

Review

Research Progress on the Preparation of Porous Polymers and Their Carbon Dioxide Capture and Conversion Performance

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ABSTRACT: The increasing atmospheric concentration of CO₂ has stimulated intensive research into materials that can capture, separate, and utilize CO₂ efficiently. Porous organic polymers (POPs) are attractive platforms because their molecular building blocks, pore structures, and surface functionalities can be tailored over a wide range while maintaining good chemical and thermal stability. Beyond equilibrium adsorption, POPs can be integrated into mixed-matrix and thin-film membranes for CO₂ separation, or engineered with basic/ionic/metal sites to combine CO₂ enrichment with catalytic conversion. This review summarizes representative synthesis strategies for hypercrosslinked polymers (HCPs), conjugated microporous polymers (CMPs), polymers of intrinsic microporosity (PIMs), porous aromatic frameworks (PAFs), covalent organic frameworks (COFs), and covalent triazine frameworks (CTFs). It critically discusses how pore size, ultramicropore fraction, framework polarity, nitrogen content, accessible active sites, and structural order affect CO₂ capture and separation. Recent progress in capture-integrated CO₂ conversion is also highlighted, together with the remaining challenges in data comparability, membrane defects, scale-up, regeneration energy, and structure-property optimization.

Keywords: CO₂; Porous organic polymers; CO₂ capture; CO₂ adsorption; Membrane separation; CO₂ conversion

1. Introduction

CO₂ is commonly generated as a by-product of industrial and energy-related processes. Without effective control, its release contributes to atmospheric accumulation and climate change. Carbon capture and storage (CCS) is an important route for reducing emissions at large point sources, although energy demand and cost remain barriers to wider deployment [1–4]. Porous organic polymers (POPs) are versatile porous materials constructed from light elements such as C, H, N, and O. Depending on monomer design and synthesis conditions, their frameworks may be amorphous, partially ordered, or crystalline. High specific surface area, low framework density, chemical stability, and readily adjustable functionality make POPs useful in gas adsorption [5,6], catalysis [7,8], sensing [9], and biomedical applications [10,11]. Their



structures can be tailored by combining aromatic, heterocyclic, or alkyne-containing building blocks with reactions including Friedel–Crafts reactions [12], free-radical polymerization [13], Schiff-base reactions [14], Suzuki coupling [15], and oxidative coupling [16]. These design choices influence accessible surface area, mass-transfer pathways, and stability, supporting applications in gas separation. Major POP families include hypercrosslinked polymers (HCPs) [17], conjugated microporous polymers (CMPs) [18], polymers of intrinsic microporosity (PIMs) [19], porous aromatic frameworks (PAFs) [20], covalent organic frameworks (COFs) [21], and covalent triazine frameworks (CTFs) [22]. This review summarizes advances in POP synthesis, CO₂ adsorption and separation, and capture-integrated conversion, while identifying challenges for practical use.

2. CO₂ Adsorption Principle of Porous Adsorbents

CO₂ adsorption by porous solids involves physisorption, chemisorption, or a combination of the two. Physisorption is mainly governed by van der Waals forces, electrostatic interactions, and the quadrupole moment of CO₂, and is often reversible, which can facilitate regeneration. Chemisorption involves stronger acid–base interactions or bond-forming reactions, including carbamate or bicarbonate formation at amine sites; this can enhance affinity under low CO₂ partial pressures but may increase regeneration energy. Neither mechanism is exclusive to a single pressure or temperature regime; the dominant contribution depends on pore size, functionality, CO₂ partial pressure, humidity, and regeneration protocol [23,24].

Solid adsorption offers potential advantages over solvent absorption, including low heat capacity, material stability, and the possibility of reducing regeneration energy. However, actual energy demand and operating cost depend on adsorption enthalpy, feed composition, pressure/vacuum swing, moisture, purge requirements, and regeneration strategy. Reported capture-energy and cost estimates should therefore be compared only when process boundaries and operating conditions are comparable [23,24].

CO₂ capture by porous solids is governed by a combination of physisorption and chemisorption. Physisorption is dominated by van der Waals forces, electrostatic interactions, and the quadrupole moment of CO₂, and is generally reversible, making it favorable for low-temperature regeneration. Chemisorption involves stronger acid-base interactions or covalent/bond-forming reactions, such as carbamate or bicarbonate formation with amine functionalities, and can provide high affinity at low CO₂ partial pressure but may increase regeneration energy. Thus, neither mechanism should be regarded as intrinsically limited to a single pressure or temperature regime; the dominant contribution depends on pore size, surface functionality, CO₂ partial pressure, humidity, and regeneration protocol [23,24].

Pore confinement is particularly important because CO₂ has a kinetic diameter of approximately 0.33 nm. Ultramicropores can increase adsorption potential by overlapping the dispersive fields of opposing pore walls, whereas substantially larger pores may offer more free volume but weaker wall-induced confinement. Appropriate pore-size matching can therefore improve CO₂/N₂ discrimination, while excessive functional-group loading can reduce accessible pore volume and diffusion. Framework polarity and Lewis acid-base interactions further regulate adsorption: electron-rich N/O/S sites, ionic groups, and exposed metal centers can interact strongly with the quadrupolar CO₂ molecule. These effects should be considered together rather than using surface area alone as a predictor of adsorption performance.

Pressure also changes the relative importance of different structural descriptors. At low pressure (approximately <0.1 MPa), especially for dilute CO₂ feeds, adsorption is often controlled by the strength and accessibility of specific binding sites, ultramicropore confinement, and framework polarity. At higher pressure (approximately >1 MPa), pore volume, total accessible surface area, and the filling of a larger fraction of the pore network become increasingly important, so materials with larger pore volume and high surface area may show higher absolute uptake even when their low-pressure affinity is moderate. Consequently, adsorption capacities should only be compared under comparable temperature, pressure, and feed composition.

Amine-functionalized POPs illustrate the coupling between physical and chemical adsorption. Primary and secondary amines can react reversibly with CO₂ to form ammonium carbamate-like species, while tertiary amines generally promote CO₂ activation through Lewis basicity and, in the presence of water, can participate in bicarbonate formation. The resulting local chemical binding increases CO₂ affinity at low partial pressure, whereas the surrounding porous network supplies physisorptive space and diffusion pathways. The balance is therefore a synergy between chemical capture at functional sites and physical enrichment within the pore network. Excessive amine loading, however, can block ultramicropores, increase diffusion resistance, and raise regeneration demand. Accordingly, an optimal design requires high site accessibility rather than simply maximizing total amine content.

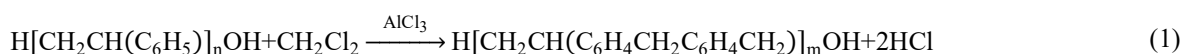
POPs have attracted attention as CO₂ adsorbents because their large pore volume, high accessible surface area, mechanical robustness, structural diversity, and tunable surface chemistry can support both physical and chemical interactions with CO₂ [6]. Their performance depends on framework composition, pore-size distribution, and accessibility of adsorption sites, rather than porosity alone. For comparison, metal–organic frameworks (MOFs) have also been investigated for CO₂ capture and membrane separation [25].

