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## Review

## Covalent organic frameworks as heterogeneous catalysts

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## ABSTRACT

Covalent organic frameworks (COFs), established as an emerging class of crystalline porous polymers with high surface area, structural diversity, and designability, attract much interest and exhibit potential applications in catalysis. In this review, we summarize the use of COFs as a versatile platform to develop heterogeneous catalysts for a variety of chemical reactions. Catalytic COFs are categorized in accordance with the types of active sites, involving single functional active sites, bifunctional active sites, and metal nanoparticles (NPs) embedded in pores. Special emphasis is placed on the deliberate or incidental synthesis strategies, the stability, the heterogeneity, and the shape/size selectivity for COF catalysis. Moreover, a description of the application of COFs as photocatalysts and electrocatalysts is presented. Finally, the prospects of COFs in catalysis and remaining issues in this field are indicated.

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## 1. Introduction

Covalent organic frameworks (COFs) are a class of crystalline porous materials that allow the atomically precise integration of pure organic units to create predesigned skeletons and nanopores based on reticular chemistry [1–8]. Different from metal-organic frameworks (MOFs), which could be obtained via the coordinative assembly between metal ions and organic ligands as the building units [9], COFs are linked to form through irreversible covalent bonds, which can be formed, broken, and reformed, allowing reaction systems with “error checking” and “proof-reading” characteristics to result in the formation of the most thermodynamically stable structures [2]. In 2005, Yaghi and co-workers demonstrated the first successful examples of COF synthesis [10]. Since this landmark paper, COFs have attracted extensive interest, and have become

one of the fastest-growing fields in both materials science and chemistry during the past decade. Depending on the dimension of building units, COFs can be categorized into two- (2D) and three-dimensional (3D) structures. 2D COFs are easier to be prepared than 3D COFs because of their structural simplicity. The covalently bonded planar sheets are stacked together through  $\pi$ - $\pi$  interactions, leading to the formation of eclipsed or staggered one-dimensional (1D) columnar arrays in 2D COFs. In contrast, 3D COFs are generally constructed based on a  $T_d$ -structure building block. 3D COFs possess not only extremely high surface areas, but also extraordinarily low densities, and, furthermore, the entire material is accessible for adsorbed molecules to “see” all the atoms of the framework. Both 2D and 3D COFs have an open network structure, which results in accessible channels or nanopores with uniform sizes ranging from angstroms to nanometers. Their unique structure is

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therefore attractive for many applications, including gas storage and separation [11–15], drug delivery [16–18], and energy conversion and storage [19–22]. In addition, through decoration with functional moieties, COFs can also be endowed with unique optical [23–27] and optoelectronic [28–30] properties. The structural and functional versatility and diversity of the constituent organic units create immense possibilities in COF materials.

The high porosity, functional versatility, easy modification, and outstanding stability of COFs make them ideal materials for catalysis applications. In particular, the assembly of COFs can be achieved by various designable and tailorable organic building blocks, which gives innumerable structural topologies and diversified porosities. Therefore, in contrast to traditional activated carbon and zeolites, the assembly approach endows COFs with unlimited structural models from “designable” crystal engineering. Meanwhile, using COFs as heterogeneous catalysts could have the following advantages, including (1) enhanced catalyst reactivity due to the spatial separation of multiple catalytic sites in the framework, endowing COFs with cooperative catalysis character; (2) permeable channels, allowing the facile access of substrates to the catalytically active sites within the COF pores, endowing the chemical reactions with shape-, size-, chemo-, or enantio-selectivity; (3) due to the flexibility and dynamics of the framework in the solid state, external stimuli, with a either physical, chemical, or environmental method, could bring new COF applications, like transition-state recognition. Furthermore, similar to other heterogeneous catalysts, the ability to separate for cycle utilization is highly attractive in large-scale reactions, especially when separation and waste disposal are costly.

