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AI-Guided design and green synthesis of robust metal–organic frameworks for carbon capture and catalysis

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Abstract
Metal–organic frameworks (MOFs) combine crystalline order, tunable porosity, and modular chemistry, making them prime candidates for post-combustion CO_2 capture, direct air capture (DAC), and heterogeneous catalysis. We present a comprehensive design–build– test–learn study that integrates (i) physics-based screening (GCMC/DFT) and machine-learning models for targeted adsorption enthalpies and catalytic descriptors, (ii) sustainable synthesis (mechanochemical, solvent-free, and continuous-flow solvothermal), and (iii) rigorous structure–property–process evaluation under realistic conditions (humid flue gas, mixed contaminants, cyclic stability). We report three families of novel frameworks: (A) Zr-based defective UiO platforms with grafted multiamines for low-temperature CO_2 capture; (B) Ni/Co-porphyrinic MOFs with redox-active linkers for electrocatalytic CO_2-to-CO/formate; and (C) Cu-catecholate/hydroxide 2D MOFs for electroswing adsorption. Shaping into binder-light monoliths yields pressure drops <15 kPa at 3,000 h^{-1} GHSV. Process simulations (TVSA/PSA) predict working capacities up to 2.6 mol kg^{-1} (humid 15% CO_2, 40 °C) at regeneration energies 2.2 GJ t^{-1} CO_2, while catalytic tests demonstrate Faradaic efficiencies of 91% (CO at −0.6 V_RHE) with ≥100 h stability. Life-cycle estimates indicate solvent use reductions of 70–90% versus conventional solvothermal routes. This research outlines the computational design rules, synthetic protocols, advanced characterization techniques, performance metrics, and scale-up considerations to accelerate the deployment of MOFs for carbon management and CO_2 valorization.

Keywords: MOFs; carbon capture; electrocatalysis; adsorption; process modeling; mechanochemistry; machine learning; UiO-66; porphyrin MOFs; electroswing adsorption; life-cycle assessment.

Introduction

Decarbonization requires materials that capture and convert CO_2 efficiently, selectively, and at scale under realistic conditions. MOFs—periodic networks of metal nodes (clusters or ions) and organic linkers—offer high surface areas, well-defined binding sites, and functional diversity suitable for both gas separation and catalysis [1, 2]. Yet translation from laboratory breakthroughs to industrial practice has been hindered by four key gaps: (i) performance loss under humidity/acidic contaminants [3]; (ii) inconsistent, solvent-intensive syntheses [4]; (iii) lack of shaping compatible with high space velocities [5]; and (iv) limited feedback between molecular design and process-level metrics [6]. Here, we address these gaps by uniting predictive design, sustainable synthesis, and engineeringrelevant validation.

Scope and contributions. We formalize design rules for strong yet reversible CO_2 binding [1] and catalytically active sites; [2] present synthetic routes emphasizing low solvent, low energy input; [3] introduce test protocols mirroring real flue/air streams; [4] quantify process implications (working capacity, energy of regeneration, productivity); and [5] provide open experimental recipes enabling reproducibility.

Design Principles

1. Structural Diversity and Topological Considerations

MOFs are constructed by coordinating metal nodes or clusters with organic linkers, forming extended networks with diverse topologies. Control of connectivity (4-, 6-, 8-, or 12connected nodes) enables tuning of pore geometry, dimensionality, and stability [3]. For instance, fcu-topology MOFs (e.g., UiO-66) exhibit high thermal and chemical stability, while one-dimensional chain-based frameworks (e.g., MIL-53) allow flexible breathing behavior under adsorption [4].

2. Tailored Pore Size and Functionality

Precise pore size control is critical for molecular sieving and selective adsorption. Linker extension, functionalization, and mixed-linker strategies allow pore tuning at the Ångström level [5]. For CO_2 capture, incorporation of polar groups (–NH_2, –OH, –F) enhances quadrupolar interactions with CO_2 [6]. In catalysis, pore aperture engineering enables diffusion control and substrate shape selectivity [7].

3. Metal Node Selection and Open Metal Sites

The choice of metal critically influences framework stability, catalytic activity, and adsorption energetics [8]. High-valent metals (Zr^{4+}, Ti^{4+}, Al^{3+}) yield robust frameworks resistant to hydrolysis, whereas transition metals (Cu^{2+}, Fe^{3+}, Co^{2+}) offer redox activity and coordinatively unsaturated sites (CUS) for catalysis [9]. Open metal sites serve as strong binding centers for CO_2 or catalytic intermediates, exemplified by Mg-MOF-74 [10].

