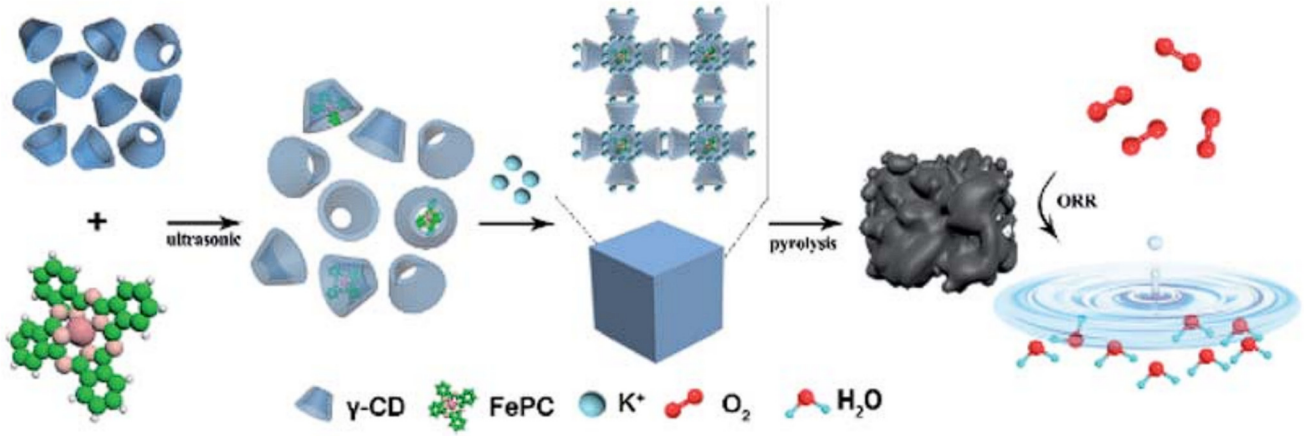


Figure 5. Synthesis method of encapsulating iron phthalocyanine molecules with γ-CD-MOF to prepare the catalysts. Reproduced with permission from [5]. Copyright 2022, The Royal Society of Chemistry.

In another study (Figure 6), the researchers investigated the synthesis and characterization of a composite catalyst, ZnO/CCM, for photocatalytic degradation of organic dyes. The composite is developed using CD-MOF as a building block and modifying it with glycol glycidyl ether for improved water stability. The Fourier transform infrared (FTIR) spectra of CD-MOF, CCM, and ZnO/CCM-3 reveal similar spectral characteristics. CD-MOF and CCM exhibit three characteristic peaks associated with stretching vibrations of -OH groups, absorption bands of -CH2- groups, and vibration absorption of -C-O-C- groups. The introduction of methylene from the cross-linking reaction between EGDE and γ-CD of CD-MOF broadens the peaks in CCM. ZnO/CCM-3 shows additional peaks related to the skeletal vibration of -OH groups from CD-MOF, the characteristic peak of ZnO, and bond vibration of Zn-O, confirming successful ZnO immobilization. XRD studies confirm the crystalline nature of CCM and the combination of ZnO with CCM. XPS spectroscopy and elemental analysis support the successful immobilization of ZnO on CCM. Morphological analysis through microscopy indicates that CD-MOF and CCM maintain their structure and stability even after various treatments. ZnO/CCM-3, after photocatalytic reaction, retains its original morphology, demonstrating good stability. UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS) reveals that ZnO/CCM-3 exhibits a wider spectral response range compared to CD-MOF and pure ZnO, indicating improved light energy utilization. Electron spin resonance (ESR) spectra confirm the production of free ·OH during photocatalytic degradation. Thermal stability tests show that ZnO/CCM-3 is stable up to 270 °C, with the introduction of ZnO making the MOF structure denser. Water stability experiments indicate that CCM has better water stability than CD-MOF. Nitrogen adsorption–desorption isotherms suggest that the materials maintain high porosity, making them suitable for adsorption and catalysis of organic matter. Photocatalytic and antibacterial properties are evaluated using methylene blue (MB) degradation and E. coli sterilization under simulated sunlight. ZnO/CCM-3 demonstrates superior photocatalytic degradation performance, degrading at least 91.8% MB. The material also exhibits stable performance over successive cycles, indicating recyclability. Antibacterial tests show a sterilization effect of over 99.9% against E. coli. In summary, the study presents a comprehensive analysis of the synthesis, characterization, and application of ZnO/CCM composite catalysts for photocatalytic degradation. The materials show promise for wastewater treatment, combining good photocatalytic activity, stability, and recyclability [6].

