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Catalytic applications of porous organic polymers in cross-coupling reactions

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Spotlight Paper

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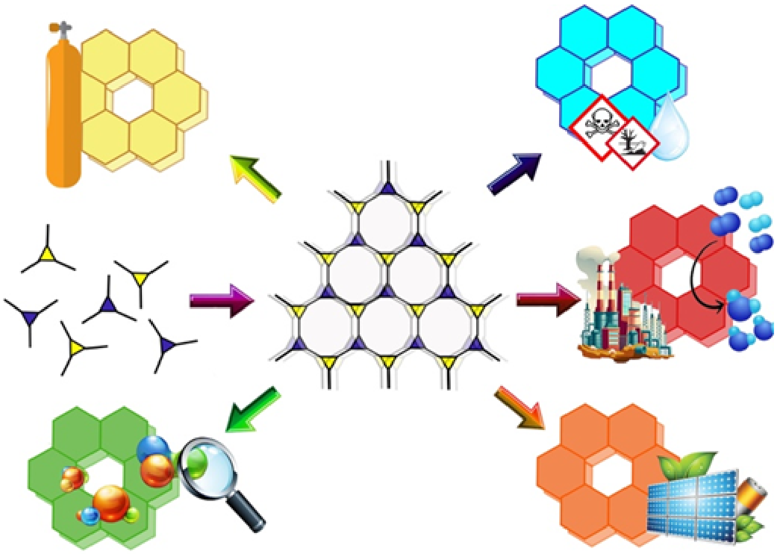
Abstract:

Erfan Abdoli was born in Kermanshah, Iran in 1997. He completed his undergraduate studies in Medical Chemistry at Azad University in Kermanshah, Iran in 2021, and he currently continues his education by pursuing a master's degree in Organic Chemistry starting in 2022, with the esteemed Professor Mohammad Ali Zolfigol as his supervisor. His research interest is the design, synthesis and characterization of porous organic polymers and exploring their potential applications in catalyzing organic functional group transformations.

Introduction

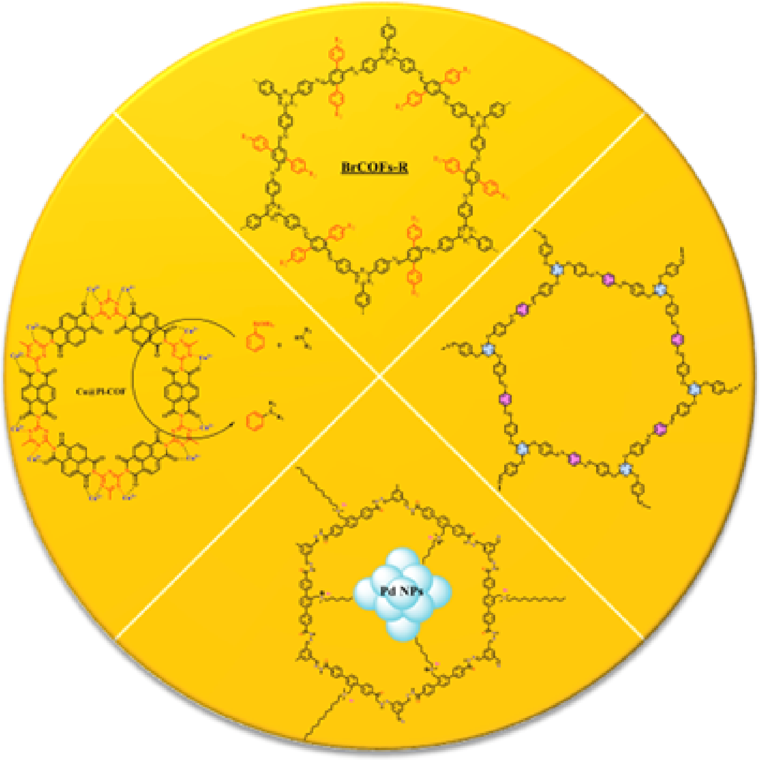
Catalysts play an important role in chemical transformations. Nearly all biological and organic reactions, as well as industrial processes, need catalysts. Nonetheless, these materials have some defects, such as the generation of highly toxic wastes and time-consuming catalyst separation [1]. Catalysts are classified into three categories: homogeneous, heterogeneous, and enzymatic systems [2–4]. A revolutionary advancement in many technologies and industries has been made through developing porous organic polymers (POPs) as a new category of porous materials. These materials possess exceptional characteristics such as high surface areas, robust physical and chemical stability, and adjustable organic functionalities [5]. Notable examples of POPs include zeolitic imidazole frameworks (ZIFs), covalent microporous polymers (CMPs), metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and nanoporous ionic organic networks (NIONs) [6]. The first COFs have been synthesized by Yaghi and co-workers in 2005. COF materials are synthesized by covalently linking organic molecules in a repetitive manner, resulting in a porous crystal structure that is ideal for gas adsorption and storage [5] Scheme 1. These reticular, sustainable as well as environmentally gentle materials possess unique properties such as high thermal and chemical stability, regulatable physicochemical characteristics, metal-free and flexible scaffolds, extremely low density, high surface area, tolerable charge-carrier mobility, and large pore sizes [7]. In catalytic applications, COFs have desirable properties. Their special channel structure and harmonic porosity provide efficient access to active sites and fast mass transfer for catalytic reactions. Moreover, the large superficiality of COFs allows the generation of well-dispersed catalytic sites reacting with substrates in a highly systematic and selective manner [8, 9]. The catalytic C-C coupling reactions are very powerful and well-known chemical tools in organic synthesis.

