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FUNCTIONALIZATION STRATEGIES FOR ENHANCING CATALYTIC PERFORMANCE IN POROUS MOFS: A COMPREHENSIVE APPROACH

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ABSTRACT

A thorough method for improving the catalytic activity of Metalorganic Frameworks (MOFs) by strategically functionalizing their porous architectures is laid forth in this paper. In order to maximize catalytic activity for different heterogeneous catalysis uses, the MOF framework is designed, and functional groups are integrated throughout the synthesis process. We investigate several functionalization approaches, such as modifying MOFs after synthesis or adding functionalized ligands during synthesis. A range of analytical methods are used to evaluate the chemical, structural, and textural characteristics of the functionalized MOFs that have been synthesized. Catalytic testing is carried out to assess how well these customized MOFs work in specific reactions. The findings prove that the all-encompassing method is effective in crafting MOFs with enhanced catalytic activity, opening the door to their potential use in environmentally friendly and cost-effective catalytic procedures.

Keywords: Metalorganic Frameworks (MOFs), Functionalization, Heterogeneous Catalysis, Post-synthetic Modification (PSM), Catalytic Performance, Porous Structures, Synthesis Strategies

I. INTRODUCTION

Potential applications for metalorganic frameworks (MOFs) in gas storage, molecular separation, and heterogeneous catalysis have been highlighted in recent years [1-14]. MOFs are made of modular metal nodes and organic ligands. The fast transit of guest molecules and the encapsulation of macromolecules are made possible by the vast open channels of MOFs with enormous cavities, attracting much attention recently [15–19]. Fig. 1a shows that unmodified MOFs have poor separation performance and undesirable by-products because of their possible selectivity problems versus substrate molecules of comparable sizes [20]. It is crucial to provide porous MOFs with selectivity towards distinct substrates with comparable physical or chemical characteristics to tap into the whole functionality of these materials in a range of real-world applications. To produce substrate-selective porous MOFs, it is common practice to use bottom-up synthesis or post-synthetic modification to generate a framework with a substrate-specific accessible void [21–23]. "Hybrid materials with enhanced properties have been produced thus far by successfully incorporating different surface capping agents onto the external surface of different MOFs." These agents include polymers, phospholipids, phenylsilanes, and biomacromolecules like proteins and oligonucleotides [24-30].

As an example, the Janiak group achieved MOF-CB6 composites with improved CO2 adsorption and gas separation ability by encapsulating cucurbit[6]uril (CB6) with MIL-101 [27]. "The modified MOFs demonstrated enhanced solvent dispersibility and colloidal stability when Li et al. covered their surface with various organic macrocycles and polymers [28]." Regardless of these successes, the majority of the methods that have been documented so far alter the external surface using nonporous capping agents, which in turn impacts the host framework's porosity and associated properties (Fig. 1a). "Discovering the perfect surface capping agent with built-in porosity for easy guest molecule transport and tunable functions for accurate recognition is of the utmost importance for improving MOF characteristics and adding new functionalities via surface modification while preserving structural porosity." Here, we are interested in discrete supramolecular cage structures with inherent voids, called porous coordination cages (PCCs) [31–37]. These structures may be metalorganic polyhedrons (MOPs) or cages (MOCs).

Host-guest chemistry, catalysis, and chemical reactions with region selectivity have applications for PCCs [31–37]. "One possible use for PCCs is as surface-capping agents to alter the external surface of MOF particles; this could result in multicomponent porous materials with improved functionalities and preserved accessible voids, thanks to PCCs' inherent porosity and highly tunable properties like charges, sizes, and functional groups." In the few studies that have looked at functionalizing MOFs using molecular cages, the focus has been successfully enclosing the molecular cages inside the host framework's cavities [38–40]. One study that demonstrated enhanced stability in the oxidation of benzyl alcohol to benzaldehyde was conducted by Li et al. [38]. They reported encapsulating the Pd6L4 cage inside the cavity of MIL101. However, most of the "Cage-MOF" hybrids that have been reported up to this point have been made by non-covalent encapsulation, which involves inserting tiny cages into the cavities of the host MOF. This might compromise the porosity of the MOFs since the cages are arranged randomly within the host voids. Concerns about the "Cage-MOF" hybrid material's stability in harsh environments may also arise from non-covalent interactions.

