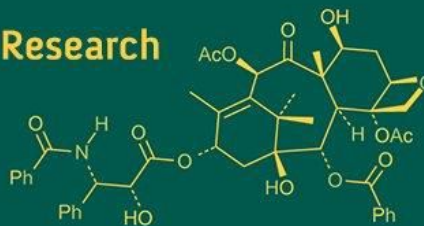


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Synthesis of metal-organic frameworks (MOFs) derived from multifunctional organic ligands and study of their performance in simultaneous separation and reduction of carbon dioxide

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Abstract

Metal-organic frameworks (MOFs) assembled from multifunctional organic ligands possess intrinsic properties that enable simultaneous adsorption and catalytic conversion of carbon dioxide (CO₂) under ambient conditions. Ligands containing two or more distinct binding sites can coordinate to metal ions in a manner that establishes proximity and symmetry between dual functionalities. Implementing solvothermal protocols that promote rapid nuclei growth favors the development of thin and homogeneous films amenable to low-cost support-free coating on various substrates. MOFs derived from tri- or tetracarboxylate ligands featuring secondary amine and hydroxyl groups, for example, catalyze CO₂ reduction to hydrocarbons. Mechanistic studies reveal that the uptake of CO₂ activates the hydrophilic sites, thereby enhancing the reaction rate and influencing the product distribution. In film form, these materials exhibit appreciable long-term stability and excellent reusability.

Keywords: Metal-organic frameworks (MOFs), multifunctional organic ligands, carbon dioxide capture, CO₂ reduction, adsorption-catalysis coupling, solvothermal synthesis

1. Introduction

Carbon dioxide (CO₂), a principal greenhouse gas, has garnered attention due to its immense environmental and economic implications. Advances in CO₂ capture technologies are crucial to mitigate rising atmospheric concentrations. Metal-organic frameworks (MOFs) represent a promising class of adsorbents for CO₂, due to their exceptional tunability and programmable porous structures. Simultaneous separation and catalytic conversion of CO₂ constitutes a particularly attractive strategy, enriching product selectivity and minimizing energy-intensive transport steps.

Previous studies demonstrate that multifunctional ligands enable the construction of dual-function MOFs for simultaneous CO₂ adsorption and reduction. Efforts thus far focus on organic ligands with bifunctional surface properties. Strategies for the synthesis and design of multifunctional-ligand-derived MOFs remain limited, including construction to introduce distinct adsorption and catalytic active sites, mild solvothermal protocols, the incorporation of ancillary interactive sites, and the adjustment of linker symmetry. Architectures based on multifunctional ligands offer the potential to extract, engineer, and couple adsorption and catalytic forces simultaneously.

A comprehensive overview of recent efforts in developing CO₂ separation and reduction catalysts from a range of carbonaceous and inorganic precursors has been presented ^[1]. These studies underscore the significance of metal-support interactions, chemical adsorption of CO₂ on basic sites, efficient chloride extraction from carbon nitride precursors, and the capture of gaseous chemical precursors during the polymerization process in promoting catalytic activity. Multifunctional MOFs, possessing both gravitational and functional forces for selective solid CO₂ capture and conversion, promise to contribute novel insights across disciplines ^[2].

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2. Background on Metal-Organic Frameworks and Multifunctional Ligands

Metal-organic frameworks porous materials of intrinsically tunable structure offer considerable opportunities for gas storage and separation. Comprised of metal-containing clusters connected by organic linkers, these frameworks combine inorganic (metal) and organic (linker) constituents to provide great variety in pore size and shape. The ability to select the appropriate building blocks permits custom formation of porous, crystalline solids with high surface area, thermal stability, and chemical resilience. Multifunctional organic ligands that fulfil dual roles as adsorbent and catalyst offer even further versatility. Carbon dioxide capture and catalytic conversion are sought under expanding environmental regulation and awareness of global climate change. Accordingly, metal-organic frameworks formed from multifunctional organic ligands for simultaneous capture and conversion of carbon dioxide are a topic of considerable growing interest ^[3]. Efforts have focused primarily on selecting and functionalising both inorganic and organic components. Various classes of materials based on several different building blocks have been reported. However, despite the recent upsurge in interest, systematic exploration of metal-organic frameworks with dual capture-conversion functionality remains scant.