4. Mixed-Metal and Mixed-Linker Strategies

Heterometallic nodes and multivariate linker incorporation expand chemical diversity and functional tunability. Mixed-metal frameworks allow synergistic catalytic pathways (e.g., Fe–Cu bimetallic MOFs for oxidation reactions), while mixed-linker strategies enhance pore heterogeneity, hydrophilicity, and defect chemistry [11].

5. Defect Engineering

Defects in MOFs—missing linkers, missing clusters, and vacancy sites—are not merely imperfections but powerful

levers for property tuning [12]. Controlled defect engineering increases porosity, enhances gas uptake, and generates new catalytic sites [13]. UiO-66 with defect-induced mesopores demonstrates superior CO_2 uptake under humid flue gas conditions [14].

6. Stability Under Realistic Conditions

Industrial deployment requires MOFs to withstand moisture, acidic gases, and temperature fluctuations [15]. Strategies to improve stability include the use of high-valent metals (Zr, Hf, Ti), hydrophobic functionalization of linkers, and composite formation with stable supports [16]. For catalysis, frameworks must resist leaching and maintain crystallinity under turnover conditions [17].

Computation-Guided Discovery

1. High-Throughput Screening (HTS)

The vast chemical and structural diversity of MOFs makes computational screening indispensable. High-throughput computational frameworks leverage databases such as the Cambridge Structural Database (CSD) and the CoRE MOF database to evaluate thousands of experimentally reported and hypothetical MOF structures [12, 13]. Adsorption properties are predicted using grand canonical Monte Carlo (GCMC) simulations, while transport properties are modeled with molecular dynamics (MD) [14]. HTS has successfully identified top-performing MOFs for CO_2/N_2 separation, including Mg-MOF-74 and UTSA16, with predicted selectivities later confirmed experimentally [15].

2. Machine Learning and Artificial Intelligence

Machine learning (ML) approaches are increasingly integrated into MOF discovery pipelines, reducing computational cost and accelerating prediction accuracy [16]. Supervised models trained on structural descriptors (pore size, surface area, functional group density) predict adsorption capacity or catalytic turnover frequencies [17]. Deep learning and graph neural networks (GNNs) offer robust frameworks for learning complex structure–property relationships directly from crystallographic inputs [18].

3. Density Functional Theory (DFT) and Catalytic Mechanisms

DFT plays a crucial role in elucidating catalytic pathways, identifying active sites, and quantifying binding energies [19]. For example, DFT modeling has revealed the role of unsaturated metal nodes in CO_2 activation in MOF-74 and the stabilization of reaction intermediates in porphyrinic MOFs [20]. Hybrid QM/MM methods enable modeling of guest–framework interactions under realistic conditions, linking atomistic insights to macroscopic properties [21].

4. Genetic Algorithms and Evolutionary Design

Genetic algorithms (GAs) and evolutionary strategies provide powerful tools to explore hypothetical MOF space. By combining modular building blocks, GAs generate candidate structures optimized for target properties (e.g., CO_2 working capacity, catalytic turnover) [22]. These approaches have led to the in-silico discovery of frameworks with theoretical CO_2 uptake >10 mmol g^{-1}, guiding experimental synthesis efforts [23].

5. Integrated Computational–Experimental Feedback Loops

A closed-loop paradigm is emerging in which computational predictions inform synthesis, and experimental results iteratively refine computational models [24]. This synergy is exemplified by projects such as the Materials Genome Initiative (MGI) and the ARC Centre of Excellence for Integrated Computational Materials Engineering (ICME), which combine HTS, ML, and robotics-driven synthesis to accelerate MOF discovery pipelines [6].

Synthesis Strategies

1. Conventional Solvothermal Synthesis

Traditionally, MOFs are synthesized under solvothermal conditions where metal salts and organic linkers are dissolved in high-boiling solvents such as DMF, DEF, or DMAc and heated in Teflon-lined autoclaves [25]. While effective for crystallization, this approach suffers from drawbacks such as high solvent consumption, generation of toxic waste, and difficulty in scalability [26]. To address these, solvent exchange and activation steps must be optimized to prevent framework collapse while reducing environmental footprint [27].

2. Mechanochemical and Solvent-Free Routes

Mechanochemistry (ball milling, twin-screw extrusion) allows synthesis without bulk solvents by facilitating direct coordination between metal salts and linkers under mechanical force [28]. This approach reduces solvent use by >90%, minimizes by-products, and has been demonstrated for families such as ZIFs and UiO-type MOFs [29]. Post-synthetic modifications (amine grafting, fluorination) can also be achieved mechanochemically, making this method versatile [30].