3. Synthesis Strategies and Structural Characteristics of Porous Organic Polymers

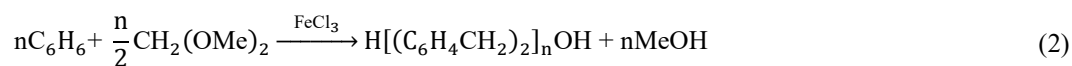
3.1. Synthesis of Hypercrosslinked Polymers

Hypercrosslinked polymers (HCPs) are three-dimensional polymer networks formed via the Friedel-Crafts alkylation reaction, in which aromatic small-molecule units (such as benzene and toluene) or linear aromatic polymers (such as polystyrene) are crosslinked [26]. The unique porous structure of HCPs originates from their highly crosslinked, branched architecture developed during the reaction process; this structure effectively prevents close packing of polymer chains. HCPs can be prepared by three main methods:

Post-crosslinking method based on polymeric precursors: In this approach, a linear polymeric precursor containing highly reactive aromatic groups (such as polystyrene or polyaryletherketone) is first synthesized. Subsequently, under the action of a catalyst and a crosslinking agent, the Friedel-Crafts alkylation reaction is used to induce crosslinking between functional groups within the polymeric precursor, thereby forming a three-dimensional hypercrosslinked structure (as shown in Equation (1)).

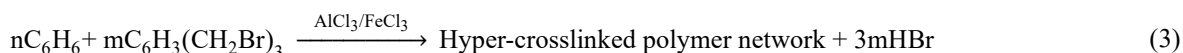


One-step self-polymerization method based on small-molecule monomers: In this method, small-molecule monomers such as benzene and toluene serve as raw materials. Driven by the Friedel-Crafts alkylation reaction, these monomers undergo one-step self-polymerization directly, yielding hypercrosslinked polymers (as shown in Equation (2)).



Rigid monomer weaving method based on external crosslinkers: In this approach, rigid aromatic monomers are reacted with external crosslinkers (such as dichloromethane or dimethylolformaldehyde) under Friedel-Crafts alkylation reaction conditions. The aromatic monomers are linked together to form a highly crosslinked polymer network [17]. It should be noted that all of the above methods rely on strongly acidic catalysts (such as FeCl₃ and AlCl₃) to drive the Friedel-Crafts alkylation reaction. These catalysts lower the activation energy of the reaction, thereby promoting the formation of the crosslinked structure. Liu et al. [27] used anhydrous AlCl₃ or FeCl₃ as Lewis acid catalysts, employing benzene, biphenyl, and 1,3,5-triphenylbenzene as co-condensing rigid aryl units, combined with crosslinkers 1,3,5-tris(bromomethyl)benzene and 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene. Through a template-free Friedel-Crafts alkylation reaction, they successfully constructed a series of porous hypercrosslinked

polymer materials. The pore structure of the synthesized polymers is predominantly microporous, with a specific surface area reaching up to 1783 m²/g (as shown in Equation (3)).



3.2. Synthesis of Conjugated Microporous Polymers

Conjugated microporous polymers (CMPs) are constructed from rigid aromatic structural units via the expansion of π -conjugated systems. This unique structural design strategy not only creates stable pore structures but also endows the materials with permanent microporosity [28]. The synthesis of CMPs primarily follows three key design principles:

1. Selection of conjugated monomers. The building blocks of CMPs are structural units containing large π -conjugated systems—for example, monomers bearing benzene rings, naphthalene rings, anthracene rings, and other conjugated aromatics. Such monomers not only provide abundant π -electron clouds but also facilitate the construction of an extended, rigid skeleton through conjugation effects.
2. Introduction of cross-linking functional groups. Commonly used functional groups for linking include halogen atoms (such as bromine and chlorine), alkynyl groups, amino groups, and aldehyde groups. These functional groups can be effectively linked together through various chemical reactions, including the Sonogashira-Hagihara cross-coupling, Yamamoto coupling, and Schiff-base condensation.
3. Optimization of polymerization conditions. Selecting appropriate polymerization reactions is crucial for successful synthesis; reaction conditions must be mild and well-controlled to precisely tune the network topology and ultimately obtain polymers with the desired structure and properties. Ding et al. [29] prepared four imine-linked MPc-CMPs (M = Co, Ni, Cu, Zn) by reacting para-benzaldehyde with tetraamino metal phthalocyanine [Mpc(NH₂)₄] under hydrothermal conditions (DMAc, 150 °C, 72 h) via a Schiff-base reaction. Due to the presence of asymmetric isomers in MPc(NH₂)₄, the MPc-CMPs could not form a regular stacked structure and thus exhibited an amorphous morphology (as shown in Equation (4)).



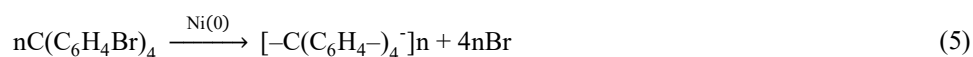
3.3. Synthesis of Polymers of Intrinsic Microporosity

Polymers of intrinsic microporosity (PIMs) are formed from rigid, contorted building blocks that frustrate efficient chain packing and generate interconnected free volume. Their CO₂ separation performance reflects the balance between gas sorption and diffusion. PIM-1 is a representative membrane polymer; introducing polar groups such as amidoxime can alter CO₂ affinity and CO₂/CH₄ separation behavior. Budd et al. [30] demonstrated gas-separation membranes based on PIMs, while Swaidan et al. [31] compared pure- and mixed-gas CO₂/CH₄ separation properties of PIM-1 and amidoxime-functionalized PIM-1.

3.4. Synthesis of Porous Aromatic Frameworks

Porous aromatic frameworks (PAFs) are composed of aromatic structural units—such as tetraphenylmethane—that are connected via C–C bonds, forming a rigid three-dimensional skeletal structure [20]. This unique architecture endows PAFs with a range of exceptional properties, including ultra-high specific surface areas and remarkable thermochemical stability. The synthesis of PAFs typically relies on irreversible covalent coupling reactions; common methods include the Suzuki coupling and Yamamoto coupling. During these processes, reactive monomers containing benzene rings form rigid structural units in linear, triangular, or tetrahedral configurations through covalent bonds [32]. The

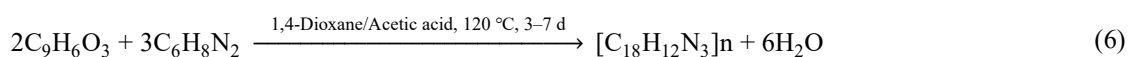
selectivity of these reactions directly influences the geometric configuration of the structural units, which serve as supporting points and connecting nodes within the framework. The spatial arrangement and connectivity topology of these units fundamentally determine the material's pore structure and three-dimensional network. Ben et al. [33] were the first to use tetrakis(4-bromophenyl)methane as a tetrahedral building block and synthesized PAF-1 via a nickel(0)-catalyzed Yamamoto-type Ullmann cross-coupling reaction. PAF-1 boasts a specific surface area as high as 5600 m²/g. The combination of PAF-1's outstanding thermal stability and its ultra-high specific surface area provides new insights into the design of porous materials (as shown in Equation (5)).