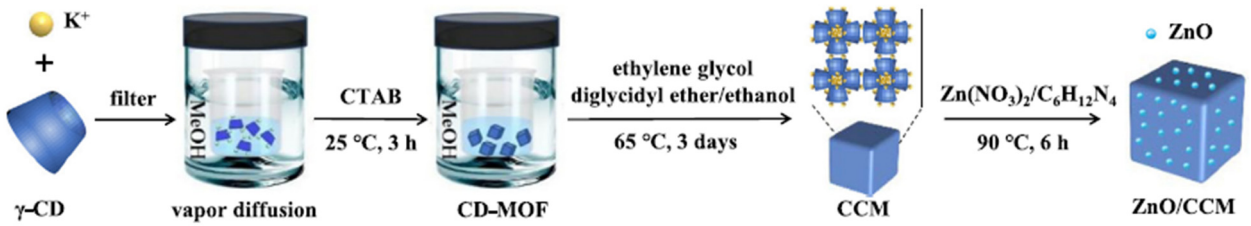


Figure 6. Synthetic procedure of CCM and ZnO/CCM. Reproduced with permission from [6]. Copyright 2023, Elsevier.

Another study synthesized a novel gold nanocluster, Au_{40}(S-Adm)$_{22}$, and characterized its unique structural and catalytic properties. The choice of this nanocluster was based on the model's protecting ligand, adamantanethiol (Adm-S-), which has gained significant attention due to its large spatial blockade. The synthesis involved a two-step method with slight modifications, resulting in the formation of nanocluster crystals with distinct absorption bands in the UV–Vis/NIR spectrum. The nanocluster's structure was determined through various techniques, including NMR, ESI-MS, and SCXC. The Au_{40}(S-Adm)$_{22}$ nanocluster exhibited a triclinic crystal structure with a unique kernel packing mode, unlike other gold nanoclusters protected by adamantanethiolates. The kernel consisted of a Au_{16} unit and a Au_{13} unit, forming a quasi-icosahedron structure with specific Au–Au bond lengths. To enhance the water solubility of the nanoclusters for potential catalytic applications, a host–guest chemistry approach was introduced. A γ-cyclodextrin metal–organic framework (γ-CD-MOF) was synthesized and mixed with Au_{40}(S-Adm)$_{22}$, resulting in Au_{40}/γ-CD-MOF. The catalytic properties of this inclusion compound were explored in an enzyme-mimicking reaction, specifically the horseradish peroxidase (HRP)-mimicking reaction. The catalytic efficiency of Au_{40}/γ-CD-MOF was found to be pH-dependent, with an optimal pH of 4. Additionally, kinetic data indicated that the nanocluster had lower affinity toward H_2O_2 compared to HRP but higher affinity toward the substrate 3,3′,5,5′-tetramethylbenzidine (TMB). Comparative studies with other inclusion compounds, Au_{38}/γ-CD-MOF and Au_{44}/γ-CD-MOF, demonstrated the efficiency and universality of the dual-purpose strategy. The study also explored the mechanism of the HRP-mimicking catalysis using density functional theory (DFT) calculations. The proposed mechanism involved the interaction of H_2O_2 with the metal surface of Au_{40} through the interstice left by the rigid ligands, leading to the production of hydroxyl radicals and subsequent oxidation of TMB. In summary, the study presents a comprehensive exploration of a novel gold nanocluster, Au_{40}(S-Adm)$_{22}$, its unique structure, and its catalytic properties in enzyme-mimicking reactions. The introduction of a water-soluble component through host–guest chemistry opens up avenues for potential applications in water-phase catalysis, showcasing the versatility and efficiency of the proposed strategy. The study also contributes valuable insights into the catalytic mechanism of gold nanoclusters, laying the foundation for future developments in nanocatalysis [7].