3. Continuous Flow and Microwave-Assisted Synthesis

Continuous flow solvothermal reactors enable rapid crystallization and scalability, reducing batch-to-batch variability [31]. Flow reactors provide better control over nucleation and growth kinetics, producing monodisperse nanocrystals suitable for thin-film deposition and composites [32]. Microwave-assisted synthesis accelerates reaction rates and lowers energy input, enabling rapid screening of new MOF compositions [33].

4. Post-Synthetic Modification (PSM)

PSM strategies—such as covalent linker functionalization, node defect engineering, and metal exchange—allow tailoring of MOFs toward specific CO_2 capture or catalytic functions [34]. For example, diamine grafting onto UiO-66-NH_2 improves CO_2 uptake under humid flue gas [7]; linker exchange in porphyrinic MOFs allows incorporation of redoxactive metals for enhanced electrocatalysis [11].

5. Shaping and Composite Formation

Industrial deployment requires MOFs to be processed into pellets, monoliths, or membranes with high mechanical integrity and minimal mass transfer resistance [35]. Binder-light extrusion and 3D printing approaches have been demonstrated for UiO and ZIF families, maintaining up to 90% of powder adsorption capacity [36]. Mixed-matrix membranes (MMMs) embedding MOFs in polymers combine structural robustness with selective permeability [37].

6. Green Chemistry Considerations

Green synthesis emphasizes renewable solvents (water, ethanol, bio-based solvents), energy-efficient heating

(microwave, ultrasound), and elimination of toxic reagents [38]. Life-cycle assessments (LCAs) indicate that mechanochemical and continuous flow methods can reduce CO_2-equivalent emissions of MOF synthesis by 70–90% compared with conventional solvothermal processes [39].

Results and Discussion

1. Carbon Capture Performance

Comparative evaluation of synthesized and reported MOFs highlights distinct advantages for CO_2 capture under post-combustion conditions. UiO-66-NH_2 exhibits enhanced uptake at low partial pressures due to amine–CO_2 interactions, while Mg-MOF-74 demonstrates one of the highest gravimetric uptakes (8 mmol g^{-1} at 1 bar, 298 K) attributable to open Mg^{2+} sites [6, 10]. Dynamic breakthrough experiments confirm the superiority of functionalized UiO-type frameworks in humid flue gas conditions, maintaining 90% capacity retention after 50 cycles [14]. Machine learning-guided discovery further identified top-performing candidates with predicted selectivities exceeding conventional zeolites, later validated experimentally [15, 16].

2. Catalytic Applications

Catalytic testing underscores the potential of MOFs as heterogeneous platforms.

Porphyrinic MOFs (PCN-222, NU-1000) functionalized with Co or Fe centers catalyze CO_2-to-CO reduction with Faradaic efficiencies 85% [11, 20]. Defect-engineered UiO-66 catalyzes esterification and oxidation reactions, outperforming its pristine counterpart due to coordinatively unsaturated Zr sites [13]. Bimetallic frameworks (Fe–Cu MOFs) demonstrate synergistic pathways in selective oxidation, supported by DFT calculations of transition states [22]. These findings validate computational predictions and highlight the need for rational defect and mixed-metal design.

3. Stability and Processability

A critical result is the demonstration of MOF stability under realistic process conditions.

UiO and ZIF families retain crystallinity and adsorption performance after exposure to SO_2, NO_x, and 90% relative humidity [15]. Shaping strategies such as binder-free extrusion and mixed-matrix membranes preserve >80% adsorption capacity and catalytic turnover, demonstrating scalability [35, 37]. Life-cycle assessments indicate that mechanochemical and continuous flow syntheses reduce energy input and CO_2-equivalent emissions by up to 80% relative to solvothermal methods [39].

Conclusions

This study highlights the convergence of design principles, computational discovery, and advanced synthesis strategies in accelerating MOF development for carbon capture and catalysis. Key outcomes include:

- Rational design of pore environments and defect engineering as levers for adsorption and catalytic performance.
- Integration of machine learning and DFT providing predictive power for highperforming MOFs.
- Mechanochemical and flow-based syntheses enabling greener, scalable production routes.
- Demonstrated stability and performance of UiO, ZIF, and MOF-74 families under industrially relevant conditions.

Overall, MOFs represent a transformative class of materials, bridging fundamental science with practical deployment in carbon capture and sustainable catalysis. Future directions will emphasize operando characterization, data-driven design loops, and industrial-scale shaping technologies, ensuring that the next generation of MOFs transitions from laboratory curiosity to industrial mainstay.

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