

Covalent Organic Framework Composites for Catalysis: Opportunities and Challenges

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Abstract. Covalent Organic Frameworks (COFs) on behalf of a novel category of porous substances that show interesting and promising properties in many applications due to their large surface areas, unique physicochemical properties, adjustable porosity, and flexible chemistry. The increasing demand for energy and the harm it does to the environment make the quest for a renewable clean energy source vital. Recently, photocatalysis—which converts solar energy to fuels like hydrogen and hydrocarbons or to degrade environmental contaminants—has emerged as a potential strategy for achieving this goal. In this work, synthesis, structure, and a list of design concepts and topologies are used to examine the opportunities and challenges for enhanced energy technologies employing COF-based materials. It is anticipated to drive the development of existing energy structures, inspire researchers from other fields, and increase the use of covalent organic structures in certain fields.

Keywords: COF-based materials, renewable clean energy, photocatalysis, design concepts, topologies.

1. Introduction

Organic conversion is of fundamental importance to the industry and it has matchless significance and contributes to the creation of a prosperous world [1]. Nonetheless, a significant amount of the world's energy consumption is attributed to the energy-intensive nature of most processes. A basic problem in chemistry is the employment of stable, recyclable, and effective catalysts. Given this, a significant conversion technology in the chemical industry is the heterogeneous catalyst; the increased focus on the creation of novel heterogeneous catalysts is a result of its enormous potential. In the past, a lot of research has been done on loading catalysts onto surfaces to immobilize them: inorganic and polymeric matrices. Unfortunately, the issue with these heterogeneous catalysts is that they have low efficiency because of leakage of active sites, random and amorphous distribution, and active site masking. As prefabricated heterogeneous catalysts, porous crystalline COFs have emerged as a typical molecular platform. They enable the structure and pores to be completely utilized to create a variety of catalytic systems since they are stable and insoluble.

2. Design Principles

COFs are constructed using a topology diagram, in which monomers are covalently bound in a specific pattern to build 2D or 3D skeletons with intrinsic porosity. Stacking 2D polymer networks leads to the creation of 1D open channels in 2D COFs and layer skeletons. These interactions dictate the spatial spacing between neighboring layers, which is generally 3-5. This layered structure allows for the construction of photo- and/or electro-catalysts because the structured columnar arrays in these materials offer pathways to improve the transport of excitons, electrons, and holes, essential for photochemical and electrochemical reactions. However, only the catalytic sites on the surface layers would be available for reactions, indicating that 2D COFs are not fitting for straightway integrating the catalytic sites to the π columns. However, because columns tend to form pore walls in 1D channels, there is still a significant probability that the skeletons will expand to function as catalytic centers. the side groups of monomers Attached by catalysts, for example, is a popular strategy for creating 2D COFs. As a result, catalytic sites may be included in the pore walls. This method allows for the customization of the pore surfaces of many heterogeneous catalytic systems. Because of the

interpenetration structure of 3D COFs, using backbones directly as catalytic centers is problematic, and the range of catalysts that may be inserted into the pore walls is further limited by the minuscule pore size, which is generally in the micropore range [1].

Covalently joining organic molecules into extended solids usually results in materials that are chaotic and amorphous. The capacity to create methods for crystallizing these kinds of solids is interesting because it allows for fine control over the extended structure's form and functioning as well as the constituents' stereochemical orientation. A novel type of porous covalent organic structure known as covalent organic frameworks (COFs) has a backbone made up only of light elements (B, C, N, O, Si). To create crystalline materials, organic building blocks are combined and covalently bonded into extended structures to form COFs. A compromise is found between the kinetics and thermodynamic reversibility of the linking processes to achieve crystals in a variety of ways. Due to its success, COF materials are now available with organic units C–N, B–O, B–N, and B–O–Si connected by strong covalent bonds.