A group of researchers succeeded in preparing the CD-MOF in which water-soluble porphyrin (tetrakis (4-carboxyphenyl) porphyrin, TCPP) was encapsulated in hydrophilic nanopores by methanol vapor diffusion of methanol to the mixed solution of γCD, KOH, and TCPP. Co(II)TCPP/CD-MOF, a cubic crystal with a maximum size of 150 μm and a crystallization yield of 76%, was obtained. The Co(II)TCPP content in Co(II)TCPP/CD-MOF can be controlled by adjusting the vessel's opening area during methanol vapor diffusion. Two types of Co(II)TCPP/CD-MOF with catalyst loadings of 5.1 wt% and 9.8 wt% were prepared, corresponding to 0.49 and 0.94 Co(II)TCPP molecules per (γ-CD)$_6$ unit, respectively. In comparison, when TCPP was introduced into CD-MOF, there were 2.1 TCPP molecules per (γ-CD)$_6$ unit, suggesting that a pair of TCPP molecules may be located in the hydrophilic nanopore. This implies that CD-MOF, when used as a support for organometallic catalysts, facilitates the creation of heterogeneous catalysts with high dispersibility and loading. The crystallinity of Co(II)TCPP/CD-MOF was confirmed by

X-ray diffraction (XRD), showing maintained peaks corresponding to CD-MOF even with the introduction of Co(II)TCPP. The BET specific surface area of CD-MOF was 970 m^2/g, while Co(II)TCPP/CD-MOF had a lower surface area of 682 m^2/g. The study found that homogeneous Co(II)TCPP catalyst exhibits high catalytic activity in an O_2 atmosphere, with negligible activity in N_2. The use of Na_2CO_3 and NaOH as bases at a 0.2 mol% catalyst concentration results in nearly 100% conversion after a 24 h reaction. Co(II)TCPP/CD-MOF, with a particle size of 5–20 μm, slightly reduces the reaction rate, achieving a 92% conversion. The study also explores the effects of catalyst concentration and crystal size on conversion, revealing higher rates with increased concentration and smaller particle sizes. Overall, the study showed that Co(II)TCPP can be successfully introduced into the hydrophilic nanopores of CD-MOF, forming a heterogeneous catalyst with high dispersibility and loading. The catalytic activity of Co(II)TCPP/CD-MOF in the oxidative coupling of creosol is comparable to that of homogeneous Co(II)TCPP, demonstrating the potential of CD-MOF as an effective support material for organometallic catalysts. Further investigations are suggested to analyze the diffusion effects on the reaction, especially in catalysts with larger particle sizes [8].

2.2. CD-MOFs as a Catalyst

With the discovery of CD-MOFs based on transition metals, they emerged to be powerful catalysts for various applications. A study (Figure 7) explored the synthesis and characterization of Cu-β-CD-MOF, formed by incorporating beta cyclodextrin (β-CD) and copper ions (Cu) through a vapor diffusion method. FTIR spectra were conducted on β-CD and Cu-β-CD-MOF to investigate the involved functional groups. In β-CD, characteristic peaks corresponding to O–H, C–H, and C–O–C vibrations were observed. Cu-β-CD-MOF exhibited similar peaks, confirming the presence of cyclodextrin in the MOF, consistent with previous β-CD-MOFs. The UV–visible absorption spectra of Cu-β-CD-MOF revealed a band gap energy of 2.23 eV. This narrow band gap suggests that Cu-β-CD-MOF is a good photosensitive material, encouraging photocatalytic activity and positioning it as an efficient photocatalyst. XRD analysis confirmed the crystal structure of Cu-β-CD-MOF, showing sharp peaks for β-CD and additional peaks attributed to the presence of copper ions. The diffractogram indicated high crystallinity, consistent with previous studies on β-CD-MOFs. Morphological assessment through SEM revealed that Cu-β-CD-MOF exhibited a rod-like structure with cuboidal-shaped smooth crystals. The average particle size was determined to be 1.07 μm. EDX analysis confirmed the elemental composition of Cu-β-CD-MOF, showing the presence of carbon (C), oxygen (O), and copper (Cu). TGA was employed to evaluate the thermal stability of β-CD and Cu-β-CD-MOF. The latter demonstrated enhanced thermal stability compared to β-CD, attributed to the insertion of metal ions. Cu-β-CD-MOF was evaluated for its photocatalytic activity in the reduction of nitroaromatic compounds (NACs), specifically 4-NP, NB, 2-NP, and 4-NA. The catalytic reduction reactions were monitored by UV–visible spectroscopy. Cu-β-CD-MOF exhibited an ultrafast reduction of NACs, reducing them in less than 4 min. The catalytic rate constants were determined using pseudo-first-order kinetics. A plausible mechanism for the catalytic reduction of NACs was proposed. The Langmuir–Hinshelwood model was suggested, involving four steps: adsorption of hydrogen radicals, adsorption of NACs on the catalyst surface, electron transfer, and desorption of reduced aromatic amino compounds. The study concludes that Cu-β-CD-MOF, synthesized through a sustainable and green approach, possesses remarkable photocatalytic activity in the reduction of NACs. The material exhibits enhanced thermal stability, a small band gap, and efficient catalytic performance, making it a promising candidate for wastewater treatment and environmental remediation. The results contribute to the understanding of MOFs in sustainable catalysis and their potential applications in green chemistry [9].