The number of coupling reactions is Miyaura-Suzuki (boron-mediated), Corriu-Kumada-Tamao (magnesium-mediated), Kosugi-Migita-Stille (tin-mediated), and Neghishi (zinc-mediated). Sonogashira (copper-mediated), Heck-Mizokori (Pd-mediated), and Hiyama (Pd-mediated) [11, 12]. The most widely used reaction for the formation of carbon-carbon bonds is the Suzuki cross-coupling reaction, Suzuki cross-coupling reactions, that has been discovered by Nobel laureate Akira Suzuki [13, 14]. Due to the primacy of gentle synthetic conditions, high tolerance



Scheme 1. Several applications of COFs [5].

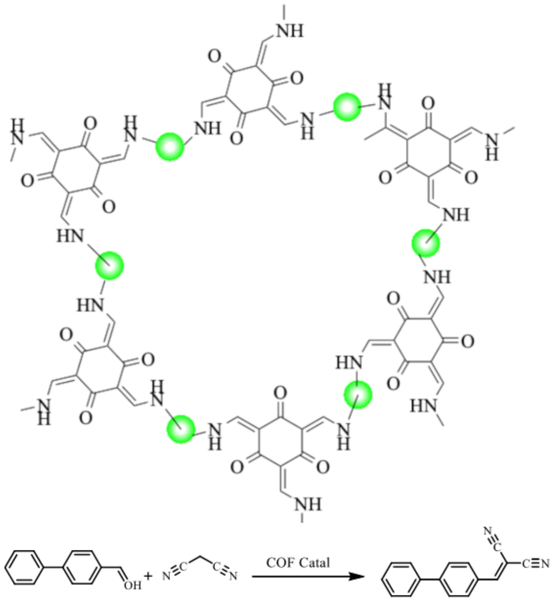
to functions, ease of transportation and severance, stability of precursors, as well as orthogonality, the Suzuki-Miyaura cross-coupling is particularly useful in the application of synthetic and natural materials [10] (Scheme 2). Nickel, gold, and palladium are essential for the synthesis of complex and functional allylic molecules via cross-coupling techniques. In recent decades, a variety of solid-supported palladium catalysts have been developed using materials such as activated carbon, inorganic oxides, metal-organic frameworks (MOFs), silica, and porous organic polymers (POPs) to enhance both their catalytic activity and stability. A successful solid-supported metal catalyst must ensure that metals like palladium are evenly dispersed to avoid aggregation. To achieve this supports often incorporate chelating groups, including phosphine ligands and amine groups, or feature heteroatoms such as nitrogen, sulfur, and phosphorus. These modifications not only improve the chemical and electrical properties of the support but also strengthen its interaction with metal catalysts. Notably, extensive research has shown that nickel-based catalysts exhibit greater versatility and effectiveness in facilitating C–C, C–N, and C–P bond-forming reactions with a wide range of electrophiles, particularly in scenarios where palladium catalysts may face challenges [15–18].