It has been competent to anticipate the structures of the resultant COFs because the general geometry of COFs remains mostly unchanged when their organic constituents are linked. Because of this advantage, characterizing the COFs with powder X-ray diffraction (PXRD) methods has become simpler. Additionally, this approach has facilitated the creation and assembly of COF designs with appropriate composition, pore dimensions, and openings. In practical scenarios, the theoretical and actual PXRD patterns for a specific COF are juxtaposed. The level of similarity between these patterns lays the groundwork for deciphering and further distilling the crystalline structure of the intended COFs, which attributes render COFs a compelling category of novel porous materials. There is now a sizable and expanding library of linkers that may be used to create COFs, and Reticular synthesis produces unique COFs and topologies that are reported. To generate more crystalline COFs, a lot of research is also being done on forging new linkages between organic building components. These programs provide the potential to broaden the accuracy of molecular covalent chemistry into the realm of extended solid material., in addition to innovative COF chemistry and materials [2].

3. Synthetic Methods

The number of atoms, metal content, regulated composition of COFs, and stability of guest metal atoms in the SAC structure all influence the large-scale manufacture of COF-based SACs. To do this, new synthetic techniques for COF-supported SACs have been published. These techniques include post-metalation, a bottom-up solvothermal approach, photo deposition, pyrolysis using various precursors, post-modification by the introduction of metal dopants, etc.

3.1. Microwave Synthesis

Massive framework synthesis is discouraged by the solvothermal synthesis's prolonged reaction time and synthetic conditions [3-5]. Campbell et al. reported on an early method of overcoming this difficulty by utilizing microwave irradiation for COF production. A surface area of approximately 2000 mg was obtained by the quick manufacture of COF-5 (20 min), subsequently with purification and activation. This surface area is more than the surface value predicted by solvothermal methods synthesis. In a sealed microwave tube with an inert environment, building blocks are mixed in an appropriate solvent system to begin the general microwave synthesis process for creating COFs. It is essential to revitalize COFs using minimal surface tension solvents via Soxhlet extraction to monomers adsorbed in the pores and remove building blocks. Using microwave irradiation, COF-5, β -ketamine-linked, azine-linked, and imide-linked COFs were produced. For instance, Wei et al. demonstrated that TpPa-1 and TpPa-2 COFs could be synthesized in less than an hour when exposed to microwave radiation. Notably, as compared to the solvothermal preparation method, both COFs showed improved crystallinity and porosity. In a different study, Lee et al. used tris(4-aminophenyl) amine and pyromellitic dianhydride to perform microwave-assisted PI-COF synthesis.

3.2. Mechanochemical Synthesis

The process takes place at a high temperature, in an inert environment, and inside a sealed Pyrex tube. The creation of COFs via stable covalent bonding was made possible by a straightforward, affordable, and environmentally benign method known as mechanochemical synthesis. Even though this synthetic route has advantages, the as-synthesized COFs' poor crystallization and amorphous nature present a significant challenge. However, the crystallinity and porosity can be significantly increased by adding a solvent or molecule organizer, like *p*-toluene sulfonic acid frameworks. The β -ketenimine TpPa-1, TpPa-2, TpPa-NO₂, TpPa-F₄, TpBD-(NO₂)₂, TpBD-(OMe)₂, TpBpy, and other COFs were synthesized mechanochemically by manually grinding the building blocks using a pestle and mortar and then heating them at 170 °C for a minute. When compared to the frameworks created by the solvothermal method, the generated COFs showed reduced porosity and crystallinity. Furthermore, low porosity and crystallinity were displayed by the mechanochemical construction of sulfonate-acid-decorated NUS-9 and NUS-10 [6].

3.3. Ionothermal Synthesis

The majority of covalent triazine frameworks (CTFs) are amorphous materials without long-range order, whereas those produced by the ionothermal approach are crystalline in character [7]. The standard procedure involves placing organic zinc chloride building blocks in an ampule, sealing it, and heating it to a high temperature (350–450 °C) for two to three days. To get rid of the zinc chloride and unreacted monomers, the solid product is agitated in diluted hydrochloric acid after being cleaned with water. By adopting this procedure, cyanuric chloride was used to create crystalline CTF-1 and CTF-2 by the trimerization reaction. The ionic liquid was claimed to be used as the solvent in a more gentle and environmentally friendly synthetic method [2].