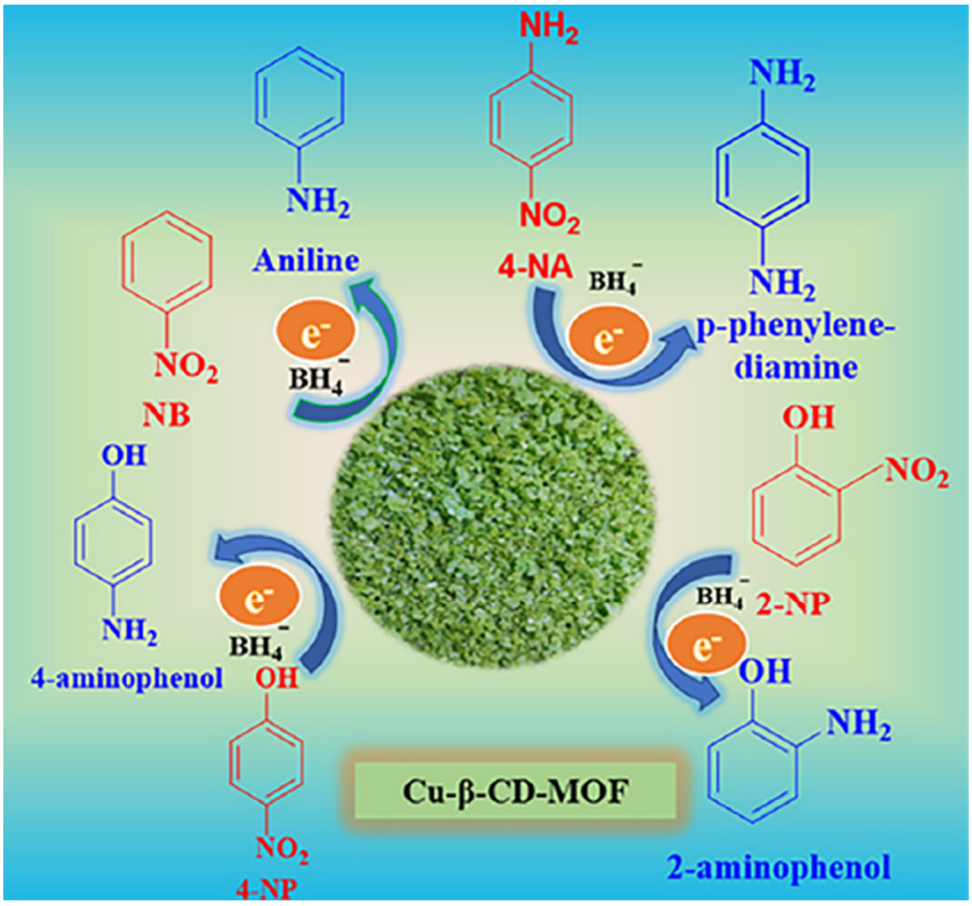


Figure 7. Photocatalytic reduction of different NACs to their derivatives by Cu-β-CD-MOF. Reproduced with permission from [9]. Copyright 2023, Elsevier.