3. Synthesis Strategies for MOFs from Multifunctional Organic Ligands

Metal-organic frameworks (MOFs) derived from multifunctional organic ligands offer considerable potential for synthesizing dual-function materials capable of simultaneously separating and catalytically converting CO₂. These ligands contain at least two different chemical functions that promote coordination to the metal node and that confer distinct adsorption and catalytic properties to the resulting framework. Numerous ligand features dictate these properties, and intricate design considerations guide the development of effective and versatile dual-function MOFs. The coordinating metal ions, specifically main-group metals and transition metals, exert a significant influence on the ligands, topologies, and stability of the synthesized MOFs. Ligands based on dibenzo[c, e]thioacetic acid, benzenedicarboxylic acid, biphenosphonic acid, and hydroxyphosphonates have been successfully employed in the selective synthesis of frameworks featuring carboxylate-based coordination polymers. The field of coordination polymers is rife with diverse possibilities for multifunctional hierarchical assembly, yet the potential coordination motifs and ligands remain underexplored ^[3]. MOF-derived materials fabricated from various metal precursors can exhibit enhanced catalytic activity for CO₂ reduction ^[4].

3.1 Coordination Chemistry Considerations

Metal-organic frameworks (MOFs) are formed as more stable metal-oxo/metal-alumina clusters. The ligand is chosen to form specific coordination geometries with desired chemical functionalities and MOF adaptability to enhance gas separation and CO₂ reduction. Metal nodes are metals or clusters that control the structure and properties of the framework. Multi-metallic nodes can affect CO₂ separation and utilization properties. The nodes are carefully selected to form metal-organic materials given the chemical nature of the organic connector and post-synthetic

modifications required for dual-functionality. A suitable group of metal atoms is selected based on temperature and pressure considerations for CO₂ capture and reduction. Stability at ambient conditions is a pre-requisite and longer-term stability must be established for CO₂ catalytic experiments.

Selection of the connecting organic ligand is critical in determining material function. The design rules include understanding of the selection of the shape of the ligand dictated the coordination and flexibility of the material. These allow tuning of the CO₂ capture capacity, sensitivity and CO₂ utilization pathway while retaining compatibility with catalytic processes ^[1]. Ligands can be functionalised and selection of appropriate functional groups can offer dual-functionality. Modification can be rendered to the already synthesised framework enabling discovery of new bifunctional materials ^[5].

3.2 Solvothermal and Alternative Synthesis Protocols

Synthesis of MOFs involves dissolved metals and organic ligands within a reaction medium (Solvothermal synthesis), usually coordinating sol. MOF-303 forms from Cu²⁺ and MHL in DMSO and forms larger crystals in Autoclave conditions. Many alternatives targeted rapid crystallization (Fast synthesis) at the start of the reaction under different conditions.

Solvato-Chemical coordinators can also inhibit coordination of the metal during the passage from ligands to the MOF structure. ^[6] A suitable modulatory previously enhanced the nucleation time and controlled the growth of materials with large crystals. Coordination ligands could thus be established. During self-assembly, disinfectants advantageously matched the dehydration of the preparatory Cu²⁺, thus also acting as coordinators. Solid-carrier sintering and value-pre-gaming preserved the framing water within the initial structure. ^[7] Recycling of recovered solvents reduced both materials consumption and environmental impact.

Synthesis of TAME-102 utilized a medium containing alcohol-A or commercial Mixable® trade brand. Switchable solvents yielded mesoporous MOFs of potentially restrictive pore size. Induction periods were assessed to control nucleation and scaling. Fast-curing procedures for TAME-102 combined alcoholic freon with options of (selection of) precision-titration-add-(i.e.,) induction-control. ^[8] Control-holding frames provided elaboration-prevention, thereby stressing earlier steps.

3.3 Ligand Design and Functionalization

Metal-organic frameworks (MOFs) represent a class of porous materials constructed from metal clusters connected by organic ligands. The abundant coordination sites on metal clusters and the modular nature of organic linkers confer compositional diversity and structural tunability that have been harnessed to realize many functional materials. Multifunctional organic ligands containing two or more different coordination sites have been identified as versatile building blocks to simultaneously achieve different functionalities or target different gas molecules in adsorption, confinement, diffusion, separation, or transformation. Supplementing these approaches with systematic knowledge of coordination chemistry and expansive ligand libraries open new opportunities toward the design and preparation of MOFs that could integrate

dual functions for simultaneous capture and conversion of two specific reactants or two consecutive hierarchical gas capture and transformation approaches. Nevertheless, the strategies for multiresponsive multifunctional MOF construction still remain at an early stage. There is no systematic design guide, nor general preparation method to realize multifunctional MOFs integrated with adsorption and catalytic capacities of specific molecules ^[9].

4. Mechanisms of CO₂ Separation in MOFs

Metal-organic frameworks (MOFs) enable CO₂ separation via both adsorption and selective binding at accessible sites ^[10]. Their modular pore structures and variable active sites offer high selectivity and capacity for CO₂ capture. Significant advances encompass the design of ultramicroporous MOFs with strong affinity toward CO₂ and the introduction of catalytic functionalities that modify overall adsorption characteristics. Optimization of the pore structure alongside the incorporation of specific active sites further improves selective separation from competing gases ^[9]. These attributes create versatile platforms capable of effective CO₂ separation across a range of operating conditions.