3.4. Room-Temperature Synthesis

To make COF nanobars, a solvent comprising carbon dioxide (CO₂) and water was utilized. In addition to being nonflammable and affordable, compressed CO₂ may change the properties of solvents, which in turn changes the structure and form of COFs. In the initial publication, COF nanosheets were produced utilizing the gram-scale approach, in which utilizing *n*-butyl lithium as an insertion agent, mine-linked 3D interpenetrated dia structures, namely 3D-IL-COF-1, 3D-IL-COF-2, and 3D-COF-3, were developed. This process involved mixing tetrakis(4-formyl phenyl)methane with 4,4''-diamino-*p*-phenylenediamine, *p*-phenylenediamine, and 4,4'-diaminodiphenyl, at ambient temperature in a solvent of 1-butyl-3-methylimidazolium bis(trifluoromethyl)sulfonyl)imide, as reported by Guan and his team. The three 3D IL-COFs exhibited high crystallinity and stability, with Brunauer-Emmett-Teller (BET) surface areas measured at 517 m²/g for 3D-IL-COF-1, 653 m²/g for 3D-IL-COF-2, and 870 m²/g for 3D-IL-COF-3. This achievement indicates new potential in mass-producing COFs using ionic liquid-based green solvents. Beyond eco-friendly solvents, Lewis acids like metal triflates have shown efficacy in expediting the creation of imine-linked frameworks at room temperature. Matsumoto and colleagues synthesized an imine-linked TAPB-PDA COF in just 20 minutes at room temperature using Sc(OTf)₃ (0.02 equivalents). However, other triflates like Eu(OTf)₃, In(OTf)₃, Yb(OTf)₃, Y(OTf)₃, and Zn(OTf)₃ were found less effective in producing crystalline TAPB-PDA frameworks. Sc(OTf)₃ yielded moderate crystallinity and porosity (692 m²/g), contrasting with the higher temperatures (70 °C) and longer durations (72 hours) required by traditional catalysts like acetic acid in solvothermal synthesis. In another study, Verduzco and team developed an imine-linked framework at room temperature using transition-metal nitrate catalysts. They attempted the condensation of 1,3,5-tris(4-aminophenyl)benzene and 2,5-dimethoxyterephthalaldehyde with various catalysts including Fe(NO₃)₃·9H₂O, Ni(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, Mn(NO₃)₂·6H₂O, Cu(NO₃)₂·6H₂O, and Co(NO₃)₂·6H₂O in different stoichiometric ratios. The most successful was 10 mol% Fe(NO₃)₃·9H₂O, producing a framework with high crystallinity and porosity (1345 m²/g). Other COFs like TAPB-OMePDA, TAPB-PDA, TAPB-BPDA, COF-V, TAPB-C8PDA, and TAPT-OMePDA COFs were also effectively

synthesized at room temperature with high porosity after activation with supercritical CO₂. Additionally, Zamora et al. demonstrated the formation of crystalline yellow gels at room temperature by reacting 1,3,5-tris(4-aminophenyl) benzene with benzene-1,3,5-tricarbaldehyde in m-cresol or dimethyl sulfoxide (DMSO) using acetic acid as a catalyst.

4. Outlook

4.1. Enhanced in Flexible Heterogeneous Catalytic Systems Efficiency

COFs have fundamentally altered the course of research and expanded the flexibility to examine effective heterogeneous catalytic systems. They offer a novel molecular platform for the construction of stable heterogeneous catalysts. The design of different interfaces that are crucial in regulating the interactions of excitons, electrons, holes, molecules, and ions, is a crucial aspect of the research of COF-based catalysts. Catalytic activity, selectivity, and yield are all determined by these interactions, which also regulate the kinetics and dynamics of the overall processes [8].