2.3. CD-MOF-Derived Catalysts

CD-MOF-based catalysts have also found their way into catalytic applications. In a study (Figure 8), a bifunctional catalyst derived from γ-CD-MOF was synthesized for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The synthesis involves preparing γ-CD-MOFs through a solvent evaporation method, followed by the introduction of Co^{2+} ions. The resulting Co-CD-MOFs undergo carbonization at 750 °C, producing Co–N,O–C@C_3N_4 through a molten-salt-assisted pyrolysis strategy. The Co–N,O–C@C_3N_4 catalyst is characterized by a cubic morphology with a particle size of 2 µm. The structural changes induced by Co2+ incorporation are elucidated through XRD and FT-IR, demonstrating effective anchoring of Co^{2+} ions to γ-CD-MOFs. Carbonization with melamine introduces disorder, observed in Raman spectra, which enhances electrochemical reactivity by creating more active sites. The resulting Co–N,O–C@C_3N_4 exhibits a large BET surface area of 243 m^2 g^{-1} with mesoporous structures, providing favorable conditions for rapid substance transmission and active site accessibility. SEM and TEM images illustrate the cubic morphology of Co–N,O–C@C_3N_4, surrounded by a folded sheet structure. High-resolution TEM and SAED images reveal the polycrystalline features of Co–N,O–C@C_3N_4, indicating the presence of Co_3O_4, CoN, and Co species in the porous carbon matrix. XPS analysis further confirms the composition and chemical valence of Co–N,O–C@C_3N_4, showcasing the presence of atomically dispersed metallic Co centers and nitrogen-doping. The electrocatalytic performance of Co–N,O–C@C_3N_4 is evaluated for both OER and ORR. The catalyst displays remarkable OER activity, outperforming Co–O–C and Co–O–CMS, with a lower overpotential and Tafel slope. The presence of defects resulting from melamine addition contributes to enhanced electrochemical reactions. For ORR, Co–N,O–C@C_3N_4 exhibits a positively shifted cathodic peak and superior catalytic performance compared

to Pt/C, with a smaller Tafel slope indicating faster reaction kinetics. The bifunctional catalyst is integrated into a Zn–air battery, demonstrating an open-circuit potential of 1.43 V, outperforming Pt/C + RuO2. The Co–N,O–C@C_3N_4-based battery exhibits higher power density, specific capacity, and energy density, along with excellent cycling stability over 200 cycles. In summary, the study presents a comprehensive approach to the synthesis and characterization of γ-CD-MOFs and their transformation into a high-performance bifunctional catalyst for both OER and ORR, showcasing their potential in sustainable energy applications, particularly in Zn–air batteries. The unique combination of structural features, compositional elements, and electronic interactions contributes to the exceptional electrocatalytic properties of Co–N,O–C@C_3N_4 [10].