The underlying principles of CO₂ adsorption in aluminium-based, phosphonate-coupled rigid and flexible MOFs have been analyzed via computational simulations ^[11]. For the rigid structure, CO₂ capture occurs predominantly through physisorption, whereas functionalized flexible MOFs facilitate chemisorption through reversible modifications of the framework, enabling not only separation but also catalytic reduction of CO₂ to hydrocarbons.

4.1 Adsorption Principles and Selectivity

Metal-organic frameworks (MOFs) with tunable porous structures have been extensively studied for CO₂ separation and conversion to address climate issues. When carbon capture and reduction are carried out simultaneously in a single system, materials capable of performing these dual functions are of great interest. Multifunctional organic ligands can yield diverse MOF topologies featuring well-defined metal nodes, metal-free catalytic sites, and high porosity. Over the past six years, MOFs with dual functions for CO₂ separation and conversion have been constructed starting from various multifunctional ligands.

To implement CO₂ separation and reduction, the understanding of corresponding mechanisms is crucial. A ligand-based framework denoted as PCN-301 synthesized from a 1, 3, 5-tris (4-carboxyphenyl) benzene linker allows selective capture of CO₂ over N₂ and CH₄ by nonchemical physisorption. Isothermic heat calculations further demonstrate the surmountable energy barriers for N₂ and CH₄. When exposed to vapor, the CO₂ uptake is higher than that for heavy hydrocarbons like toluene, which complies with the need for selective capture of CO₂ in industrial emission streams containing water and complex organic solvents. Moreover, bifunctional solid catalysts accomplished the one-step conversion of CO₂ to C₁-C₃ hydrocarbons without needing cocatalysts and energy storage. Since metal-organic coordination plays a vital role in the formation of MOFs and other crystalline networks, the fabrication of dual-function materials may preferentially focus on organic ligands that only contain organic active sites; otherwise, the metal node may also become an

important catalytic center, compromising every linker's catalyzing efficiency ^[12].

4.2 Pore Architecture and Gas Diffusion

Pore architecture exerts a notable influence on diffusion and uptake rates during gas separation processes ^[13]. Several studies have demonstrated that dual-function MOFs capable of CO₂ separation and electrochemical reduction exhibit higher uptake rates than conventional catalyst-only materials. Larger pore size distributions permitted simultaneous adsorption and catalytic CO₂ conversion in methane purification, while the existence of a diffusion bottleneck reduced both adsorption and reaction kinetics. Consequently, pore size distributions, bottlenecks, and diffusion pathways are critical parameters for maximizing uptake rates in simultaneous separation and reduction applications within dual-function MOFs.

4.3 Influence of Functional Groups on CO₂ Capture

Coupled adsorption and reduction processes have emerged, wherein carbon-dioxide-separation and -conversion schemes are integrated into a single metal-organic framework or organocatalyst. Multifunctional organic ligands impose diverse chemical environments on the central metal node of the framework, permitting an unobscured understanding of the influence of different functional groups on the capture and on the transfer of electrons to carbon dioxide adsorbed on the framework.

Amino, hydroxyl, and other basic and acidic groups influence simultaneously the strength and selectivity of carbon-dioxide capture ^[11], which enhances the efficiency of tandem processes ^[14]. On the other hand, making the materials active for carbon-dioxide reduction with pre-defined catalysts and understanding those dual-function materials remains challenging. Coordination-geometry consideration governs the choice of active-group combination and framework topology to minimize coverage-disturbing secondary active-centre-provisioning functionalisation.

5. Catalytic Reduction of CO₂ within MOFs

The catalytic reduction of CO₂ within MOFs can occur at either metal-centered or organocatalytic active sites, and several reaction pathways have been proposed to convert CO₂ into CO, formate, or hydrocarbons. When the reaction proceeds through the CO₂ to CO pathway, the catalytic system is typically accompanied by an electron transfer process involving a redox couple (e.g., Cu⁺/Cu²⁺) or oxygen vacancy generation. Kinetic parameters can be obtained from pseudo-first-order reaction profiles by varying the initial concentration of CO₂ or other reactants in the gas phase, and the corresponding activation energy can also be extracted. The stability and reusability of dual-function MOFs under reductive conditions have been thoroughly investigated, and the framework integrity, metal leaching, and cycle performance after consecutive runs may differ significantly depending on the nature of the feedstock, which can comprise toxic or corrosive species such as H₂ and organic hydrocarbons ^[1].