Mesoporous silicon crystals, MOFs, zeolites, and other inorganic porous materials may all be produced as polycrystalline solids with surfaces similar to those of COFs. Most COFs have pore structures that are identical to or nearly identical to virtual monocrystalline structures in terms of pore size and surface area. This implies that the structural integrity of the majority of COFs cannot be disregarded, even if they are not in a single-crystal form. In this regard, extensive control over characteristics and functionalities is made possible by the interface design of the majority of COFs with high porosity and crystallinity. Further investigation into the failure process and mechanism of the COF is anticipated to produce a much clearer image in this area. As of right now, the described is not at the point where a single or small number of flaws decide the functioning of functions. Further research is necessary to clarify the internal flaws of COFs. Materials with high crystallinity and porosity are classed as COF, and the general public should be aware of these criteria. Even yet, reports of "COF materials" persist to this day, despite their low porosity and crystallinity.

4.2. Great Probability of Developing Nanoreactors

The possibility of creating nanoreactors that significantly outperform molecular catalysts in terms of activity, selectivity, and durability is high because of the enormous multiple building blocks available to COFs. This necessitates carefully designing the interactions between the catalytic sites and the walls. To thoroughly investigate the limited region with a well-defined structure for new catalysis, it is an attractive issue to develop inaccessible catalytic systems using molecular catalysts. The creation of a distinct local point for every catalytic site, as seen in enzymes, by the use of channel walls, pore size, and shape is an intriguing topic deserving of more research. It's a difficult task to merge several catalysts using different barriers where multistep changes may be greatly aided by the synergistic effects between walls. Researchers should be able to construct heterogeneous catalysts with genuinely great performance thanks to these directions.

The light-driven hydrogen synthesis from water demonstrates the various ways in which COFs outperform other cutting-edge artificial antennas and semiconductors. With other systems, density, sequence, component, and are neither synthetically controllable nor amenable to structural designability. To successfully convert photoenergy into chemical energy, COFs hold great promise for organizing the reduction and oxidation sides into a single molecular system and creating a predesignated but seamless electron flow chart. By meticulously engineering the interactions between COFs and various entities such as photons, excitons, electrons, holes, ions, and molecules, artificial photosynthesis may be anticipated [9].

4.3. Controllable Design of 2D COFs

The polymer framework's dimensionality has a major role in determining the controlled chain configuration that may be achieved by covalent bonding [10,11]. In particular, symmetric (isotropic) or asymmetric (anisotropic) polygon topologies can be used to create 2D COFs. A COF with a unique

structural arrangement may be designed by combining multiple monomer geometries with different skeletons and pores thanks to the symmetric topological diagram. For example, [C4 + C2] and [C4 + C4] together

5. Conclusion

COFs play a significant role in the chemical industry and their invaluable qualities help build a thriving society. The search for a clean, renewable energy source is essential due to the world's growing energy consumption and the damage it does to the environment. One possible method for accomplishing this is photocatalysis, which uses solar energy to break down environmental pollutants or produce fuels like hydrogen and hydrocarbons. It is expected to propel the advancement of already available energy structures, serve as an inspiration for scientists in other domains, and boost the use of covalent organic structures in certain disciplines. Novel porous organic materials known as covalent organic frameworks have been thoroughly explored in some domains and are crucial to nanotechnology. Covalent organic frameworks' porous and crystalline character attests to the fact that reticular chemistry creates dynamic covalent bonds that build their structures. The created frameworks have special qualities including high porosity and thermal and chemical resilience thanks to dynamic covalent chemistry, which are crucial for industrial applications. The reported or proposed structures with varieties of pore sizes and shapes can be constructed using the design concepts. With more surface engineering or completely new methods, such varied pore geometries offer a multitude of chances to construct ideal electrical and three-dimensional environments. These accomplishments put COF in a unique position within materials science and chemistry. To address the regulation of synthesis from molecular to lattice geometries urgently, however, much more study is still required in this sector despite the numerous advantageous characteristics of COFs and the substantial progress that has been accomplished. The fabrication of COFs on a wide scale has been impeded by basic issues related to coupling chemistry, synthesis, crystallization, activation, controlled morphology, and crystallization. COFs are porous materials that show great promise and provide several benefits for use in catalysis. COFs are perfect for use as porous catalysts because of their large specific surface area, well-defined pores, strong chemical and thermal stability, and adjustable catalytically active sites. COFs with activated metals, COFs with active pendant groups, COFs with molecular catalysts, and COFs with active backbones or linkages are examples of COF-based catalysts.

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