II. LITERATURE REVIEW

One kind of porous crystalline material that is created by coordinating organic ligands with inorganic metal ions (or clusters of metals) is called a metalorganic framework (MOF) [41–46]. They are perfect host matrices for biomolecule immobilization because of their intrinsic features, which include ordered and controllable porosity, good crystallinity, and large surface areas: 1) With the abundance of MOFs with big holes discovered in the last several years, it is clear that their enormous surface area and porosity make them ideal for biomolecule loading [41–42]. 2) The architectures of MOFs are open. The guest biomolecules may interact with the external environment via the passage of substrates and products through the pores. 3) MOFs have many metal nodes, ligands, and topological configurations. A well-designed, application-specific shape and set of attributes is possible. 4) As a result of their porous and surface-distributed nature, MOFs have the potential to interact with biomolecules in a way that prevents or significantly reduces their leaching. "5) When studying the interaction/mechanisms of MOFs with guest molecules, it is vital to have access to the defined networks and unambiguous structural information provided by their high crystallinity." Due to their exceptional features, MOFs may provide remarkable support for including biomolecules for advanced applications. Composites made of biomolecules and metalorganic frameworks (MOFs) may combine the best features of both components. "Not only may MOFs facilitate the separation and recovery of biomolecules from products, but they can also provide stabilizing microenvironments for biomolecules,

which improves their performance under perturbation conditions." In addition, MOFs' heterogeneous feature makes biomolecules worthwhile in several areas, including separation, catalysis, and sensing. However, MOFs may be functionalized by immobilized biomolecules, which adds new features to biomolecules-MOFs composites and opens up new technological possibilities for MOFs, particularly in biocatalysis and biomedicine [47-50]. Incorporating biomolecules into MOFs expands the advanced applications of both sectors and the two components, MOFs and biomolecules, in hybrid materials, are complimentary and necessary. "Numerous biomolecules, ranging in size from nucleic acids to enzymes, have been effectively embedded in MOFs by various methods such as pore encapsulation, surface attachment, covalent coupling, and in-situ encapsulation" [51-52].

Mesoporous (>2 nm) pore size tuning is possible for MOFs, which may range from ultra-microporous. That is why MOFs can hold various biomolecules in their pores. Pore encapsulation is the most common and easy way to combine biomolecules with MOFs so far [53, 55]. Achieving extensive loading of biomolecules is made easier with this effective postmodification method. "This post-synthetic modification technique may include biomolecules under moderate circumstances and mainly prevent the effect on biomolecules' structures and activities, which is particularly advantageous since the synthesis of MOFs is often conducted under severe conditions (e.g., high temperature, organic solvents)." In addition, the pores of MOFs provide a shield that may stop biomolecules from clumping together and even further reduce the impact of denaturation factors. The methods used to produce MOFs have made great strides in recent years. Many mesoporous MOFs have recently come to light, expanding the horizons for immobilising giant molecules beyond the microporous MOFs. Hierarchical pores are an intriguing property of certain MOFs that allows them to selectively trap substrates, enzymes, or cofactors into distinct pores, which opens up exciting possibilities for their advanced uses [56]. For this pore encapsulation technique, MOFs must have suitable window widths and excellent water stability. Many studies have focused on three-dimensional (3D) MOFs with polyhedral cages to entrap biomolecules. Compared to the cages' diameters, the narrow windows of these structures make it easier to capture guest molecules and provide the restricted regions necessary for specific applications, making them a desirable choice in particular cases [57]. The incorporation of biomolecules with MOFs by pore encapsulation has been shown in several research to be an efficient and adaptable method. Enzymes and other biomolecules undergo conformational changes when they enter MOF pores, allowing them to function differently from their native or denatured forms [58]. Using hierarchical cavities of 3.9 and 4.7 nm in diameter, we immobilized micro peroxidase-11 (MP-11) into mesoporous Tb-mesoMOF for the first time in 2011. [53]. Unlike enzymes encased in mesoporous silica, those contained in other materials may keep working and, in some cases, even outperform them. While the mechanism was being encapsulated, we continued to reveal it. With more window diameters of 1.3 nm and 1.7 nm, Tb-mesoMOF was able to entrap cytochrome c (Cyt c), a protein with molecular dimensions of 2.6 nm 3.2 nm 3.3 nm. We thought that the protein's pliability was responsible for this occurrence. The translocation of cytochrome c molecules into the interior of the MOF via the relatively narrow pore window may cause a substantial change in their shape. Fluorescent research confirmed this hypothesis [59]. Thanks to this study, researchers uncovered the intricate mechanism of biomolecule translocation, which provided a theoretical framework. In addition, building on prior research, we used confocal Raman spectroscopy to examine MP-11's interaction with Tb-mesoMOF and explained the enzyme's ability to remain within MOFs [58-59].