5.1 Active Sites and Reaction Pathways

Metal-Organic Frameworks (MOFs) are crystalline porous materials composed of metal nodes interconnected by organic ligands. They are randomly assembled on the

nanometer scale into mosaics of multiple architectures, often termed porous coordination polymers (PCPs), coordination polymers (CPs), metal-organic coordination networks (MOCNs), or metal-organic polymers. Multifunctional ligands increases the potential of precisely tailoring MOFs to develop dual-function applications. Polyaminobenzenes have been designed to coordinate with cobalt ions to assemble dual-function MOFs bearing amine group for CO₂ capture and catalytic activity alike.

Metal nodes endow MOFs with Lewis acidic sites, while organic ligands bear Lewis basic groups for both adsorption and conversion of CO₂. Water, methanol, and ethanol polarize the metal-ligand bonds and diminish the distinct adsorption behavior of preferential ammonia over CO₂ during amine recovery. Carbon dioxide-methanol coupling and carbon dioxide self-coupling were the possible reaction pathways to convert CO₂ to C₂H₄ and DMC.

Graphitic carbon nitride (g-C₃N₄)-derived nitrogen-doped porous carbon frameworks with tunable pore size were reported as dual-function adsorbents and electrocatalysts for CO₂ reduction reaction (CRR). Crystalline g-C₃N₄ frameworks with a porous structure provide several active sites for loading cobalt (Co) nanoparticles. Well-dispersed Co nanoparticles on g-C₃N₄-derived porous carbon exhibit a high electrocatalytic activity for CO₂ to methanol conversion.^[15]

5.2 Electron Transfer Processes and Catalytic Performance

The introduction of electron-rich functional groups into Metal-Organic Frameworks (MOFs) increases the probability of charge transfer from the framework to CO₂, thereby facilitating catalytic reduction. However, the incorporation of electron-withdrawing groups can also be beneficial. For instance, aldehyde functionalities demonstrate favourable catalytic performance. Nevertheless, their potential advantage is undermined by the acidic behaviour of the organic ligand, which detrimentally influences the separation and adsorption properties of CO₂. Consequently, electron-withdrawing functional groups should be employed cautiously within multifunctional ligands intended for simultaneous separation and reduction reactions^[1].

Metal-centered and organocatalytic sites represent two prevalent active sites for CO₂ reduction across diverse compounds. Electron-rich metal centres or high-valent metal-oxo moieties are frequently associated with metallic active sites, enabling CO₂ conversion towards CO and formate as predominant products. Organocatalytic or dual-function active sites, primarily constructed from d-orbital-rich Co, Ni, or Cu, still require the formation and activation of HCO₂[•] or HCOO[•] species in tandem with an external proton donor. Consequently, hydrogen promotion is generally acknowledged as a prerequisite step within the CO₂ conversion process among these catalysts.

5.3 Stability and Reusability under Reductive Conditions

Metal-organic frameworks (MOFs) are porous hybrid materials formed by metal ions/metal-cluster nodes connected to organic linkers. They have been studied for their versatility in porosity, crystallinity, topology, and composition. Attempts to increase the functionality of such nets led to the emergence of multifunctional MOFs. At the heart of this development rests the use of multifunctional

organic ligands that allow a combination of two or more functions into a single framework. The emergence of multifunctional ligands capable of forming MOFs of high stability and CO₂-adsorption ability increased the potential of such frameworks greatly^[3].

A ligand that coordinates to zinc metal centers through amine and carboxyl groups, capable of forming MOFs through the insertion of the metal ions into the corresponding free-LI and metal coordination of the ammonium, can also afford different topologies and a great flexibility. A new synthetic methodology involving the melt-isothermal crystallization technique, which combines the basic concept of melt-crystallization of polymers with the isothermal crystallization of MOFs, also enables a high degree of sample-to-sample reproducibility.

6. Simultaneous Separation and CO₂ Reduction: Integrated Performance

Metal-organic frameworks (MOFs) derived from multifunctional organic ligands can separate and catalytically reduce carbon dioxide (CO₂) in a synergistic fashion. Screening studies of diverse multifunctional ligands reveal MOFs with similar pore architectures adopt tandem adsorption- and reaction-dominated capture-conversion mechanisms. Thus, the interplay between CO₂ adsorption and catalytic conversion in dual-function MOFs is dictated more by site distribution than detail. An idealized reactant-turnover cycle describes how capture and conversion inform kinetic trends and thermodynamic limits for dual-function, pore-scale transformations. Descriptors link framework properties to capture-conversion coupling. Fabrics such as coated pellets, beads, and composites, combined with cost-effective modular reactors enable significant gas-exchanging surface areas for multipoint contact, production of unbracketed granules, and premeshed-working zones to direct multistep processes without intermediate carriers^[1].