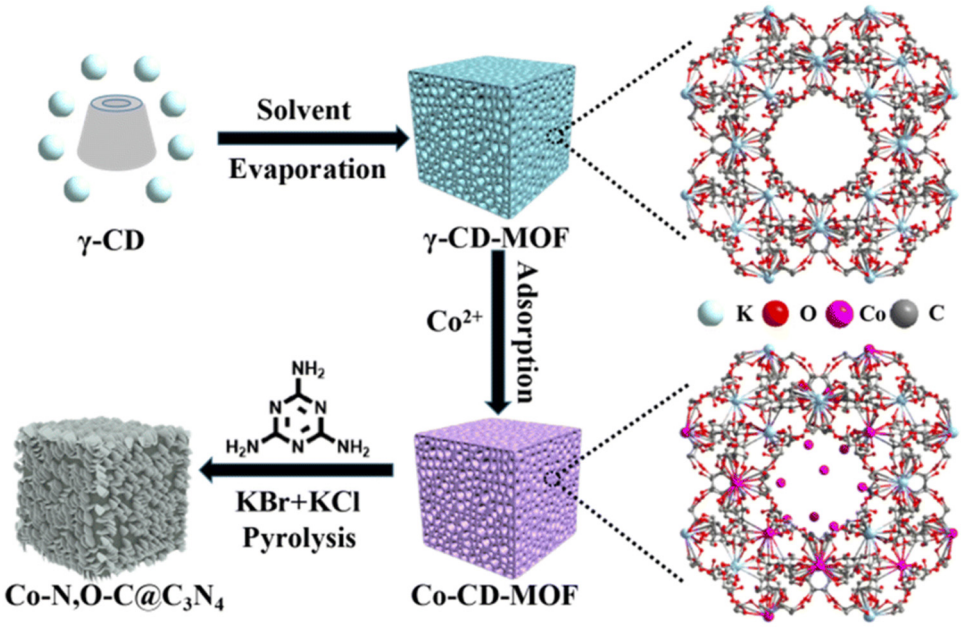


Figure 8. Schematic illustration for the preparation of Co–N,O–C@C_3N_4. Reproduced with permission from [10]. Copyright 2023, The Royal Society of Chemistry.

3. Research Gaps

Cyclodextrin-based metal–organic frameworks (CD-MOFs) have emerged as a class of porous materials with tunable structures and unique properties, primarily due to the combination of cyclodextrins with metal ions through coordination bonds. These materials have garnered significant attention in the field of catalysis due to their versatility, sustainability, and intriguing catalytic properties. However, despite the progress made, there remain several research gaps that hinder the comprehensive utilization of CD-MOFs in catalytic applications. One of the most critical challenges lies in understanding the structure–function relationships within CD-MOFs, particularly in how the type and nature of the metal ions used in these frameworks influence their catalytic performance, stability, and scalability. Additionally, there are important considerations related to commercial viability and the environmental impact of CD-MOFs, which align with the principles of green chemistry.

The metal ions chosen in CD-MOFs play a central role in determining their catalytic behavior. Metal ions serve as coordination centers that bind cyclodextrin molecules, creating a robust and structured framework. The specific properties of the metal ions, including their electronic configuration, oxidation state, coordination geometry, and bonding characteristics, have a profound impact on the catalytic properties of the MOF. Different metal ions confer distinct catalytic functions, making the choice of metal ions crucial in designing CD-MOFs for specific catalytic applications.

A deeper understanding of the structure–function relationships within CD-MOFs is essential for the rational design of materials with enhanced catalytic properties. The

specific arrangement of metal ions and cyclodextrin molecules within the MOF framework can greatly influence the catalytic activity, selectivity, and efficiency of the material. While many studies have demonstrated the catalytic efficacy of CD-MOFs, few have provided detailed mechanistic insights into how the arrangement of these components affects catalytic performance. To fully harness the catalytic potential of CD-MOFs, it is imperative to investigate how variations in metal ion coordination, pore size, and framework topology impact catalysis. Advanced spectroscopic and computational techniques can be employed to elucidate the reaction pathways, identify active sites, and understand the role of each component in the catalytic process. Such studies will provide valuable insights for the rational design of CD-MOFs, allowing for the optimization of their catalytic properties for specific applications.

While CD-MOFs show great promise for catalytic applications in laboratory settings, the transition to large-scale production presents significant challenges. The synthesis of CD-MOFs on a commercial scale requires methods that are not only scalable but also cost-effective and reproducible. One of the key challenges in scaling up the production of CD-MOFs is maintaining the unique properties of the material, such as its porosity and catalytic activity, without compromising structural integrity. In addition to scalability, the cost of the metal ions used in CD-MOF synthesis is a major consideration for commercial viability.

One of the main advantages of CD-MOFs is their potential to contribute to sustainable chemical processes by providing efficient and reusable catalysts. However, the sustainability of CD-MOFs depends not only on their catalytic performance but also on the methods used to synthesize them. Traditional methods for synthesizing MOFs often require the use of toxic solvents or energy-intensive processes, which can offset the environmental benefits of using these materials in catalysis. Therefore, there is a need for the development of greener synthesis methods for CD-MOFs that minimize the use of hazardous chemicals and reduce energy consumption. Additionally, the recyclability of CD-MOFs is a critical factor in their sustainability. Catalysts that can be easily recovered and reused contribute to more efficient chemical processes, reducing waste and minimizing the consumption of raw materials. Research should focus on understanding the factors that affect the stability and recyclability of CD-MOFs under catalytic conditions, as well as developing strategies to enhance their robustness.