The physical adsorption of biomolecules onto MOFs has proven a success; however, under certain circumstances, the biomolecules may slowly leak out of the matrix due to the weak connections between

them. Covalent bonding may immobilise biomolecules to prevent leaching [60-68]. "In biomolecules, nucleophiles like amino, carboxylic, phenolic, thiol, imidazole, indole, and hydroxyl groups can make covalent bonds with the organic linkers in MOFs. A broad array of functional groups, such as free carboxyl, amino, and hydroxyl groups, may link with reactive groups of biomolecules on the surface of MOF crystals." Three methods of covalently linking biomolecules to MOFs have been used so far: 1) to create a self-assembled monolayer (SAM) on MOF surfaces, linker molecules like glutaraldehyde may cross-link biomolecules. 2) Covalent bonds may be formed between biomolecules and the active groups of MOFs. 3) biomolecules can become MOFs by being pre-covalently linked to organic ligands. Then, these MOFs may self-assemble.

It is well-known that enzymes are natural catalysts that are both very effective and selective. Nevertheless, enzymes' sensitivity to organic solvents, poor heat stability, and restricted pH tolerance ranges limited their usefulness in real-world applications. Because of their unique chemical and structural characteristics, MOFs are ideal host matrixes for enzyme immobilization [69]. The many benefits of enzyme-MOF composites as a novel platform for heterogeneous biocatalysis have led to their use. These advantages include improved catalytic selectivities, ease of product separation, and excellent stability and reusability. The enzymes-MOF composites used for catalysis often include heme proteins (such as myoglobin, horseradish peroxidase, cytochrome c, and micro peroxidase) with porphyrin prosthetic groups. This is likely because these proteins have high activities, appropriate dimensions, and a dark colour that makes them easy to track. The first enzyme encapsulation in MOF cavities was reported in 2011 by us (MP-11@Tb-mesoMOF). "Using H2O2 as a catalyst, the MP-11@TbmesoMOF facilitated the oxidation of 3,5-di-tert-butylcatechol." The immobilization process improved the enzymatic catalysis performances over the mesoporous silica version. Additionally, myoglobin (Mb) was effectively immobilized inside the Tb-mesoMOF. Compared to free Mb, the Mb@MOF composite showed superior catalytic activity towards tiny substrate oxidation and intriguing size-selective biocatalysis [70]. “Enzymes (such as horseradish peroxidase, cytochrome c, and MP-11) were encapsulated by a series of mesoporous MOFs (e.g. PCN-333(Al)) created by the Zhou group using the same methodology.” With the help of enzymes bound to PCN-333(Al), 2- 20 -azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) or o-Phenylenediamine were oxidized in H2O2. Mesoporous MOFs provide size selectivity that is otherwise difficult to achieve and improve enzyme stability. Regarding size-selective catalysis in enzyme-MOF composites, the porosity must be well organized or homogeneous, and MOFs' strong crystallinity makes this possible. Catalysts' enhanced selectivity is essential for practical uses in industry. Microporous ZIFs, such as ZIF-8 and ZIF-90, are another popular option for in-situ enzyme immobilization alongside mesoporous MOFs. Another option for in-situ synthesis is to encapsulate guest molecules within MOFs, which will serve as a protective shell, as their size exceeds that of the MOFs' pores. Lyu et al. used a one-pot co-precipitation technique to incorporate Cyt c into ZIF-8. Compared to free Cyt c, the peroxidase activity of the resultant composite was ten times higher. It was a quick, easy, and compassionate way to detect organic peroxides at low concentrations [71]. In addition, the Falcaro group showed that ZIF-8 might be immobilized with various biomolecules using the de novo synthesis process. Ribonuclease A, urease, lipase, haemoglobin, lysozyme, HRP, trypsin, oligonucleotide, and human serum albumin were the many biomolecules used by the writers. Despite extreme environments, enzymes@ZIF-8 maintained their enzymatic activity, as shown in the data. 14). Later, the Ge group used this in-situ synthesis approach to encapsulate horseradish peroxidase (HRP) within ZIF-8. The catalytic activity of the produced HRP-MOF composite, which had an average size of around 30 nm, was higher than that of the original