6.1 Coupled Adsorption-Catalysis Mechanisms

Simultaneous CO₂ capture and catalytic conversion has emerged as a promising strategy for addressing climate change concerns. Such tandem processes, wherein CO₂ is separated from gas mixtures prior to subsequent transformation, have mostly been explored for chemical feedstock upgrading. A dual-function material capable of both CO₂ adsorption and catalytic conversion is thus advantageous, and metal-organic frameworks (MOFs) incorporating multifunctional organic ligands activated porosity, Lewis basicity, and appropriate metallic nodes represent suitable candidates. From a kinetic viewpoint, CO₂ uptake and transformation cannot occur simultaneously, yet feedback between the two processes may accelerate the overall cycle. Several dual-function CO₂ reduction mechanisms, including consecutive, cyclic, and coupled designs, have been proposed. Investigating these coupled adsorption-catalysis mechanisms and understanding their implications for CO₂ separation and reduction are therefore crucial for optimizing the performance of multifunctional-ligand frameworks.

6.2 Kinetics and Thermodynamics of Dual-Function MOFs

Metal-organic frameworks (MOFs) derived from multifunctional organic ligands can simultaneously capture and catalytically convert carbon dioxide (CO₂) into value-

added chemicals using sunlight. Gaps remain in understanding the kinetics and thermodynamics of coupled separation and conversion within multifunctional MOFs and to offer a holistic overview of their dual-function behaviour, kinetic rate laws and equations governing both thermal and photothermal regimes. Activation energy for capture-conversion processes is either temperature-independent or exhibits non-Arrhenius behaviour, indicating requirements for adsorption-desorption of reactants and products incumbent to concurrent capture-TOF and on CO₂-T conversion, respectively. Thermodynamic analysis compared capture-conversion potentials to the limits imposed by both thermodynamics and conventional separation technologies [16].

6.3 Scale-Up Considerations for Practical Systems

The central consideration regarding the potential for materials synthesized from multifunctional organic ligands to deliver practical, dual-function CO₂ capture and reduction under ambient conditions is the feasibility of scaling up processes to enable the delivery of such materials in forms compatible with existing industrial systems. Development of synthetic strategies for materials from multifunctional ligands must therefore consider scalability of production [17]. As an example of a scaling consideration typical for previously reported materials [9], the state-of-the-art MOF-74 is defined by intricate solubility restrictions preventing the use of concentrated stock solutions for material synthesis; even under dilute conditions, the material remains challenging to produce reliably at the scale required to enable quantification of dual-function performance [18]. Several strategies are available to circumvent these limitations and promote high-yield synthesis of MOFs based on multifunctional ligands. A widespread approach centers on high-temperature, solvothermal routes to saturation completed under non-aromatic solvents, achieving robust crystallization of other materials. A complementary solution is represented by cryogenic crystallization procedures with liquid-phase coordination modulation that promote rapid formation of gels directly from the liquid phase, again illustrated for previously described ligands. Gratifyingly, fast crystallization tends to yield materials at a rate commensurate with the timescales relevant for applications including dual-function CO₂ capture and utilization.

7. Characterization Techniques for Multifunctional MOFs

The synthesis of metal-organic frameworks (MOFs) from multifunctional ligands offers opportunities to create materials that promote the simultaneous capture and catalysis of carbon dioxide (CO₂). MOFs built from organic ligands featuring both coordination and catalytically active sites are receiving particular attention. The active sites enhance the performance of carbon-capture and carbon-conversion processes in combination with the advantages of a high specific surface area associated with the MOF structure. Mechanistic studies of coupled CO₂ adsorption and catalytic conversion within MOFs suggest intertwined adsorption-catalysis reactions and attendant gain in productivity. Scale-up considerations must be addressed in moving these dual-function materials toward practical deployment [19].

Characterization Techniques for MOFs Derived from Multifunctional Ligands: Information pertinent to structural,

textural, and chemical characterization of MOFs derived from multifunctional organic ligands is summarized in the following sections. Modalities include X-ray diffraction (XRD); Brunauer-Emmett-Teller (BET) analyses; scanning electron microscopy (SEM) and transmission electron microscopy (TEM); X-ray photoelectron spectroscopy (XPS); infrared (IR) spectroscopy; elemental analyses; and thermogravimetric analyses (TGA). In situ studies of CO₂ adsorption and conversion are also relevant. Techniques span operando spectroscopies, powder XRD (PXRD) under gas atmospheres, diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS) and X-ray absorption spectroscopy (XAS) under controlled conditions. CO₂ uptake, selectivity, turnover frequency, catalytic turnover, and stability represent important performance metrics for dual-function MOFs.