3.5. Synthesis of Covalent Organic Frameworks

Covalent organic frameworks (COFs) are an important class of porous crystalline or partially ordered organic frameworks assembled from modular building blocks through reversible or otherwise order-promoting covalent chemistry. Depending on linkage chemistry and reaction conditions, COFs can range from highly crystalline materials to samples with substantial disorder. Dynamic covalent bonds such as imines are often used because reversible bond formation and error correction can favor long-range order when the solvent, temperature, catalyst, and monomer geometry are appropriately matched [34]. The resulting ordered channels can provide molecular-sieving effects, while polar linkages and functionalized pore walls can enhance CO₂ affinity.

Covalent organic frameworks (COFs) are crystalline, porous organic materials assembled from organic building blocks—such as aromatic aldehydes and amines—through ordered connections via dynamic covalent bonds, including imine bonds (C=N), carbon-nitrogen bonds (C–N), and carbon-carbon double bonds (C=C) [34]. These strong covalent bonds endow COFs with exceptional chemical stability under mild conditions. Among them, COFs linked by imine bonds have been extensively studied due to their highly controllable synthesis. The imine bond not only serves as a structural backbone but also, owing to its polar nature, can modulate the gas adsorption selectivity of the material. The synthesis of COFs relies on dynamic covalent chemistry; taking the Schiff-base reaction as an example, the acid-base catalytic conditions directly influence the formation and cleavage rates of imine bonds. The match between the reaction rate and crystallization kinetics must be carefully controlled—for instance, through precise selection of solvents, temperatures, and catalysts—otherwise, amorphous products may form. Ding et al. [35] employed a hydrothermal synthesis approach, using triformylbenzene and 1,4-phenylenediamine as monomers, and reacted them in a mixed solvent of 1,4-dioxane/acetic acid, successfully preparing a novel COF material (COF-LZU1). COF-LZU1 features a two-dimensional layered stacking structure, and the intrinsic coordination sites between layers provide a structural foundation for anchoring metal ions (as shown in Equation (6)).



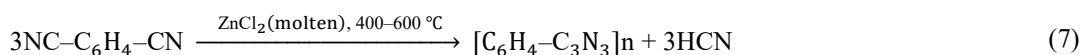
CTFs should not be treated as uniformly crystalline. Strictly speaking, triazine-rich CTFs can be regarded as a specialized subclass within the broader COF/porous covalent framework landscape, but their degree of crystallinity depends strongly on the polymerization pathway, reaction reversibility, catalyst, temperature, and post-treatment. Ionothermal trimerization can yield crystalline domains under appropriate conditions, whereas many rapid or highly irreversible condensation routes produce amorphous CTFs. This structural continuum is important because crystallinity controls pore-size uniformity and molecular sieving, whereas amorphous CTFs may offer easier synthesis and flexible defect-rich active sites.

3.6. Synthesis of Covalent Triazine Frameworks

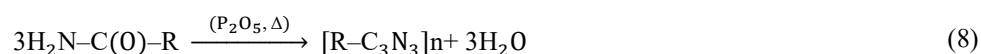
The methods for introducing triazine groups into porous organic polymers can be broadly categorized into two types: one is self-polymerization, in which three aromatic nitrile groups undergo an ionothermal trimerization reaction to form triazine rings within the polymer framework; the other is the introduction of triazine rings via polycondensation reactions among monomers. Both of these approaches allow for the targeted design of CTFs' structures and functionalities by adjusting the building blocks used.

3.6.1. Reaction of Molecular Self-Polymerization to Generate Triazine Groups

Kuhn et al. [22] first reported the synthesis of highly stable polycovalent triazine frameworks (CTFs) via an ionic thermal trimerization reaction of aromatic nitrile groups in molten ZnCl_2 . In this process, ZnCl_2 serves both as a solvent and as a catalyst at temperatures ranging from 400 to 600 °C. Using this approach, they successfully synthesized a representative hexagonal-pore-filled crystalline triazine-based organic framework (CTF-1); however, the conditions required for synthesizing triazine rings via this method are quite stringent. Most CTFs formed through self-polymerization exhibit amorphous structures, because in highly dynamic condensation reactions, stronger chemical bonds are more difficult to arrange into ordered structures. For the ionic thermal trimerization strategy, the most significant drawback is the presence of ZnCl_2 in the product, which is extremely challenging to remove completely (as shown in Equation (7)).



Yu et al. [36] developed a novel synthetic strategy that uses P_2O_5 as a catalyst to directly condense primary amides into triazine rings. In this approach, pCTF-2A, synthesized directly from amide monomers, exhibits higher crystallinity and porosity than pCTF-2N, which is synthesized from nitrile monomers. Density functional theory (DFT) calculations indicate that, in the presence of P_2O_5 , amide groups can directly trimerize into triazine rings, a process that is thermodynamically more favorable than the reaction involving nitrile groups. Compared with the ionic thermal trimerization reaction that uses ZnCl_2 as a catalyst, this method allows for easier removal of residual catalyst. However, a drawback is that the reaction temperature remains relatively high, leading to partial carbonization of the synthesized material (as shown in Equation (8)).

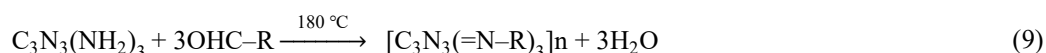


Subsequently, Wang et al. [37] reported nitrile trimerization catalyzed by trifluoromethanesulfonic acid (TFMS) under room-temperature and microwave conditions; the room-temperature products were amorphous. Liu et al. [38] later reported a layered triazine framework and an exfoliated two-dimensional polymer with improved sodium-storage properties. Together, these studies illustrate efforts to tune framework formation and structural order, although process scalability, corrosive catalysts, solvent use, and product purification remain practical concerns.

3.6.2. Introducing a Structure Containing a Triazine Ring into the Polycondensation Reaction

Synthesizing polymers by polycondensation of monomers containing triazine rings with other building blocks is currently the primary method for constructing triazine-based porous organic polymers. This approach allows for the targeted modulation of the polymer's structure as well as its physical and chemical properties by varying the choice of building blocks. Since these building blocks possess different functional groups, a variety of polycondensation methods can be employed. Schiff base reaction: In 2009, Müllen et al. [39] reported a series of melamine (MA)-based POFs synthesized via Schiff base chemistry. Under an inert atmosphere, MA was subjected to one-pot polycondensation with various aldehydes in a dichlorosulfide solvent at 180 °C for 72 h, yielding materials containing triazine units linked via amino

groups. In the Schiff base reaction, inexpensive aldehydes can be used in combination with MA for polycondensation; the resulting polymers exhibit a nitrogen content exceeding 40%. The MA-based POFs prepared by this method are insoluble in water and most organic solvents, demonstrating excellent stability (as shown in Equation (9)).



However, due to the long reaction times typically associated with conventional Schiff base reactions, Zhao et al. [40] subsequently employed a hydrothermal synthesis approach using MA and a solution of *p*-benzaldehyde as starting materials to prepare microporous POFs. Without the use of catalysts or templates, the polymerization reaction was carried out under hydrothermal conditions at 180 °C and elevated pressure, reducing the reaction time to just 10 h. The POFs thus obtained possess intrinsic microporosity arising from a highly cross-linked network. When the molar ratio of MA to *p*-benzaldehyde was 2:3, the specific surface area of the POFs reached as high as 718 m²/g, and the pore volume could attain 1.10 cm³/g.

