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Hybrid reticular chemistry-based catalysis

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Spotlight

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Milad Mohammadi Rasooll was born in Hamedan, Iran in 1995. He received his B.Sc. in pure Chemistry (2018) from Bu-Ali Sina University, Iran. He received his M.Sc. in Organic Chemistry (2021) under the supervision of Prof. Mohammad Ali Zolfigol. He was also accepted into a Ph.D. program in organic chemistry at the Bu-Ali Sina University in the same year. His research interests are the synthesis, characterization, and application of homogeneous and heterogeneous reagents and catalysts in organic synthesis.

1. Introduction

Reticular chemistry is the chemistry of linking organic and inorganic building units by strong bonds to create porous 2-dimentional2-dimensional (2D) or 3D crystalline fortified frameworks. Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), graphene oxide (GO), and carbon nanotubes are general examples of reticular chemistry-based materials. Among these, MOFs and COFs have emerged as outstanding materials in reticular chemistry, owing to their unique and invaluable properties such as high thermal and chemical stability, high porosity, and tunable post-synthetic modification capabilities. MOFs are constructed by organic-inorganic building blocks, and COFs are assembled by organic covalently strong linkages. Until about 25 years ago, the connection between organic and inorganic synthesis was underdeveloped. The instability of the resulting products and the challenge of achieving microscopic reversibility in reactions hindered the formation of extended 2D and 3D reticular structures through strong chemical bonds [1–5].

For decades, the development of reticular chemistry was largely limited to discrete molecular and one-dimensional polymeric structures. Meanwhile, inorganic reactions were typically conducted under thermodynamic conditions, where simple precursors were used to construct highly crystalline and symmetric extended architectures [9–12]. At a fundamental level, the relationship between a molecule and an atom is analogous to that between a framework and a molecule. In other words, the molecule fixes the atom in a specific geometry and spatial arrangement, and the framework fixes the molecule in a specific geometry and spatial arrangement [13].

Since the late 1980s, the arrangement of chemicals with both organic and inorganic compounds properties has led to the revolution of a new class of compounds called organic-mineral hybrids (OIHs) [14, 15]. The hybrid reticular chemistry is a contribution of both organic and inorganic components. The unique characteristic of these materials is their well-defined molecular scaffold, constructed from inorganic and organic moieties [16, 17]. Reticular hybrids combine the benefits of their parent components, making them suitable for a wide range of potential applications. Inorganic materials provide high thermal and mechanical stability, while organic components offer advanced features such as chemical selectivity, hydrophobicity, chemical stability, task-specific designability, and electronic potential applications. This class of compounds has diverse applications, including optics, gas absorption, energy storage and conversion, catalysis, environmental remediation, drug delivery, and bone repair [6–8, 18–24]. In this spotlight, recent advances in the catalytic applications of hybrid reticular compounds are reviewed (Fig. 1).

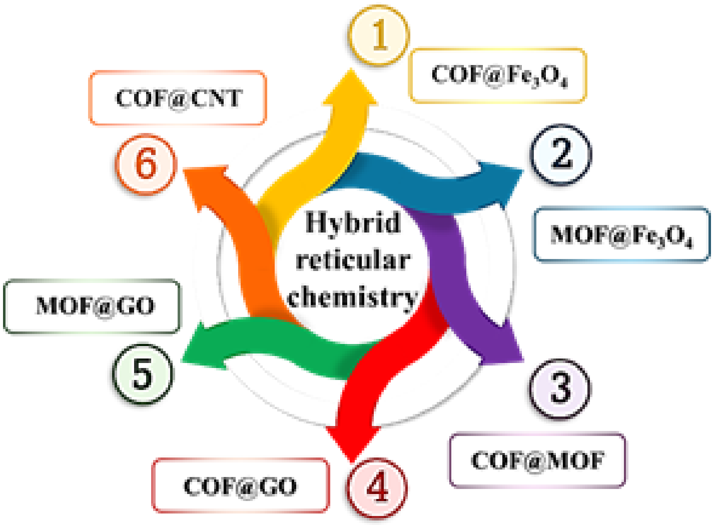
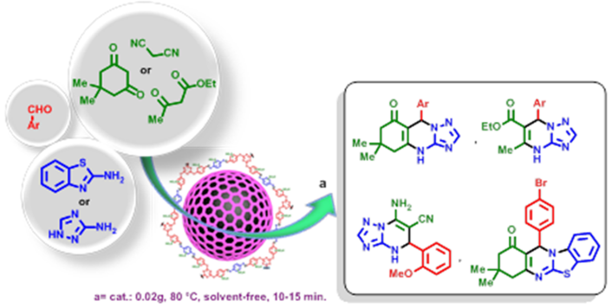