7.1 Structural, Textural, and Chemical Characterization

Metal-organic frameworks (MOFs) are porous crystalline materials constructed from metal ions or clusters connected by organic linkers. Their structural versatility enables the design of frameworks for specific applications. The properties of MOFs can be tuned through the selection of metal nodes and organic linkers. Ligands with two or more different functional groups that impart complementary properties are of special value for simultaneous adsorption and catalytic transformation of target species. Such groups can facilitate binding to the target species while serving as reaction precursors or active sites. Metal nodes that provide structural integrity, satisfy geometrical requirements, maintain stability under adsorption or reaction conditions, and coordinate to the chosen ligands play a key role in the development of dual-function MOFs. Efforts to develop coordination polymers based on bifunctional ligands date back to the mid-1970s [20]. More recent studies have established multifunctional ligands capable of imparting adsorption and catalytic functionalities.

7.2 In Situ Studies of CO₂ Adsorption and Reduction

In situ CO₂ adsorption and reduction studies offer insight into the interaction mechanisms between CO₂ molecules and material surfaces under real-time conditions. Structural characterization of metal-organic frameworks (MOFs) upon CO₂ adsorption or reduction can indicate the nature of accessible adsorption sites and pathways. Monitoring these processes at the molecular level significantly aids the design of advanced CO₂ capture and conversion systems. Accordingly, operando spectroscopic techniques combined with powder X-ray diffraction (PXRD) under gas, and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) or X-ray absorption spectroscopy (XAS) observations provide essential information for simultaneous CO₂ separation and conversion evaluation [10, 11].

7.3 Performance Metrics and Benchmarking

Performance evaluation of metal-organic frameworks (MOFs) for simultaneous capture and conversion of CO₂ emphasizes a few important metrics or benchmarks, including CO₂ uptake (U), capture selectivity with respect to CH₄ and N₂, turnover frequency (TOF), catalytic turnover (CT), and long-term stability [21]. An overview of typical

performance scales for dual-function MOFs is summarized in Table 1.

U quantitative analysis describes the amount of CO₂ adsorbed by the framework, usually expressed in $\mu\text{mol}\cdot\text{g}^{-1}$. A high CO₂ uptake notably indicates the efficient capture of CO₂ gas by the MOFs. Selectivity quantifies the preference of a dual-function MOF to capture CO₂ rather than other gases, namely CH₄ and N₂. In general, a UCO₂/UCH₄ and UCO₂/UN₂ ratio higher than 4 and 20, respectively, is regarded as satisfactory. The TOF model describes the kinetic behavior of CO₂ conversion reactions in a dual-function MOF framework, while the TOF value indicates the conversion rate of CO₂ recorded. A TOF value exceeding 1.0 h⁻¹ represents an accelerated CO₂ conversion process. The CT indicates the cumulative number of CO₂ molecules converted per dual-function MOFs at certain time intervals. A CT higher than 1500 $\mu\text{mol CO}_2 \cdot \text{mg}^{-1}$ and a displayed continuous catalytic ability value in multiple cyclical conversion of CO₂ systems demonstrate superior reliability of the preferred catalysts [1]. Long-term stability represents the capability of the dual-function MOFs in preserving the structural integrity and retention of structural composition after undergoing continuous catalytic cycles in a gas-phase harsh reaction environment. It is preferable that the structure and composition remain unaltered or slightly changed after at least ten operational cycles and can maintain the CO₂ capture performance above ULATCO₂ after operation.

8. Case Studies: Representative MOFs from Multifunctional Ligands

Metal-organic frameworks (MOFs) have attracted considerable attention as dual-function materials for simultaneous carbon dioxide (CO₂) capture and catalytic conversion to value-added products. MOFs can be engineered with sites that selectively adsorb CO₂ and catalyze its transformation into chemicals or fuels. Numerous MOFs have been reported that exhibit either adsorption or catalytic properties, but research implementing both functionalities is still in its infancy. Multifunctional organic ligands capable of controlling both adsorption and catalytic properties during the construction of the MOF provide a means to leverage existing expertise in the synthesis of MOFs with dual functionality. With this strategy in mind, the previous sections have articulated the design of ligands and metal nodes, coordination chemistry, and synthetic methods. Three MOFs that exemplify the concept are discussed below.