enzyme [72]. For the first time, in-situ synthesis was used by Shieh et al. to insert catalase into ZIF-90. Despite the presence of protease proteinase K, the produced composites exhibited vigorous activity towards hydrogen peroxide degradation [73].

III. MOFs as hosts and reaction channels

As a novel kind of heterogeneous catalyst, MOFs may mimic the process of enzyme encapsulation in proteins by acting as carriers and enclosing various active species, such as metal nanoparticles, metalorganic catalysts, metal clusters, and nonmetallic catalysts. The pores of the encased MOF catalyst may filter the reaction substrate, preventing reactants with sizes more significant than the MOFs' windows from entering the inner tunnels, thanks to the size-specific windows and channels found in MOF cages [74]. Additionally, MOF tunnels provide a unique limited space environment that controls product structure.

A. MOFs as hosts for metal nanoparticles

By providing a surfactant-free active site for metal nanoparticles to nucleate and multiply in the constrained pores, metalorganic frameworks (MOFs) restrict particle aggregation. As a carrier for attaching metal nanoparticles, MOFs are attractive due to their uniform structure, extensive range of morphologies, and internally changeable surface porosity [75]. It is possible to impregnate, initial wet, grind in solid phase, and reduce core-shell continuous deposition to include tiny metal particles into MOFs for use in catalytic processes [76]. The reaction's activity and the selectivity of the reaction products are significantly impacted by the confined space environment supplied by the pores of MOFs.

In order to encapsulate palladium precursors utilizing ligand design prior to MOF assembly, Chen et al. employed the first successful preincorporation approach. This prevented palladium particles from clumping together and made it easy for precursors to be anchored in the pores of MOFs [77]. Both the aerobic oxidation of alcohols and the reduction of nitrobenzene were catalyzed by the as-prepared Pd-in-MOF composites, showing excellent and enhanced activity. "Another simple in situ inclusion method was used to encapsulate ultrafine Pd, Ni, and PdNi alloy inside the MOF matrices." The insertion of metal precursors into the pores of MOFs was made more accessible and more convenient by this single procedure [78]. Also, the hydrogenation activity and reuse stability of PdNi-in-UiO-67 were determined to be better than those of PdNi-out-UiO-67, which showed that the MOF pores provided a confinement effect by loading metal particles outside the pores. A homogeneous core-shell structure was synthesized by encasing the Pt nano cores in MOF-177 [79]. Using powder XRD, we confirmed that the crystal structure was preserved during nanoparticle encapsulation, and we determined that the pore size of the shell of this MOF was 2.3-2.5 nm. "The Ptencapsulated MOF catalyzed the oxidation of alcohols at room temperature, without the need for an alkali." The conversion frequency of benzoyl alcohol was 968 h-1, and its catalytic yield was 50%. Since the Pt@MOF-177 catalyst became inactive after the first run due to the partial collapse of the MOF skeleton under the reaction conditions, using more stable MOFs as nanoparticle hosts is crucial. Li et al. initiated the Suzuki-Miyaura cross-coupling reaction by infusing Cr-MIL-101 with Pd nanoparticles, resulting in a 1% Pd loading [80]. The TEM analysis demonstrated that the Pd nanoparticles in Cr-MIL101 were uniformly distributed. The average diameter of the pores in the MOF is 1.9 nm, and their diameters vary from 2.9 nm to 3.4 nm. Using 4-trichloroanisole and phenylboronic acid as reactants and NaOMe as a base, a 96% yield of 4-methoxyphenyl was produced in aqueous conditions at 80 C. As catalysts, Pd2+/Cr-MIL-101, Pd/C, and Pd/ZIF-8 were all tested under the same circumstances. "With yields of 3%, 35%, and 16%, respectively, they were lower than the MOF catalyst-encapsulated Pd nanoparticles."