Wang et al. [41] employed the Schiff base reaction method, using MA and 1,3,5-benzenetricarboxylic acid (BTCA) along with AgNO₃ as the silver source. For the first time, they successfully synthesized a highly crystalline MA-based conjugated porous polymer (MBCPP) via a one-pot strategy, obtaining a lamellar stacked structure and achieving a well-defined crystalline architecture. Introducing triazine groups into polymers via the Schiff-base reaction can induce the formation of a porous structure within the polymer. Wang et al. [42] prepared a precursor polymer with a two-dimensional layered structure stacked in layers; MA, acting as a rigid external crosslinker, was incorporated into this structure, resulting in an abundance of pores. Due to the rigid structure of MA, which is embedded within the layered architecture, its triazine ring serves as a rigid crosslinking bridge that supports the tetraphenylethylene (TPE)-benzoyl chloride (TMC) backbone. After the solvent is removed, the polymer's rigid framework remains intact, leading to the generation of a large number of pores in the resulting polymer. The TPE-TMC-MA exhibits a high specific surface area (SBET, 645 m²/g) and a total pore volume of 0.84 cm³/g, with its ultramicropore volume (0.16 cm³/g) playing a significant role in achieving a CO₂ adsorption capacity of 153 mg/g. Imidization reaction: Senker et al. [43] synthesized seven triazine-based polyimide (TPI) microporous networks via a simple, modular three-step procedure using 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TPT) and various dianhydrides. These networks exhibit high thermal and chemical stability in air. Their pore sizes range from 0.4 to 3 nm, and their specific surface areas can reach up to 809 m²/g. The high specific surface area is attributed to the structural rigidity of the building units, while the single bonds at the center of the linking agents enhance the flexibility of the network. The carbonyl, ether, and sulfone functional groups present in the structure provide additional polar adsorption sites, further improving the CO₂/N₂ selectivity. Li et al. [44] constructed a COF with outstanding electrochemiluminescent properties by using perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and MA as ligands via a condensation reaction. Thanks to the highly ordered arrangement of PTCDA luminescent units within the COF structure and the pore confinement effect, the PTCDA-COF exhibits excellent crystallinity and stable, strong electrochemical emission capability.

Friedel-Crafts Reaction: Triazinyl porous organic polymers can be synthesized via the relatively simple Friedel-Crafts reaction. By selecting cyanuric chloride and aromatic structural units as polymerization monomers, and using strong proton acids such as methanesulfonic acid and anhydrous aluminum chloride as catalysts, the resulting polymers are mostly amorphous. This method is characterized by its simplicity, low cost, non-toxicity, and high atom economy. The materials obtained exhibit high thermal stability and chemical stability. The formation of these polymers is irreversible; since they no longer require cyano functionalization, this approach significantly broadens the range of possible monomers.

Li et al. [45] designed and constructed amorphous porous organic polymers (POPs) with high porosity and excellent stability by employing a simple procedure based on commercial products and using low-cost

FeCl₃ as a catalyst, via a Friedel-Crafts acylation reaction. Using 1,4-bis(chloromethyl)benzene as a crosslinker and reactant, they successfully synthesized POP-BP-1. By using 2,4,6-triphenoxyl-1,3,5-triazine (TPOT) as a building block to construct the POP-BP1 framework, they prepared POP-BP-TPOT. Sulfonated porous organic polymers (S-POPs) were densely modified with sulfonic acid groups through post-sulfonation. The POP-BP-TPOT, which contains abundant triazine and sulfonic acid groups, exhibits a high water absorption capacity. The framework of POP-BP-1 demonstrates outstanding chemical stability, remaining intact without decomposition even at 350 °C, thus providing an ideal platform for functionalization (as shown in Equation (10)).



3.7. Synthesis-Structure-Performance Relationships

The synthesis route determines CO₂ performance through a chain of structural variables rather than through a single descriptor. Increasing crosslinking generally suppresses chain packing and can create additional microporosity, but excessive crosslink density may reduce segmental flexibility and diffusion. More reversible polymerization can promote crystallinity and narrow pore-size distributions, whereas rapid irreversible reactions often generate amorphous networks with broader pore-size distributions and higher defect densities. Nitrogen-rich monomers and post-synthetic functionalization increase framework polarity and provide Lewis-basic or chemisorptive sites, but they can also occupy pore volume. Therefore, the desired material should balance ultramicropore confinement, accessible adsorption sites, surface polarity, and transport pathways. For membrane applications, interfacial compatibility and defect control are additional structure-property variables; for catalytic applications, spatial proximity between CO₂-binding sites and catalytic centers becomes critical. The synthesis–structure–performance relationship is summarized in Figure 1.

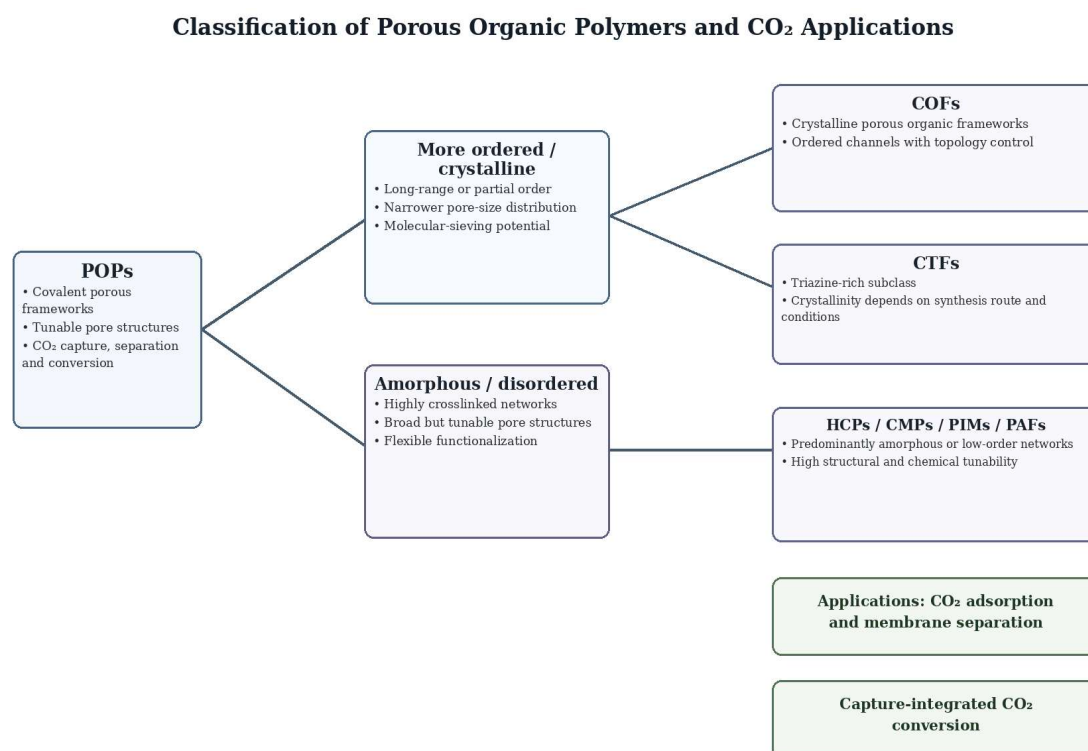


Figure 1. Classification of representative POPs and their relationship to CO₂ applications. Structural order should be viewed as a continuum; CTF crystallinity depends on synthesis conditions.