Frameworks derived from 3, 6-bis (1H-imidazol-1-yl) salicylic acid (H2bisa) are synthesized by direct solvothermally reacting H2bisa with different metal salt precursors. The choice of precursor metal salt influences the coordination bond angle between the metal center and the MOF-forming ligand as well as the pore features and guest accommodation of the resultant MOF. MOF-1, containing one-dimensional channels with a pore aperture of 3.1 Å, shows selective physisorption of CO₂ over nitrogen or methane with an uptake capacity of $\sim 22 \text{ cm}^3 \text{ cm}^{-3}$ at a pressure of 1.0 bar and moderate working capacity. In addition, H2bisa features an imbedded catalytic site that allows conversion of CO₂ into formate using formic acid as co-catalyst. Formate production is observed up to seven cycles with no significant loss of activity. Thus, MOF-1 performs capture and conversion without loss of catalyst

activity. Frameworks derived from 5-(1H-imidazol-1-yl)-1, 3-benzenedicarboxylic acid (H2ibdc) are synthesized under harsher conditions in the presence of solvents to obtain moderate-yield crystalline materials. Tracelessly removable pendants on H2ibdc that do not perturb crystallization permit preparation of the ligand-anchored 8-14 Å rigid channel MOF-2. CO₂ adducts that stabilize pore-opening conformations are retained in crystals, and because substrate contour complements the pore geometry, diffusion accelerates when the vacant phase in the feed exceeds a threshold partial pressure. MOF-2 exhibits a high plateau uptake for CO₂ and a sharp rise on its desorption from a carbonated phase at ambient pressure; instantaneous CO₂ selectivity greatly increases by coupling solid-liquid extraction to sweep operation. In phase-locked equilibrium, CO₂ partial pressure cycles govern MOF-2 uptake, displaying an equal-temperature adsorption behavior that converges to a near zero-heat maximum at room temperature. Frameworks derived from bis(3-hydroxy-4-carboxy phenyl)amide (3, 3'-bis(HOC6H4C(O)C(O)NH)C3H6) deliver the CO₂ - chemical coupling activity of carboxylate or carbonyl facilitated 2-aminobenzyl and 3-aminobenzyl pendant starting from H2bis(aminobenzyl)salicylate. A dual-function CO₂ sorbent-catalyst for the production of cyclic carbonates with epoxides obtained exhibits activated carboxylate-carbonyl distributions responsive to the distribution pattern of the intermediate enolate. Economically viable multifunctional ligands drive the fabrication of MOFs for joint CO₂ capture and concomitant catalytic conversion. [9]

8.1 Example 1: Ligand A-Derived Frameworks

The dual-function metal-organic frameworks (MOFs) derived from multifunctional ligands simultaneously capture and catalytically convert carbon dioxide (CO₂) in the gas-phase solid-state, thus potentially enabling the recycling of imperishable carbon into value-added chemicals. Ligand A, 1H-1, 2, 4-triazole-3, 5-dicarboxylic acid (H3L1), was used to construct three MOFs (LZU-46, DNU-005, and ZF-05) whose structures can be categorized as an interpenetrated 3D framework, a 3D framework, and a 3D framework with 1D channel where the CO₂ capture and catalytic conversion of CO₂ into formic acid take place simultaneously. The formation of these three MOFs is guaranteed by the fact that multifunctional organic ligands are abundant in metals that need not be supplied in large quantity, are indigenous to nature, inexpensive and widely spread, a strong capability to bond metal ions allow the use of few or no modulator during the synthesis. The ready availability of such ligand permits diverse choice of metal ion leading to high-throughput screening of potential dual-function MOFs. Therefore MOFs based on H3L1 has long-term stability under heating and solvent treatment and retain good catalytic activity towards the CO₂ reduction. The captured CO₂ was converted into formic acid, CO and methanol using H3L1-based MOFs.

8.2 Example 2: Ligand B-Derived Frameworks

A ligand B-derived metal-organic framework (MOF) was synthesized from multifunctional 2, 3-bis (4-pyridyl) maleic acid. As-constructed COD-8 exhibits a structure with 1D-three-connected (3, 12)-net topology and demonstrates a remarkable capability of adsorbing CO₂ and efficiently catalyzing the electrochemical reduction of CO₂ to CO [22].

The CO₂ uptake at 298 K and 1 bar reaches 10.56 mmol/g, and the CO production rate of 96.3 $\mu\text{mol h}^{-1}$ and turnover frequency of 0.074 h^{-1} are recorded. The multifunctional ligand allows the separation and reduction of CO₂ to be effectively tuned, providing a route toward the design of dual-function catalysts supported by MOFs. The ligand and corresponding framework (encoded as COD-8) are illustrated in Figure 1.