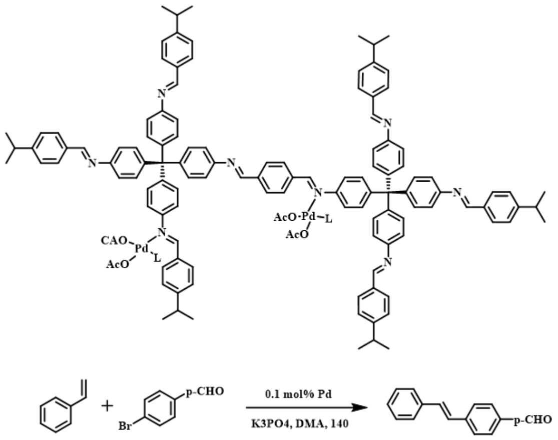
Scheme 2. Several COF-based catalysts in cross-coupling reactions [10].

Abstract:

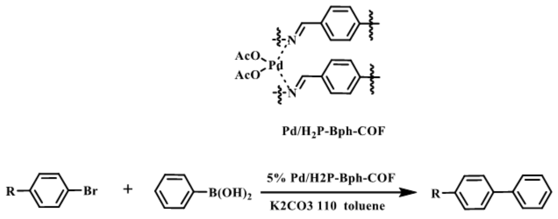
(A) In 2020, Jikuan Qiu and colleagues developed an eco-friendly method for synthesizing hyper-crosslinked covalent organic frameworks (HP-COFs) using ionic liquids (ILs). The process results in highly crystalline, stable frameworks with adjustable porosity based on the alkyl chain length of the ILs, allowing for tailored applications. Notably, these HP-COFs have exhibited enhanced catalytic activity for carbon-carbon bond formation, particularly for larger molecules, highlighting their potential in organic synthesis and green chemistry. Their synthesis is rapid, completing in just 12 hours under mild conditions [19].



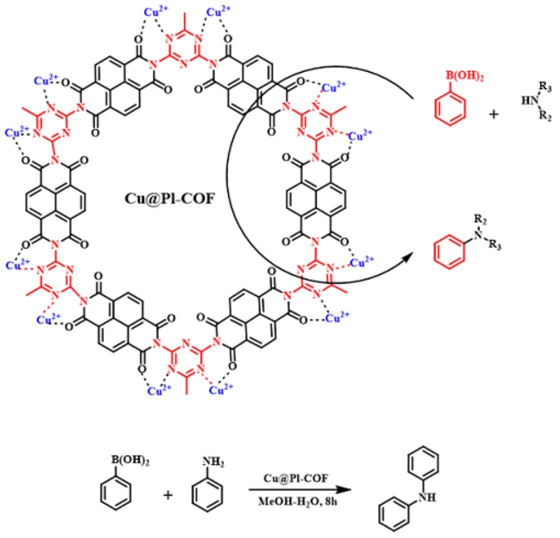
(B) In 2016, Raoni et al. explored the potential of covalent organic frameworks (COFs) in catalysis, specifically focusing on the COF-300 topology for palladium-catalyzed cross-coupling reactions. Recognizing the limited number of samples available for this application, they hypothesized that the imine groups present in the COF-300 structure could serve as effective coordination sites for palladium salts, creating a stable complex within the nanostructured material. In their study, they introduced a palladium salt-modified variant, $Pd(OAc)_2$@COF-300, and demonstrated its efficacy as a catalyst for cross-coupling reactions. This innovative approach not only highlighted the versatility of COFs in catalysis but also opened new avenues for the development of efficient and sustainable catalytic systems [20].