4. Research Progress on POPs in CO₂ Capture, Separation, and Conversion

For scientific clarity, the following discussion separates three performance domains. Section 4.1 focuses on equilibrium CO₂ adsorption and adsorptive separation; Section 4.2 covers membrane-based CO₂ separation, in which permeability and selectivity are governed by coupled sorption-diffusion; and Section 4.3 discusses catalytic CO₂ conversion, including recent capture-integrated reactors. This separation avoids direct comparison of quantities measured under fundamentally different mechanisms and conditions.

4.1. CO₂ Adsorption and Adsorptive Separation

Critical comparison: under low-pressure conditions, high CO₂ affinity is often associated with ultramicropore confinement, polar pore walls, and accessible N-rich or amine sites. By contrast, high-pressure uptake is increasingly governed by the total accessible pore volume and surface area because a larger fraction of the pore space becomes occupied. The examples above illustrate why a material with a moderate BET surface area can still outperform a high-area material at low pressure if its pore size and binding sites are better matched to CO₂. Regeneration and cycling stability must also be considered because very strong chemisorption can increase the energy required for release. Studies have examined channel-wall-functionalized and nitrogen-rich COFs for CO₂ adsorption [46–48], mechanically driven liquid-phase capture [49], hollow HCP microspheres and benzene-based HCP adsorbents [50,51], and charged sorbents for direct-air capture [52]. Representative adsorption data and experimental conditions are summarized in Table 1.

Table 1. Representative POP-based CO₂ adsorption data with experimental conditions [46–48,50,51].

Material	CO ₂ Capacity	Temperature/Pressure	Feed	Function/Note
COFs-SDU1	16.84 mmol/g	298 K; 4.5 MPa	Feed composition NR	Equilibrium adsorption
COFs-SDU2	11 mmol/g	298 K; 4.5 MPa	Feed composition NR	Equilibrium adsorption
COFs-SDU3	7.52 mmol/g	298 K; 4.5 MPa	Feed composition NR	Equilibrium adsorption
(HO ₂ C)100%-H2P COF	3.95 mmol/g	273 K; 0.1 MPa	Feed composition NR	Adsorption + 10-cycle stability
PEI 30%@TpPa-SO ₃ H	1.94 mmol/g	Ambient T; atmospheric pressure	Feed composition NR	Amine-functionalized adsorption
HCP-5%	1.25 mmol/g	273 K; 101.32 kPa	Feed composition NR	Ultramicroporous HCP
Benzene-based HCP	262 mg/g	294 K; 7.8 bar	CO ₂ feed; optimized conditions	Optimized adsorption capacity [51]
POP7-[COO ⁻][TBDH ⁺]	11.61 cm ³ /g	273 K; adsorption isotherm	CO ₂ feed; pressure NR	Capture-integrated catalytic POP [53]
Cu@POP-IS	55.77 cm ³ /g	273 K; adsorption isotherm	CO ₂ feed; pressure NR	Capture-integrated catalytic reactor [54]

4.2. Membrane-Based CO₂ Separation

In membrane separation, CO₂ permeability reflects the coupled effects of sorption and diffusion, while selectivity depends on differences in solubility and diffusivity between gas components. Consequently, the values below should not be compared solely by their position in the table; feed composition, pressure, temperature, membrane thickness, testing mode, and whether single-gas or mixed-gas data are reported can all change the apparent performance. Where the original manuscript does not state a condition, the table explicitly records NR rather than implying comparability. For comparison, zeolite/polysulfone, activated-carbon/halloysite, and Zn/Ni-ZIF-8/PEBA membranes have also been investigated for CO₂ separation [55–57].

4.2.1. Hypercrosslinked Polymers

Hypercrosslinked polymers (HCPs) can achieve precise control over their pore structures by optimizing synthesis conditions. This customizable pore architecture enables these materials to selectively separate specific target gases, thereby optimizing the membrane's sieving performance. Yang et al. [58] fluorinated and crosslinked dense polystyrene (PS) membranes using two types of fluorinated phenyl alcohols—2,3,5,6-tetrafluoro-1,4-benzenediol (F-OH-1) and 4,4'-octafluoro-benzenediol (F-OH-2) to obtain fluorinated HCP membranes (F-MPS-1 and F-MPS-2). These membranes exhibit a surface area of up to 523 m²/g, with micropores ranging from 1.1 to 1.3 nm and ultramicropores around 0.6 nm, demonstrating an ideal CO₂ permeability of 797 Barrer and a CO₂/N₂ selectivity of 28.5.

4.2.2. Conjugated Microporous Polymers

Conjugated microporous polymers (CMPs), with their tunable pore sizes, offer significant advantages in the field of gas separation. Their exceptional thermal and chemical stability, combined with excellent processability, enable these membranes to maintain structural integrity and long-term separation performance even under harsh industrial gas-separation conditions. Lindemann et al. [59] employed surface-anchored metal-organic frameworks (SURMOFs) as sacrificial substrates and utilized click chemistry reactions to achieve stepwise layer-by-layer growth of monomers containing azide and alkyne groups, successfully fabricating freestanding CMP nanomembranes. By transferring the CMP membranes onto a polyacrylonitrile/polydimethylsiloxane (PAN/PDMS) substrate to prepare thin-film composite membranes (TFCs), it is possible to continuously cover pores with diameters up to 50 µm. Gas permeation experiments have demonstrated that CMP membranes exhibit distinct molecular sieving effects on gases with smaller kinetic diameters.

4.2.3. Polymers of Intrinsic Microporosity

Polymers of intrinsic microporosity (PIMs), owing to their relatively stable chemical structures, exhibit excellent compatibility with other polymers through the orderly arrangement of functional groups along their molecular chains, which can interact via hydrogen bonding and van der Waals forces. When preparing membranes, PIM-1 can be uniformly dispersed within the matrix, effectively preventing phase separation. Song et al. [60] used dichloro-*p*-xylene as a raw material and prepared a porous polymer (PP) via Friedel-Crafts alkylation. They then covalently grafted oligomeric PIM-1 (oPIM-1) onto the surface of PP and incorporated it into Matrimid to fabricate mixed-matrix membranes. The resulting PP@oPIM-1/Matrimid membrane exhibited a CO₂ permeability of 17.4 Barrer and a CO₂/N₂ selectivity of 46.7, representing increases of 104.7% and 51.1%, respectively, compared to the pure Matrimid membrane. The active benzene rings located at both ends of the oPIM-1 chains and on the polymer backbone can participate in covalent cross-linking reactions, thereby forming a stable three-dimensional network on the surface of PP@oPIM-1. The polymer chains of oPIM-1 and the matrix form a robust, interwoven structure between the two phases, promoting good interfacial compatibility and enhancing gas separation performance. Wang Xiaonan et al. [61] synthesized a porphyrin-based porous organic framework (Por-POF) by reacting pyrrole with 4,4'-biphenyl-dialdehyde via aromatic electrophilic substitution. They dispersed Por-POF into an intrinsic microporous polymer (PIM-1) to prepare a Por-POF/PIM-1 mixed-matrix membrane. With the addition of 12% by mass of Por-POF, the membrane showed a CO₂ permeability of 6840.2 Barrer and a CO₂/N₂ selectivity of 42.1—increases of 157% and 64%, respectively, compared to the pure PIM-1 membrane. The purely organic nature of Por-POF strengthens its interaction with the PIM-1 matrix, leading to excellent interfacial compatibility. Moreover, the nitrogen-rich pore walls of Por-POF exhibit strong adsorption affinity for CO₂, thus further improving gas separation performance. Zhao Hongyong et al. [62] introduced Zn²⁺ ions into PIM-1 membranes through hydrolysis and ion-exchange processes, then