B. MOFs as hosts for metal oxide

Catalytic devices for the oxidation of carbon monoxide were developed by Li et al. [81] by accommodating metal oxides in MOF channels. The Co3O4 nanoparticles were made from cobalt nitrate and evenly distributed throughout the ZIF-8 holes since this kind of MOF is very stable and has big pores (11.6 A). At 70 degrees Celsius, the metal oxide Co3O4 showed a high reaction rate of 58.2 mmol g-1 h-1 and highly catalytic activity towards the oxidation of CO. "To remove formaldehyde from the air, Kim et al. created an effective adsorption catalysis system using a manganese dioxide/metalorganic framework (MnO2@UiO-66-NH2)." Because MnO2 covers a proportional surface area, the catalytic activity drops as loading levels rise. The catalytic effects of the combination of manganese dioxide and MOF were highly synergistic [82]. The Au-SH-SiO2@Cu-MOF electrocatalyst was created by Bagheri et al. [83] using Au-SH-SiO2 nanoparticles immobilized on Cu-MOF. "This catalyst demonstrated electrocatalytic activity in the hydrazine oxidation, a wide linear range (0.04-500 mM), and high sensitivity (0.1 mA mM-1). What is more, it was remarkably stable and reproducible."

C. MOFs as hosts for polyoxometalates

Polyoxometalates (POMs) have Brønsted acid properties and are made up of metal-oxygen octahedra. The steric environment may impact the reaction in composites made by enclosing POMs in the pores of materials like zeolites, which can then be used for catalysis. Many studies have focused on POMs because of their desirable properties, such as their thermodynamic stability and redox tunability. Perovskite encapsulation of cobalt-based heteropolyanions [PW11CoO39]5 and titanium [PW11TiO40]5 in MIL-101 pores was accomplished with success [84]. Three alkenes—a-pinene, caryophyllene, and cyclohexene—were oxidized using catalysts supported by MIL and POMs. This catalytic system achieved respectable selectivity and catalytic activity using oxidants such as oxygen and hydrogen peroxide. In addition, under moderate reaction conditions, these heterogeneous catalysts may be regenerated without sacrificing activity or selectivity. Gascon et al. used phosphotungstic acid (PTA) to create MIL-101. They then sandwiched distributed polyoxometalates (POMs) inside the MOF skeleton evenly. Since the POMs were more significant than the pentagonal windows of MIL-101, there was no POM leaching [85]. "The Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate, which they conducted using these composite catalysts, achieved high TOF values of up to 600 h1." There was no discernible decline in activity after recycling the catalysts up to eight times. Cobalt polyoxometalates (POMs) encapsulated in MOFs using Keggin-type [Co(BBPTZ)3]BBPTZ, which was a catalyst in the oxidative desulfurization process [86], was present in the compound [HPMo12O40]$24H2O. The synergistic interaction of POM moieties with the confinement offered by MOF resulted in size-selective properties and efficient catalytic activity in the system. Centrifugal separation also allows for the catalyst's reuse.

IV. MOFS AS HETEROGENEOUS CATALYSTS

A. Catalysis by metal nodes

Many metalorganic frameworks (MOFs) have metal active sites created by metal nodes after sufficient heat activation. Biological recognition and catalytic processes are enhanced by the coordinatively unsaturated metal centres that these metal nodes reveal (Fig. 4; [87-89]). The rigidity of MOFs allowed Yaghi and colleagues to show that open metal sites may exist stably [90]. The catalytic effectiveness of organic reactions and polymer polymerizations is greatly enhanced when the surrounding environment is well-understood and there are accessible active metal sites and pore channels. "Utilizing chromium(III)