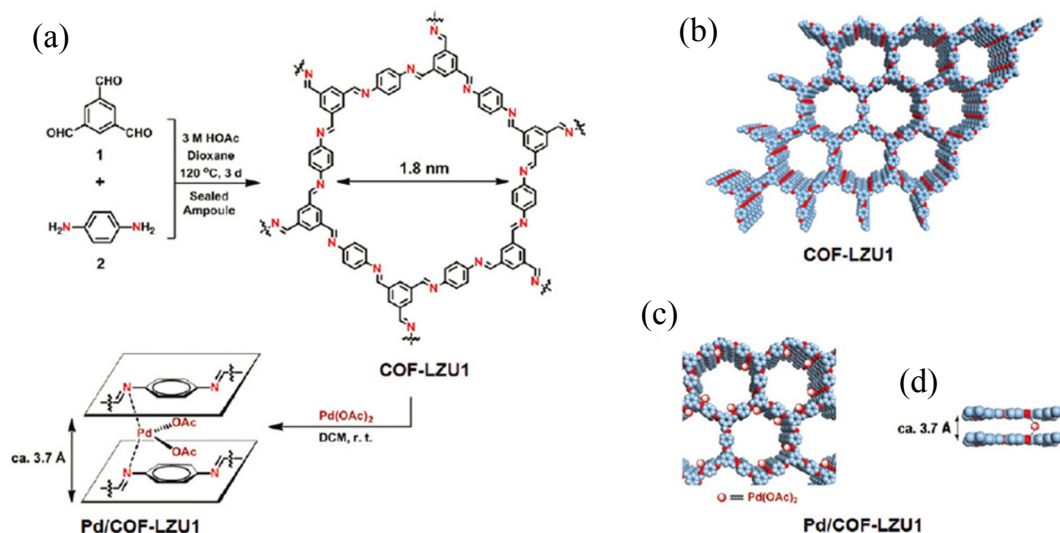
Using COFs in catalysis is a rapidly developing interdisciplinary research field. A recent review gives a short description of the preparation and functionalization of COF materials, as well as of their catalysis applications [31]. In the present paper, we present a thorough review of the recent advances in catalytic

COF materials. For the sake of discussion, COFs are categorized based on the type of catalytic sites, including single functional active sites, bifunctional active sites, and metal nanoparticles (NPs) embedded in pores. We mainly summarize the deliberate or incidental preparation strategies, the stability, the heterogeneity, and the shape/size selectivity of COF catalysts. In addition, using COFs as photocatalysts and electrocatalysts is introduced.

## 2. COFs with reactive functional group

In contrast to inorganic porous materials, COFs can be easily decorated with molecular catalysts that may acquire activities and selectivities comparable to their homogeneous analogues. Similar to MOFs, many COFs are synthesized in various fashions that easily enable straightforward incorporation of functional groups and, therefore, open a potential experimental environment for using COFs as catalysts. In general, there are two strategies that can be used for constructing catalytic COFs [31]. One methodology involves the post-synthetic integration of catalytic sites into a COF skeleton. This post-synthetic modification approach can reduce the influence of bulky catalytic sites on COF crystallinity, and the undesired effect of harsh solvothermal conditions on the catalytic sites. This is, by far, the method most used for the modification of COFs. Another is the bottom-up strategy that uses building blocks possessing catalytic sites to directly construct COFs. However, this strategy generally requires tedious solvothermal synthesis. In particular, if a bulky catalytic site is attached to building blocks, it will be difficult to obtain crystalline COFs. So far, the construction of covalently linked, yet highly active, COF catalysts still remains a synthesis challenge in the field.

A pioneer work using COFs as catalysts was reported by Wang and co-workers [32]. They constructed an imine-based COF material, COF-LZU1, and its 2D layered-sheet structure provides an exactly suitable space to coordinate with Pd(OAc)<sub>2</sub>



**Fig. 1.** (a) Schematic of the synthesis of COF-LZU1 and Pd/COF-LZU1 materials. Proposed structures of (b) COF-LZU1 and (c, d) Pd/COF-LZU1 possessing regular microporous channels (diameter of ~1.8 nm), simulated with a 2D eclipsed layered-sheet arrangement. C, blue; N, red; and brown spheres represent the incorporated Pd(OAc)<sub>2</sub>. H atoms are omitted for clarity. Reprinted with permission from Ref. [32].

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