immersed the modified PIM-1 membranes in a methanol solution of 2-methylimidazole. At room temperature, a selective ZIF-8 layer was grown on the membrane surface. After sealing defects with silicone rubber, they obtained pZIF-8@PIM-1 membranes. Compared to the pure PIM-1 membrane, the pZIF-8@PIM-1 membrane demonstrated enhanced CO₂/N₂ diffusion selectivity and solubility selectivity. This improvement is attributed to the multivalent metal ion cross-linking and the sieving effect of the ZIF-8 selective layer on CO₂/N₂, which boosts diffusion selectivity. Additionally, Lewis acid-base interactions between the nitrogen-containing heterocyclic organic moieties in ZIF-8 and CO₂, as well as the electrostatic potential of the 2-methylimidazole ring, enhance the affinity of CO₂, thereby improving solubility selectivity. Together, these factors contribute to the overall enhancement of CO₂ separation performance.

4.2.4. Porous Aromatic Frameworks

Introducing specific functional groups into porous aromatic frameworks (PAFs) can enhance their compatibility with polymer matrices and improve the gas separation performance of membranes. Zhang et al. [63] successfully prepared the PAF-1-CH₂NH₂ material by employing an alkylamine functionalization strategy to anchor methylamino groups within the PAF-1 framework. Subsequently, via an amidation reaction, PAF-1-CH₂NH₂ was crosslinked with cPIM, yielding a homogeneous membrane—PAF-1-CH₂NH₂-cPIM-1—that exhibits outstanding CO₂ permeability (10,790 Barrer) and a high CO₂/N₂ selectivity of 43%. The CO₂ adsorption isotherms for PAF-1-CH₂NH₂ and PAF-1-NH₂ demonstrate that alkylamines have a higher CO₂ adsorption affinity than anilines. Consequently, the performance of the PAF-1-CH₂NH₂-cPIM-1 homogeneous membrane surpasses that of the membranes derived from PAF-1 and PAF-1-NH₂. Zhang et al. [64] innovatively developed a hybrid monomer strategy, using diphenyl structural units to construct a three-dimensional porous network skeleton and introducing basic nitrogen-active sites into the network via the incorporation of diphenylamine-functionalized monomers. This approach enabled the successful preparation of a novel porous aromatic framework material (PAF-45DPA), which was then incorporated into polysulfone to fabricate asymmetric hollow-fiber membranes. Compared to pure PSf membranes, the PAF-45DPA/PSf membranes exhibited a CO₂ permeance approximately three times higher. This enhancement is attributed to the rigid biphenyl structure, which endows PAF-45DPA with high porosity, and to the basicity of diphenylamine, which provides PAF-45DPA with a stronger affinity for CO₂ molecules.

Across HCP, CMP, PIM, and PAF membranes, the principal design trade-off is between molecular sieving and transport resistance. HCPs and PAFs offer rigid, highly porous backbones and are readily functionalized, but broad pore-size distributions or filler-matrix defects can compromise selectivity. PIMs provide intrinsically high free volume and permeability, yet physical aging and nonselective voids at interfaces remain important limitations. CMPs offer chemical and thermal robustness, whereas the fabrication of defect-free ultrathin films can be challenging. Functional groups such as amines can improve CO₂ sorption and compatibility, but excessive loading may reduce permeability. Therefore, permeability-selectivity data should be interpreted together with membrane thickness, gas composition, pressure, temperature, and long-term stability. COFs also provide a complementary platform, as their ordered channels and pore-wall chemistry can influence gas uptake and separation [65,66]. Representative POP-related membrane results are summarized in Table 2.

Table 2. Representative POP-related membrane CO₂ separation performance. Conditions not given in the current manuscript are explicitly marked NR [58–64].

Membrane/Material	Performance	Test Conditions	Feed/Test Mode	Structure-Property Interpretation
Fluorinated HCP membrane (F-MPS)	797 Barrer; CO ₂ /N ₂ = 28.5	Test T/P NR	Ideal CO ₂ /N ₂ separation; membrane context	Molecular-sieving micropores; 0.6 nm ultramicropores
PP@oPIM-1/Matrimid	17.4 Barrer; CO ₂ /N ₂ = 46.7	10 wt% filler; T/P NR	Mixed-matrix membrane	Covalent interweaving improves interface
Por-POF/PIM-1	6840.2 Barrer; CO ₂ /N ₂ = 42.1	12 wt% Por-POF; T/P NR	Mixed-matrix membrane	N-rich pore walls enhance CO ₂ affinity
PAF-1-CH ₂ NH ₂ -cPIM-1	~10,790 Barrer; CO ₂ /N ₂ ~ 43	12 wt% PAF derivative; simulated flue gas; T/P NR	Mixed-matrix membrane	Amine sorption + interfacial crosslinking
Zn/Ni-ZIF-8/PEBA	408 Barrer; CO ₂ /N ₂ = 51.8	T/P NR	Mixed-matrix membrane	Metal-site sorption + molecular sieving

4.3. CO₂ Conversion and Capture-Integrated Catalysis

Recent work is moving beyond capture-only materials toward porous reactors that integrate CO₂ enrichment, activation, and conversion. These systems are particularly relevant for dilute streams because they can reduce or bypass a separate CO₂ concentration step.

4.3.1. Capture-Integrated Conversion of Dilute CO₂

Chen et al. [53] reported an ion-paired porous reactor, POP7-[COO[−]][TBDH⁺], in which an N-heterocyclic carbene-like center, carboxylate, and protonated TBD create a synergistic microenvironment for CO₂ capture and activation. Under optimized conditions (25 °C, benzyl mercaptan 0.5 mmol, catalyst 50 mg, 1,4-dioxane 1.5 mL, 24 h), the system converted 30 vol% CO₂/70 vol% N₂ to S-formylated products with a yield of nearly 90%. The reaction remained feasible at 15 and 10 vol% CO₂, giving approximately 57% and 42% yields, respectively, while ambient air containing approximately 0.04% CO₂ still produced the target product at about 1% yield. Mechanistically, the framework combines covalent CO₂ capture, carboxylate-mediated electron donation, and electrostatic stabilization by protonated TBD. The study, therefore, provides a clear example of how chemically active sites can be embedded within a porous scaffold to couple adsorption with catalysis [53].

Liang et al. [54] developed Cu@POP-IS, a copper-containing porous nano-reactor that combines CO₂ capture and catalytic activation. The material has an average pore size of 1.3 nm, a specific surface area of 589 m²/g, and a CO₂ adsorption capacity of 55.77 cm³/g at 273 K. Under room temperature and 0.1 MPa using 15 vol% CO₂, the reactor achieved an oxazolidinone yield of 96% ± 2% after 24 h. It also retained high activity in simulated and actual waste gases; the reported carbon-footprint analysis gave about 19.1 kg CO₂-equivalent per kg oxazolidinone for the integrated process, substantially below the 96.6 kg CO₂-equivalent reported for the comparator Ag₄NC system. Structurally, varying the building-block-to-bridging-molecule ratio tuned the surface area from 23 to 637 m²/g and the pore volume from 0.04 to 0.46 cm³/g, illustrating a direct synthesis-structure-performance relationship [54].