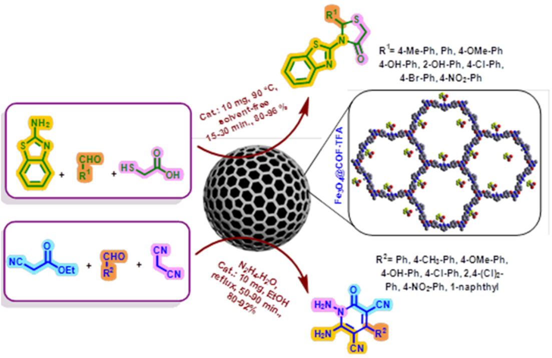
Figure 1. The number of reported hybrid reticular chemistry-based catalysis.

Abstract:

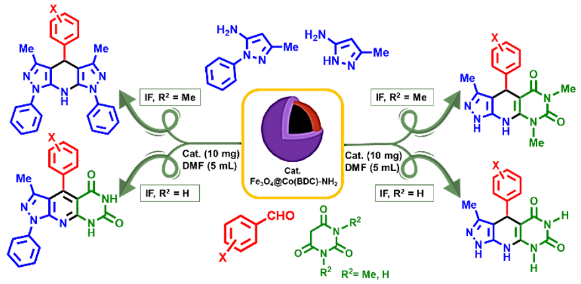
(A) In 2023, Zolfigol et al. designed and synthesized the Fe_3O_4@COF–SO_3H as a hybrid reticular catalyst and used it as an efficient heterogeneous catalyst in the synthesis of triazolo quinazolinones and 4H-pyrimidobenzothiazoles. The catalyst demonstrated high activity, easy recovery, and reusability. Moreover, the abovementioned compounds were produced under mild reaction conditions, and they have short reaction times and high yields [6].



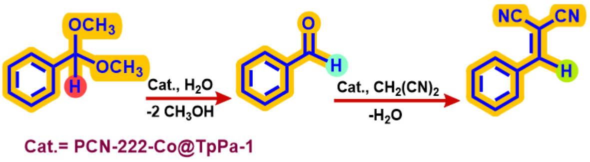
(B) In a study reported by Zolfigol's research group in 2024, a novel magnetic covalent organic framework (MCOF) decorated with trifluoroacetate as ionic segments (Fe_3O_4@COF-TFA) was designed and fabricated. This catalyst was used as a recyclable heterogeneous catalyst for the synthesis of 2,3-disubstituted thiazolidin-4-ones and N-amino-2-pyridones via a multicomponent methodology. It is noteworthy that the synthesized derivatives were obtained in excellent yields with short reaction times [7].



(C) Another class of hybrid reticular compounds is MOF@Fe_3O_4 that has been designed and synthesized as a new magnetic metal-organic framework, namely Fe_3O_4@Co(BDC)-NH_2. The mentioned MOF was used as a magnetic porous catalyst for the synthesis of new pyridines and 1,4-dihydropyridines with pyrazole and pyrimidine moieties. The newly synthesized catalyst exhibits facile workup, high efficiency, short reaction times, high thermal stability, and reusability [8].

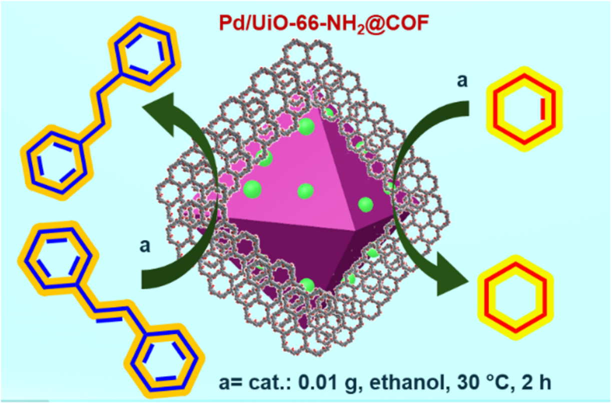


(D) Ming-Liang Gao et al., synthesized a novel bifunctional core-shell MOF@COF (PCN-222-Co@TpPa-1) via strong π-π stacking interactions. The constructed COF has imine linkages that enhance its crystalline structure. This hybrid reticular catalyst plays a dual role due to the presence of acid–base active sites, enabling it to catalyze the deacetalization–Knoevenagel condensation reaction. The platform features Lewis acid and Brønsted base active sites, which interact strongly with reactants, demonstrating that the bifunctional catalyst is highly efficient for one-pot cascade reactions. Moreover, the catalyst exhibits chemical, thermal, and recyclability stability [21].