CD-MOFs also hold potential for environmental applications, such as pollutant removal and wastewater treatment, where their porosity and catalytic properties can be used to degrade or remove harmful substances. However, a comprehensive assessment of the environmental impact of CD-MOFs is still lacking. Future research should explore the potential of CD-MOFs in green chemistry applications, such as sustainable energy production, carbon capture, and pollution abatement, to ensure that their use aligns with environmental sustainability goals.

While CD-MOFs represent a promising class of materials with significant potential for catalytic applications, several research gaps need to be addressed to fully unlock their potential. The type and nature of metal ions used in CD-MOFs are crucial to their catalytic performance, stability, and environmental impact, and further research is needed to optimize metal ion selection for specific applications. Additionally, challenges related to the scalability and commercial viability of CD-MOFs must be overcome to facilitate their widespread adoption in industrial processes. Finally, green chemistry considerations, such as the development of sustainable synthesis methods and the assessment of environmental impacts, should guide future research and development efforts to ensure that CD-MOFs contribute to more sustainable and efficient chemical processes. By addressing these challenges, researchers can propel CD-MOFs to the forefront of catalytic innovation, paving the way for their use in a wide range of industrial and environmental applications.

4. Future Research

The catalytic landscape is undergoing a transformative phase with the advent of innovative materials such as CD-MOFs. These porous structures, born from the marriage

of cyclodextrins and metal ions, exhibit unique properties that make them promising candidates for catalytic applications. As we gaze into the future, several key aspects will shape the trajectory of CD-MOFs in catalysis.

The future of CD-MOFs in catalysis lies in tailoring these frameworks for specific reactions. Designing structures with precise arrangements of cyclodextrins and metal ions can impart selectivity and efficiency, making CD-MOFs the catalysts of choice for particular chemical transformations. This tailoring requires a deep understanding of the structure–function relationships, paving the way for bespoke catalysts designed for diverse catalytic applications.

Envisioning CD-MOFs as multifunctional platforms opens new avenues in catalysis. Integrating different catalytic sites within the framework can enable synergistic effects, leading to enhanced catalytic performance. The future may witness the development of CD-MOFs with dual or multiple catalytic functionalities, capable of orchestrating complex reactions with precision and efficiency. Future research on CD-MOFs should prioritize unraveling intricate catalytic mechanisms through advanced spectroscopic and computational techniques. This deeper understanding will not only facilitate the rational design of catalysts but also enable fine-tuning of catalytic processes for optimal performance.

Sustainability is a key driver in modern catalysis. CD-MOFs, with their eco-friendly synthesis routes and potential for recyclability, align well with the principles of green chemistry. The future outlook involves further optimizing the environmental impact of CD-MOF-based catalytic processes, ensuring minimal waste generation and energy consumption. Sustainable catalysis with CD-MOFs may contribute to greener and more efficient chemical production. For CD-MOFs to make a significant impact, seamless integration with industrial processes is crucial. The future will likely see concerted efforts to scale up CD-MOF synthesis methods and adapt them to industrial settings. Bridging the gap between laboratory-scale innovation and large-scale industrial implementation will be a key milestone for CD-MOFs in catalysis.

As the field of catalysis evolves, so should the catalytic capabilities of CD-MOFs. Future research should explore uncharted catalytic frontiers, pushing the boundaries of where CD-MOFs can excel. The versatility of CD-MOFs opens doors to catalyzing novel reactions and addressing emerging challenges in various industries, from pharmaceuticals to energy production. Future applications may involve catalyzing reactions in extreme conditions such as high temperatures or corrosive atmospheres. Understanding the limits of CD-MOF stability and catalytic activity in harsh environments will expand their scope in unconventional catalytic processes.

The future outlook for CD-MOFs in catalytic applications is imbued with potential and excitement. Tailoring structures, embracing multifunctionality, advancing mechanistic understanding, promoting sustainability, integrating with industry, exploring new catalytic frontiers, catalyzing in challenging environments, and fostering collaborative initiatives are pivotal aspects that will shape the trajectory of CD-MOF research. As we navigate this path, the catalytic prowess of CD-MOFs holds the promise of contributing to sustainable and efficient chemical processes, heralding a new era of innovation at the intersection of materials science and catalysis.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained in this article.

Conflicts of Interest: The author declares no conflicts of interest.

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