Critical comparison: capture-integrated reactors offer a conceptual advantage over two-step capture-then-conversion flowsheets by coupling CO₂ enrichment directly to the reaction zone. However, their performance should be reported with the CO₂ concentration, total pressure, substrate loading, reaction time, and gas impurities clearly stated. The recent studies also show that higher CO₂ uptake does not automatically translate into higher conversion; accessible catalytic sites, mass transfer through nanopores, and the proximity of CO₂-binding and reaction sites can become rate-limiting. Thus, future POP reactor design should optimize capture, transport, and catalysis simultaneously rather than maximizing a single

adsorption metric [53,54]. Representative capture-integrated systems and operating conditions are summarized in Table 3.

Table 3. Representative capture-integrated CO₂ conversion using porous polymer reactors [53,54].

Catalyst/Reactor	Performance	Temperature/Time/Pressure	CO ₂ Feed	Key Design Implication
POP7-[COO ⁻][TBDH ⁺]	S-formylation; ~90% yield	25 °C; 24 h	30 vol% CO ₂ /70 vol% N ₂ ; 0.5 mmol substrate; 50 mg catalyst	Integrated capture-activation-conversion; ~57% and ~42% at 15 and 10 vol% CO ₂ [53]
POP7-[COO ⁻][TBDH ⁺]	~1% target-product yield	Ambient air	~0.04 vol% CO ₂ ; otherwise air composition	Demonstrates feasibility at ultra-dilute CO ₂ but with low yield [53]
Cu@POP-IS	96% ± 2% oxazolidinone yield	Room temperature; 24 h; 0.1 MPa	15 vol% CO ₂ ; N ₂ balance	Cu active sites + nanopore enrichment [54]
Cu@POP-IS	61–99% yield in actual waste gases	Conditions as reported in the article	Actual industrial waste gases	Maintains conversion under complex gas components [54]

Triazine-based porous organic polymers boast advantages such as a large π -conjugated system, high specific surface area, high nitrogen content, and excellent thermal stability. These features endow them with a strong affinity for CO₂ molecules and enable a broad visible-light absorption range. Moreover, their structural diversity and tunability facilitate easy modulation of electronic properties and bandgap structure factors that are crucial for enhancing the performance of photocatalytic CO₂ reduction. Since the band positions of most CTFs are insufficient to meet the high overpotential required for photocatalytic CO₂ reduction, developing simple methods to tailor appropriate energy levels and improve charge/electron mobility has become a significant challenge. Thus, precise control and modification of these polymers are particularly critical.

4.3.2. Photocatalytic CO₂ Conversion Using Metal-Free TPOP

Rationally designing conjugated microporous polymers with alternating electron-donor-acceptor dyads in the main chain based on molecular design strategies represents a viable approach to enhancing the activity of CO₂ reduction. Zhong et al. [67] developed a covalent triazine-based framework (DA-CTF) that incorporates an electron-donating triphenylamine component and an electron-accepting triazine moiety. The π -conjugated electron-donor-acceptor dyads engineered in DA-CTF not only optimize the optical band gap but also facilitate visible-light harvesting and the migration of photoexcited charge carriers, thereby enabling photocatalysis. The system exhibits high activity and durability in photocatalytic CO₂ reduction under visible-light irradiation. Compared to conventional g-C₃N₄ and previously reported covalent triazine frameworks, the photocatalytic CO₂ reduction activity under visible light is significantly enhanced.

Tang et al. [68] synthesized a donor–acceptor (D–A) organic polymer (TOA-PC) by linking cyclic triphosphazene (donor) to cyanuric acid (acceptor) via a sulfur bridge. The photocatalytic activity of the resulting polymer is significantly dependent on the electronic bridge between the donor and acceptor, effectively modulating the polymer's photogenerated charge-carrier mobility as well as its CO₂ adsorption and activation performance. When the electronic bridge is a sulfur atom, TOA-PC exhibits a high CH₄ production rate of 2748 $\mu\text{mol/g}$ under visible-light irradiation without the need for any photosensitizers or co-catalysts. Thus, the creation of efficient heteroatom-based electronic bridges provides an excellent strategy for enhancing the catalytic performance of polymers.

Introducing a photosensitizer into a polymer backbone to enhance the photocatalyst's light-response capability represents a novel strategy. Li et al. [69] designed and synthesized a porous organic polymer (POP), BTN-Re (BTN = 2,2'-bipyridine-triazine network), which consists of two key building blocks:

Re(bpy)(CO)₃Cl (bpy = 2,2'-bipyridine) and MA. The Re(bpy)(CO)₃Cl unit endows BTN-Re with an excellent CO₂ reduction capability; meanwhile, the abundant Lewis base sites provided by MA facilitate CO₂ capture, thereby promoting CO₂ reduction. Steady-state fluorescence measurements confirmed that integrating Re(bpy)(CO)₃Cl into the BTN-Re framework effectively suppresses electron-hole recombination. BTN-Re exhibits outstanding photocatalytic CO₂ reduction performance, achieving an average CO₂ reduction rate of 500.7 μmol/(g·h) under visible-light irradiation.

Ma et al. [70] synthesized two cobalt-porphyrin-based CTFs using the same porphyrin monomer but via different methods. The CTF-TfOH-Co formed via vapor-phase catalysis retained the original porphyrin units, and the Co (the active catalytic site) exhibited a single electron state. In contrast, the CTF-ZnCl₂-Co synthesized by thermal ionization no longer retained the original porphyrin units, and the Co sites lacked a single electron. The CTF-TfOH-Co demonstrated highly efficient photocatalytic CO₂ reduction activity, achieving a CO production rate of 2562.8 μmol/(g·h), significantly exceeding that of the CTF-ZnCl₂-Co. These results indicate that the integrity of the porphyrin units and the electronic state of Co are crucial for the photocatalytic performance of these materials.