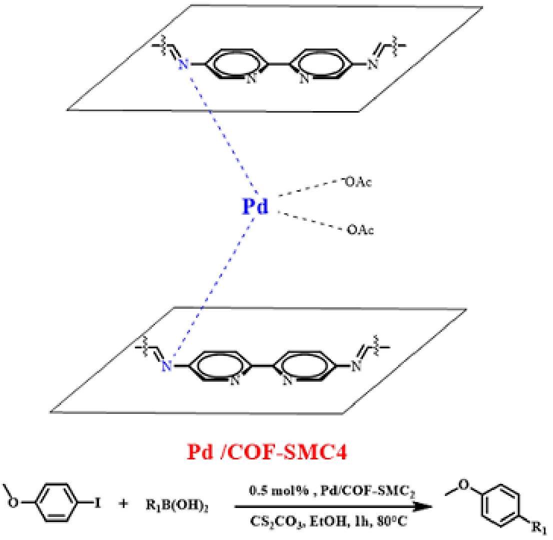
(C) In 2015, Hou et al. investigated the catalytic properties of H_2P-Bph-COF, which features a rich and periodically distributed network of nitrogen atoms. These nitrogen sites effectively stabilize and uniformly disperse palladium ions within the COF structure. This unique arrangement resulted in exceptional catalytic activity for the Suzuki coupling reaction between aryl boronic acids and bromoarenes, achieving a remarkable yield of 97.1% under mild conditions. To characterize the synthesized catalyst, the researchers employed FT-IR spectroscopy and solid-state NMR analysis, providing insights into its structural properties. Additionally, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were utilized to examine the catalyst's morphology, further confirming its promising potential for catalysis [21].



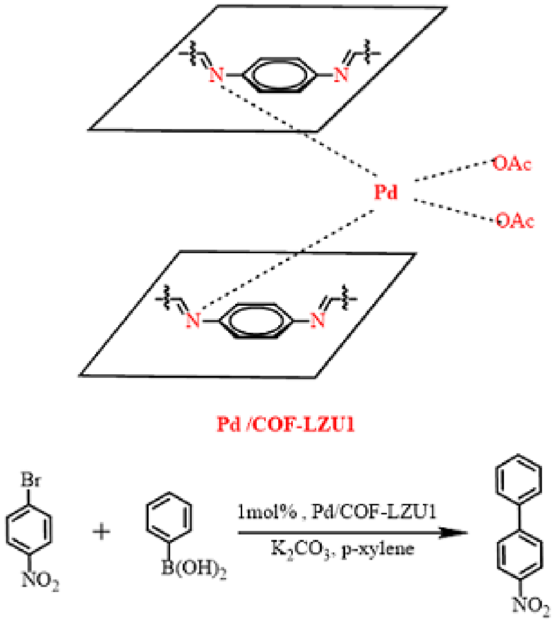
(D) In 2018, Yi Han et al. created a polyimide covalent organic framework (PI-COF) using inexpensive reagents, which demonstrated excellent chemical stability and thermal resistance. This framework served as an effective support for heterogeneous copper catalysts. The Cu@PI-COF catalyst facilitated the Chan–Lam coupling reaction between aryl boronic acids and amines without requiring bases or additives. It exhibited high catalytic activity and could be reused for at least eight cycles without structural changes, making it easily recoverable through filtration. The synthesis was cost-effective and environmentally friendly, operating solvent-free with no hazardous waste. The copper content in the framework reached 5.33 wt%, as confirmed by ICP-MS analysis, showcasing the system's efficiency [22].