carboxylate with enormous pores known as MIL-101, which was subjected to vacuum heating at 423 K to reveal trimeric chromium sites, F'erey et al. conducted the sulfoxidation of aryl sulphides. Both the catalytic activity and the selectivity towards the respective sulfoxides were very evident in the final product [91]." Additionally, oxidative competition reactions promoted by chromium(III) showed that groups releasing electrons could increase reactivity. "We have also used Cr-MIL-100/101 as heterogeneous single-site catalysts in our previous work to regulate the polymerization of isoprene under moderate conditions [92]." The addition of [PhNHMe2][B(C6F5)4] produced PhNMe2, which is associated with chromium sites, and therefore created a variety of constrained environments in nanochannels. The final result of isoprene polymerization in these limited spaces is polyisoprene with different topologies. The possibility exists that nickel-based MOFs may serve as very efficient catalysts. With the help of steric hindrance and electronic manipulation, the nickel-based MOFs improved the branching oligomer, and the catalytic system showed remarkable activity. Long et al. used two kinds of MOFs with coordinatively unsaturated Ni2+ sites to oligomerize propene: Ni2(dobdc) and Ni2(dobpdc) have the same chemical formula: 2,5-dioxodo-1,4-benzenedicarboxylate and 4,40 -dioxodo-[1,10 -biphenyl]-3-30 dicarboxylate, respectively. Both MOF types exhibited comparatively greater selectivity for linear oligomerization when subjected to identical circumstances.55 The findings demonstrated the potential of these MOFs as catalysts in the olefin-linear polymer reaction.

B. Lattice defects as active sites

One common approach to designing metalorganic frameworks (MOFs) for catalysis is to include ligands with a wide range of chemical functions or low-coordinate metal sites. Researchers have shown interest in coordination-saturated and other MOFs without these adjustable linkers because of their potential as catalysts [93]. This may be explained by the fact that various imidazolate structures might cause surface or structural flaws. To facilitate transesterification, Chizallet and colleagues used ZIF-8 as a catalyst. Based on results from FTIR and DFT calculations, they determined that the active species were responsible for the acid-basic sites on the surface or in defects. "It was determined that active sites included acid site ZnII species and surface-located basic N- and OH- moieties. In order to create a high-catalytic-ability defect site generator, Vermoortele et al created zirconium terephthalate UiO-66(Zr) and replaced partial terephthalates of this metalorganic framework (MOF) with trifluoroacetic acid (TFA) (Fig. 2)." In this case, TFA played the role of a modulator, inducing MOF crystallization and easing the synthesis of additional Lewis acid sites. Furthermore, suitable modulators such as TFA do not alter the MOF crystal size in this synthetic system. This coordinatively unsaturated UiO-66 exhibited a high conversion efficiency when utilized as a catalyst for the citronellal conversion.

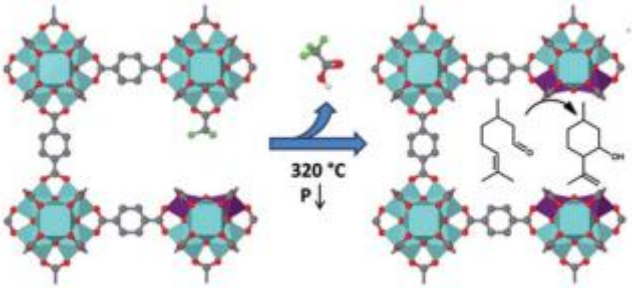

Fig. 2 A model for producing MOF lattice flaws using a modulation technique. It was modified using pe.

V. CONCLUSION

Finally, our research has shown that a whole strategy for functionalizing the porous architectures of Metalorganic Frameworks (MOFs) strategically improves their catalytic activity. We sought to optimize catalytic activity for various heterogeneous catalysis applications by adding certain functional groups into the MOF framework. In order to customize MOFs for better performance, researchers have looked at several functionalization procedures, such as adding functionalized ligands during synthesis or modifying them after synthesis.

The chemical, structural, and textural features of the synthesised functionalized MOFs were studied in depth using a battery of analytical methods. The improved activity of these customized MOFs in specific reactions was shown in catalytic testing, which further validated the effectiveness of the developed strategy.

This study's success highlights the significance of a thorough and adaptable strategy for developing materials for particular catalytic uses while also adding to the progress of MOF-based catalysts. This work presents customized MOFs that show promise for green chemistry problems, such as efficient and environmentally friendly catalytic processes. These results highlight the significance of MOFs as flexible and adjustable platforms in the quest for more sustainable chemical transformations, and they offer new opportunities for future investigation and use in various catalytic situations as functionalized MOF research advances.

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