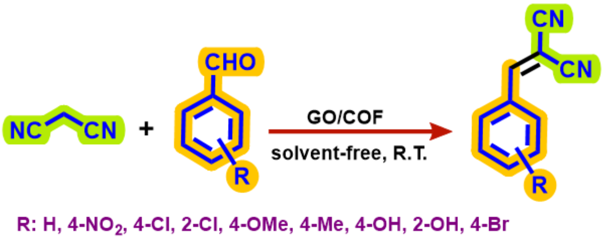


(E) Dengrong Sun's research group developed a hybrid system of MIL-125 and imine-linked COF decorated with Pd as a novel platform for photocatalysis. The catalyst shows significant photocatalytic performance in dehydrogenation and hydrogenation reactions. It demonstrates a synergistic "donor–mediator–acceptor" system among the three components: the metal serves as the active center, the MOF core functions as the electron donor, and the COF shell acts as the electron transfer medium [22].

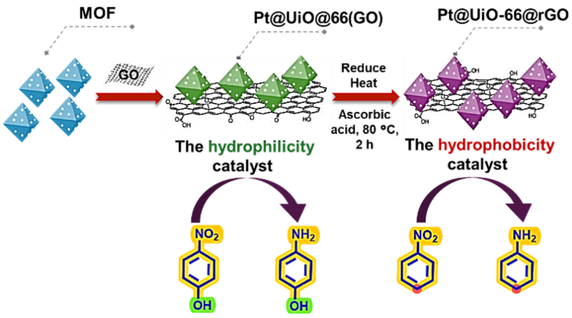
(F) Taking advantage of the extraordinary properties of MOFs and COFs, Weiqiang Zhou's research group designed and synthesized the sandwiched heterogeneous catalyst using an imine-linked COF and a Pd-decorated MOF (Pd/UiO-66-NH$_2$@COF) for the hydrogenation of olefins. The system is made of a UiO-66-NH$_2$ MOF core, functionalized with palladium nanoparticles, and then coated with COF as the outer shell [23]. This system shows high activity and excellent substrate size selectivity.



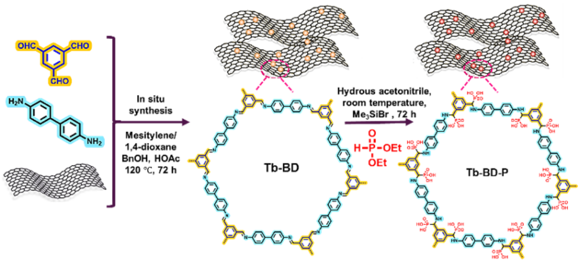
(G) In 2020, Rafiee and Monehzadeh synthesized a reticular hybrid based on GO and COF via a simple solvothermal method. This reticular hybrid was used as an excellent and cost-effective catalyst in the Knoevenagel condensation. The products were synthesized under solvent-free conditions, at room temperature, with short reaction times and high yields (84-100%). This catalyst could be reused at least 8 times without significant loss of activity [24].



(H) Xinyi Chen's research group reported the synthesis of a highly active heterogeneous catalyst: GO@UiO-66 modified with Pt nanoparticles. The catalyst showed high activity in the reduction of 4-nitrophenol but is ineffective in reducing hydrophobic compounds like nitrobenzene (controllable wettability). In contrast, Pt@UiO-66@rGO, with hydrophobic characteristics, efficiently reduces nitrobenzene, showing better performance than with 4-nitrophenol. During the chemical reduction at 80°, the hydrophilic catalyst was converted to a hydrophobic catalyst, and the color of the mixture changed from yellow to black [25].



(I) Photocatalytic reduction is a creative and effective strategy for U(VI) recovery and wastewater treatment. Recently, Qiu and coworkers investigated the photocatalytic reduction of uranium by using phosphorylated COF/rGO composite. The introduction of phosphate groups enhances the electronegativity and hydrophilicity of the material, while it benefits from the inherent thermal and chemical stability of the reported COF/rGO (Tb-BD-P/rGO). Therefore, the COF component facilitates efficient uranium transport, while the rGO component acts as an effective photothermal material [26].



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 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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