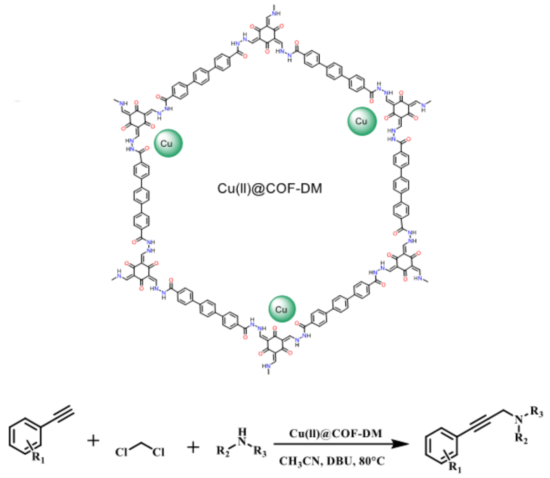
(E) In 2021, Jianguo Liu and colleagues developed a simple method to synthesize covalent organic frameworks (COFs) that support palladium (Pd) nanoparticles as catalysts. This catalyst effectively facilitates region-selective Suzuki-Miyaura coupling (SMC) reactions between aryl halides and aryl boronic acids, especially with halogenated boronic acids. The strong coordination between the COF and active Pd(II) species is crucial for its performance. The optimized Pd/COF-SMC2 catalyst shows excellent efficiency under mild conditions and with less hazardous solvents, allowing for precise regulation of the active Pd species, which improves reaction selectivity and efficiency [23].



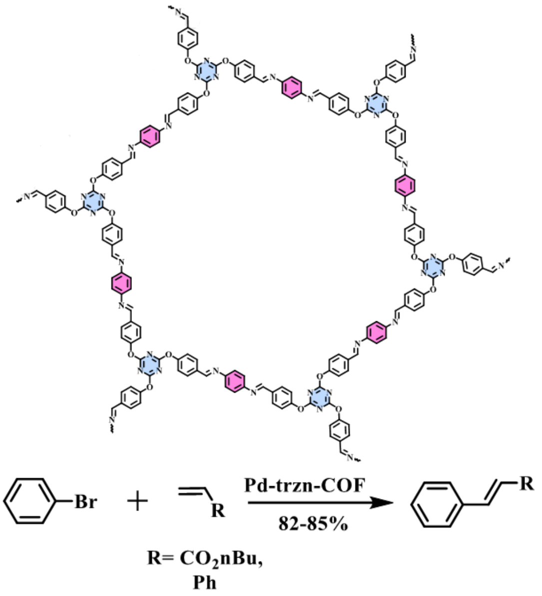
(F) In 2011, the San-Yuan Ding group developed an imine-based covalent organic framework (COF) called COF-LZU1 using accessible starting materials. Its two-dimensional structure and eclipsed imine bonds make it suitable for metal ion coordination, confirmed by spectroscopic analyses showing effective incorporation of palladium acetate ($Pd(OAc)_2$). The resulting Pd/COF-LZU1 was used as a catalyst for the Suzuki-Miyaura coupling reaction, demonstrating excellent activity, a wide range of reactants, high yields, stability, and recyclability, highlighting its potential for practical organic synthesis applications [24].



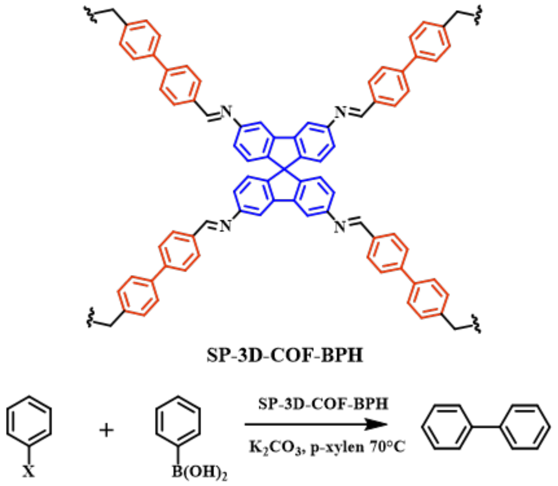
(G) In 2021, Xuan Kan and the Cowerks team synthesized a novel covalent organic framework (COF) called COF-DM, which features chelating coordination sites and can be produced at the gram scale under mild conditions. They then created a Cu(II)-loaded complex, Cu(II)@COF-DM, using a solid-state coordination method with $CuCl_2$ in acetonitrile. This complex exhibited significant catalytic activity as a heterogeneous catalyst for alkyne-dihalomethane-amine coupling reactions, demonstrating the versatility of COFs and their potential for efficient organic synthesis [25] .