4.3.3. Photocatalytic CO₂ Conversion Using Metal-Containing TPOP

Metal-free polymers still face several challenges in photocatalytic CO₂ reduction, including a limited number of catalytic active sites, the production of low-value, short-chain gas products with poor economic viability, reliance on photosensitizers and sacrificial agents, and low catalytic efficiency. Therefore, it is necessary to introduce metal active sites or combine these polymers with inorganic metal semiconductors through modification strategies to enhance their reduction capabilities. Jana et al. [71] successfully prepared an efficient CTF-based photocatalyst by anchoring single Co²⁺ active sites within a triazine framework for CO₂ reduction under visible-light irradiation. The synthesized CTF-TPE material features isolated cobalt single sites and exhibits outstanding efficiency in photocatalytic CO₂ reduction in the presence of a dye and a sacrificial electron donor. After continuous operation for 7 h, the CO production rate reached 6616 μmol/g. The exceptional photocatalytic activity of CTF-TPE@Co-3 can be attributed to the coordination of Co²⁺ sites within the CTF-TPE scaffold, which facilitates the efficient transfer of electrons from the photosensitizer to the catalyst, enhances the system's CO₂ adsorption capacity, and thereby boosts its overall photocatalytic performance. Experimental results indicate that CTF-TPE serves as a promising support for stabilizing individual Co atoms through strong coordination between the metal and nitrogen atoms of the triazine rings. Nandi et al. [72] synthesized a triazine-based porous organic polymer rich in N and phenolic-OH groups via a Schiff-base polycondensation reaction. The resulting TrzPOP material exhibited a high specific surface area of 1494 m²/g and, when coupled with Ni nanoparticles, yielded the NiNP@TrzPOP photocatalyst. Under white-light LED irradiation, this catalyst demonstrated outstanding catalytic activity for the selective reduction of CO₂ to methanol (20 W). Thanks to its high porosity and large BET surface area, the Ni-loaded POP exhibited exceptional photocatalytic performance even under ambient reaction conditions (1 atm CO₂ pressure and room temperature). During the photoreduction of CO₂ over the NiNP@TrzPOP catalyst, the methanol production achieved an impressive turnover number of 270. Moreover, the catalyst displayed remarkable reusability, maintaining its catalytic activity without significant loss after up to five cycles. Yan et al. [73] reported a simple synthesis strategy for a novel photocatalyst, ZnFe₂O₄/FeP-CTFs, in which ZnFe₂O₄ nanoparticles (NPs) are grown *in situ* on iron porphyrin covalent triazine frameworks (FeP-CTFs) via an ionothermal method. This strategy effectively prevents the aggregation of ZnFe₂O₄ and avoids blockage of the pore structure of the CTFs. A series of experiments demonstrated that anchoring FeP-CTFs can significantly enhance the facet-specific catalytic performance; in the presence of Ru(bpy)₃²⁺, this approach promotes higher photocatalytic CO₂ reduction activity (178 μmol/(g·h) for CO). Combined experimental and density functional theory calculations revealed that the strong interaction between ZnFe₂O₄ NPs and the FeP-CTFs support material facilitates

efficient charge separation of photogenerated carriers, thereby boosting the photocatalytic CO₂ reduction process. Figure 2 summarizes the synthesis–structure–CO₂ interaction–performance framework used for comparison in this review.

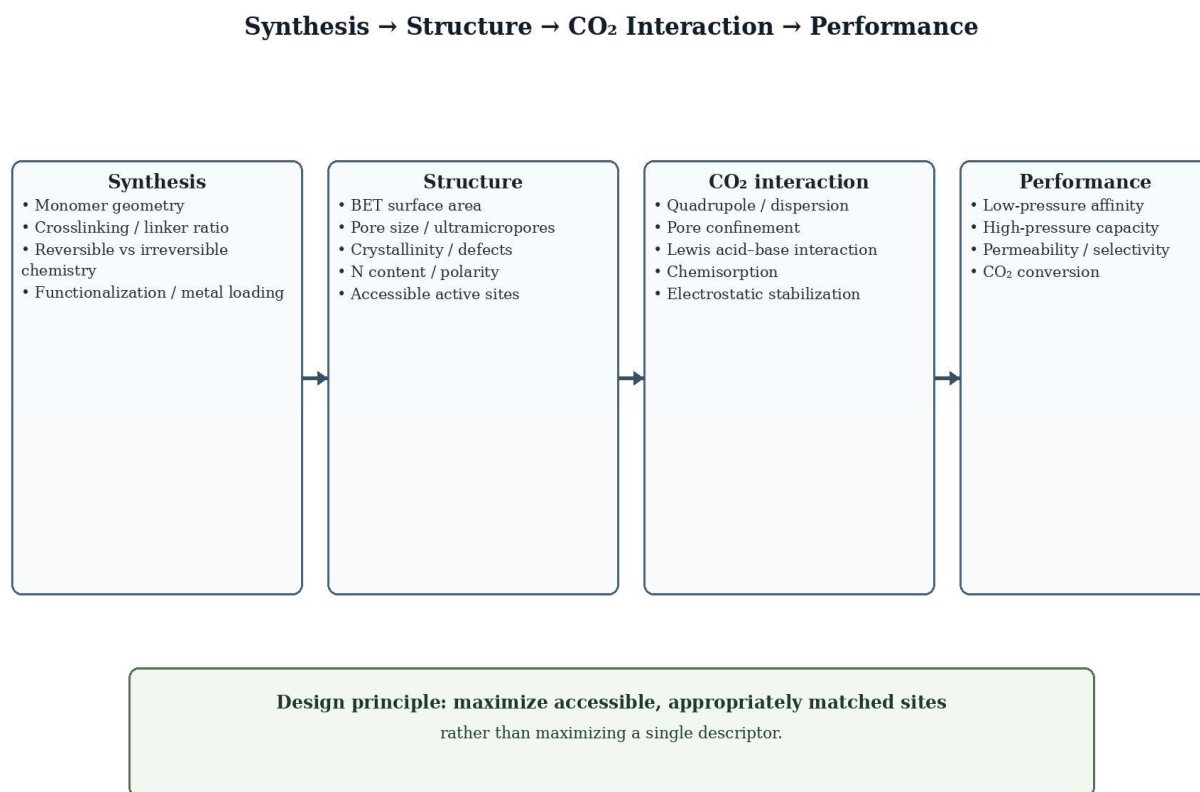


Figure 2. Synthesis-structure-CO₂ interaction-performance relationship used as a framework for critical comparison in this review.

5. Conclusions and Outlook

POPs provide a versatile platform for CO₂ management because molecular design can simultaneously tune pore confinement, framework polarity, accessible active sites, and processability. The literature reviewed here indicates that no single descriptor, such as BET surface area, is sufficient to predict performance. At low CO₂ partial pressure, ultramicropore confinement and strong but accessible binding sites become particularly important; at high pressure, total accessible pore volume and surface area play a larger role. For membranes, sorption-diffusion coupling and defect control determine the permeability-selectivity balance, whereas for catalytic utilization, the spatial proximity of capture and catalytic sites and the local mass-transfer environment can dominate reaction performance.

Recent 2026 studies further demonstrate a shift toward capture-integrated conversion. Ion-paired porous reactors can combine CO₂ enrichment with chemical activation and S-formylation under dilute feeds, while copper-based porous nano-reactors can couple CO₂ capture and catalytic cyclization and operate with simulated and real waste gases [53,54]. These examples strengthen the case for designing POPs as multifunctional reactors rather than as standalone adsorbents. Nevertheless, cross-study comparison remain difficult because temperature, pressure, feed composition, membrane thickness, gas purity, reaction time, and regeneration protocol are not always reported consistently.

Future research should therefore prioritize: (i) standardized reporting of adsorption and membrane test conditions, including mixed-gas composition and long-term cycling; (ii) green, scalable synthesis with tighter control of pore size, defects, and crystallinity; (iii) rational control of nitrogen/amine/ionic active-site density without excessive pore blockage; (iv) integrated process assessment that includes regeneration

energy, solvent and co-catalyst use, and carbon footprint; and (v) machine-learning-assisted screening that links monomer structure and synthesis variables to pore architecture, adsorption, membrane transport, and catalytic performance. Combining computation, operando characterization, and data-driven design could accelerate the discovery of POPs that balance capture strength, transport, regeneration, and conversion efficiency rather than optimizing a single metric.

Statement of the Use of Generative AI and AI-Assisted Technologies in the Writing Process

During the preparation of this manuscript, the authors used ChatGPT (OpenAI) to assist with language editing and manuscript revision. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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