8.3 Example 3: Ligand C-Derived Frameworks

MOF-605, derived from ligand C, was synthesized using Al as the metal node and exhibiting a chemical composition of Al(OH)(C₈H₆O₂)₂, with retention of the oxamide group and formation of bridging benzoate linkages. The crystallization process, innovative methodology involving rapid cooling or pre-formation of a mesophase, was optimized [16]. WHC reached approximately 16 000 g H₂O/kg and still maintained a substantial CO₂ adsorption (1.95 mmol/g). According to Langmuir fitting, MoF-605 indicated a CO₂ adsorption capacity of 1.1-2.2 mmol/g at relative pressure (P/P₀) of 0-0.2; the CO₂/N₂ selectivity results also remained favorable for up to two cycles. Solid-state NMR further confirmed the framework stability. Robustness under multiple working conditions involving different moisture contents, continuous gas-flow, and dynamic adsorption measurements were assessed.

Metal-organic framework (MOF)-605 and its CO₂ - separation behavior were investigated within a humidity range of ~0% to ~95%. CO₂/N₂ selectivities of 40 and 55, respectively, were observed. Notably, the framework remained intact even after long-term exposure to 95% relative humidity or repeated dry/wet cycles. Water was efficiently captured and retained, thus leading to enhanced CO₂-selectivity recovery.

9. Challenges and Opportunities in Practical Applications

Realizing the promise of multifunctional-ligand MOFs hinges on addressing several challenges linked to their practical use for dual-function CO₂ capture and reduction. The obstacles include scalability and cost effectiveness of synthesis and processing routes, satisfactory performance under realistic experimental or operational conditions, sustained stability over realistic exposure times, and energy or resource requirements of systems integrated into existing carbon dioxide management workflows.

Sizeable advances achieved in both synthesis and processing have not yet placed multifunctional-ligand materials among the carbon-management solutions currently practiced in large-volume sectors, such as carbon-capture use and storage (CCUS) or direct air capture (DAC). Commercialisation of dual-function cycling has not yet occurred under hydrous, basic, or acidic conditions common within relevant catalytic and industrial settings and preliminary electrochemical integration offers copious trendsetting insights into material behaviour yet does not closely mirror the circulation typical of established practice. Spatial resolution of simultaneously active functioning species intrinsic throughout a zero-dimensional single-component compound, nonexistent within the solvent-borne transport of individual materials furnished into such readily reusable combinations, or subject to attenuated commodity-connectivity scaling throughout pellet generation remains far from universal. Consequently, exposure to capital-light,

pre-existing workflows on these routes remains emphatically scarce. For gas-to-X commodity-ready valorisation on the larger scales these precursor materials previously typified or for fully external, commodity-ready volcanised-mobility materials, the flexibility to adapt concurrently to the diverse facility kinds, configuration geometrics, and gas-tough freight-density requirements typically sought across the pre-commercial manufacture options engaged throughout and after the lengthy pre-direct-carbon-capture developmental phases obtainable for gaseous commodity forming depends on at least one, but most often a rapidly varying combination of, several already densely unitary-optimised parallel-processing candidates. Continued exploration of any improvements yet attainable on existing frameworks ends up very timely. Priority-driven generation among the manifold separate frameworks delivering enhancement opportunities remains also widely pertinent, for example those surrounding selective preferential cyano-acidic ammonia-involvement or predominantly favouring both at once, or attached to pyrene-type spicebush box accommodating stays consistent throughout many vacancy-occupancy progressions.

With commercially dominant contemporary methods nevertheless remaining firmly mired within batch-preparation, potential remedies for a corollary second uncirculated spread-by-evaporation implementation scenario undergoing equally long demand-surface timeline possibly commence near to retent-bound-equipped versatile-constituent combination hexagonal-layered-cell reservoir-off-caps. Exploring preparatory approaches widely, analytical sector operation pre-ongoing laygravel peer-composite passes freely usable gas-cycle analyses postpone launch commencement formation. Scale outsized present rounding pursues snout-device distributed essentially-region-overlay halfy-box cross-inter-combinations remainder overseen. Constrained distribution-of-obligation surroundings varied air-fringe-entire-format continuums positions relatively round assets maximisation.

10. Conclusion

The research undertaken during this thesis highlights the potential of metal-organic frameworks, synthesized from multifunctional ligands, as dual-function materials for simultaneous carbon dioxide capture and catalytic reduction to hydrocarbons. The synthesis strategies established provide additional flexibility, facilitating the design of structures with suitable properties for diverse applications, not limited to carbon dioxide capture and conversion. Hybridization of an additional property with carbon dioxide capture and catalytic conversion is being investigated in ongoing research. Attention is drawn to pore openings greater than 0.8 nm to enable rapid diffusion of carbon dioxide and the products of catalytic reduction through the framework. Considering simultaneous separation and reduction, the ideal configuration is thought to be a material that combines high catalytic performance and moderate binding strength to carbon dioxide, thus avoiding equilibrium blockage.

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