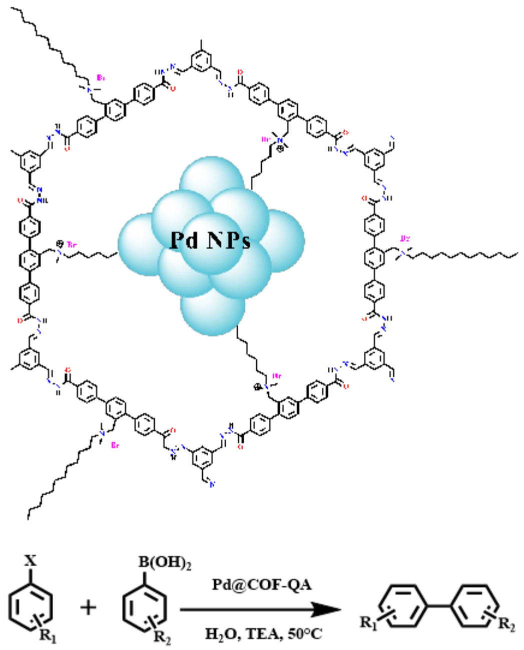
(H) In 2015, Dinesh Mullangi and colleagues developed a nitrogen-rich triazine-based covalent organic framework (trzn-COF) designed for the efficient single-step loading of palladium (Pd^0) nanoparticles. The triazine structure effectively mimics the fundamental pyridyl classification, facilitating the reduction of Pd^{2+} to Pd^0 in an alcoholic medium. The resulting Pd-trzn-COF exhibits remarkable hydrolytic stability, ease of handling, and excellent recovery, making it highly suitable for a wide range of Heck-type reactions and carbon-carbon bond formation processes. Furthermore, its recyclability enhances its appeal as a versatile catalyst in organic synthesis [26].



(I) In 2020, Yamei Liu and colleagues created a novel three-dimensional covalent organic framework (3D COF) called SP-3D-COF-BPY, using spirobifluorene and bipyridine as building blocks. This framework showed great promise in heterogeneous catalysis, particularly as a support for Pd(II) catalysts. Its structure, characterized by powder X-ray diffraction and computational simulations, features a sevenfold interpenetrated diamond-like architecture with high densities of Pd(II) coordination sites. The framework includes unobstructed one-dimensional channels that allow easy access to reactants. The SP-3D-COF-BPY achieved a high Pd(II) loading of about 15 wt%, resulting in the Pd(II)@3D-COF-BPY composite, which enhances its catalytic efficiency and positions it well for various organic synthesis applications [27].



(J) In 2020, Wang et al. developed a new catalyst system by loading palladium nanoparticles (Pd NPs) onto a covalent organic framework (COF) modified with N, N-dimethyl dodecyl ammonium bromide, named Pd@COF-QA. This composite was integrated into a chitosan aerogel-based continuous flow reactor, proving effective as a phase-transfer catalyst for the Suzuki-Miyaura coupling reaction in water under mild reaction conditions and at gram-scale. The Pd NP-loaded COF was created via an in-situ reduction method, and the quaternary ammonium salt improved its catalytic performance. Pd@COF-QA effectively facilitated the coupling of phenyl chloride and phenylboronic acid, demonstrating its versatility. This COF-based integration enhances the efficiency and sustainability of C-C coupling synthesis, showcasing the potential of COF materials in the catalytic processes [28].



Availability of data and materials
The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Conflict of interests
The author 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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