

Zr-based Metal-Organic Frameworks (Zr-MOFs): As multi-purpose catalysts

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

In recent years, metal-organic frameworks (MOFs) are an emerging class of porous materials that have expanded rapidly. This category of porous compounds has a high design ability due to the variety of ligands and metals that are the main structure of these materials [1,2]. The basis of forming these porous materials is organic-inorganic hybrid crystalline materials that include a metal core connected to organic ligands by strong coordination bonds. To produce MOFs based on different structures and characteristics, various synthetic methods such as slow diffusion, with the help of microwaves [3-6], chemical mechanics [7-9], and electrochemical methods [10,11], heating and ultrasonic waves [12], as well as the conventional hydrothermal and solvothermal method, can be used [13,14]. However, many other synthetic methods and parameters, such as temperature, reaction time, pressure, pH, and solvent must also be considered [15]. Metal-organic frameworks are among the most interesting materials due to their high chemical, physical and thermal stability compared to other

porous compounds [16]. MOFs can be summarized in various fields, including catalytic, photocatalytic, and environmental applications such as batteries, sensors and separation, adsorption or removal of hazardous substances, and biological applications such as drug delivery, and optical devices (**Fig. 1**) [17,18]. The most important reason for the widespread use of these materials is their high surface area and porosity, which has given these compounds distinctive characteristics compared to other similar compounds [19-21]. One of the most important classes of metal-organic frameworks is Zr-based MOFs. Zr-based MOFs have shown excellent thermal stability and high chemical resistance. Zr-based MOFs have different morphologies and topologies, such as bcu, csq, ftw, etc. These differences are due to the diversity in the selection of different ligands [22, 23]. One of the most important applications of MOFs is the catalytic and photocatalytic use of this type of porous material, and Zr-based MOFs have been widely expanded in this field [24-26]. In this study, an

attempt has been made to briefly investigate the catalytic and photocatalytic applications of MOFs based on Zr metal in chemical processes. Zr-based MOFs as a photocatalyst and catalyst application in various reactions, including hydrolysis,

hydrogenation, cross-coupling reactions oxidation, reduction, synthesis of spiroxindoles, multicomponent reactions, ring-opening reactions, and epoxidation are investigated (Fig. 2).



Fig. 1. Different applications of metal-organic frameworks.

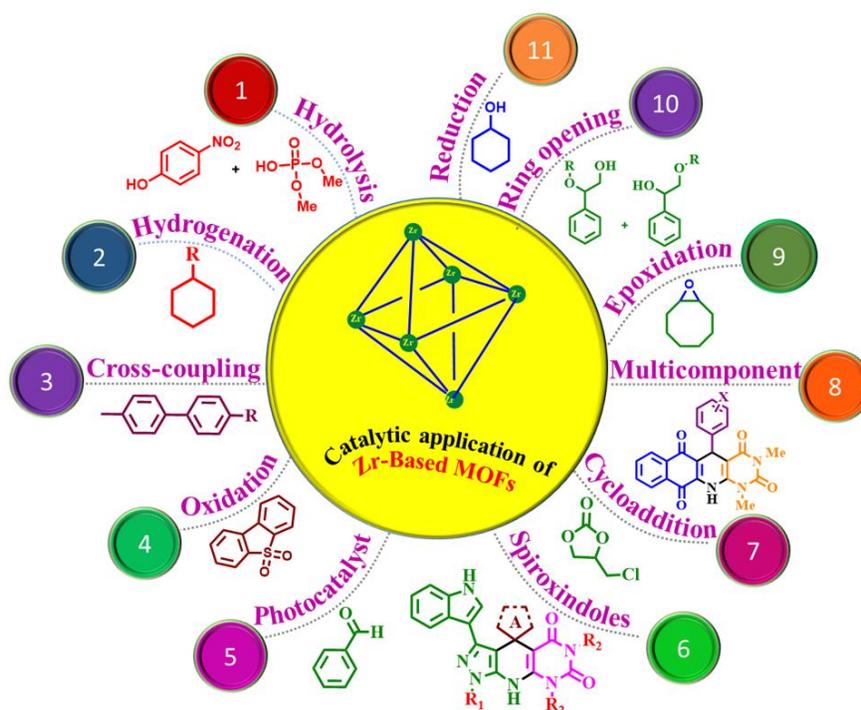
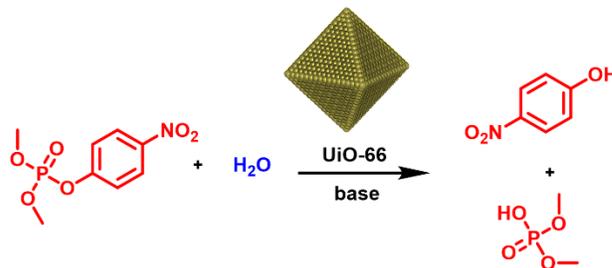


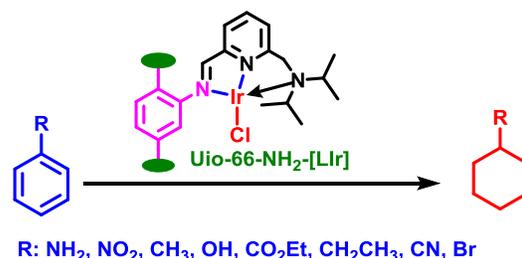
Fig. 2. Various catalytic applications of Zr-based MOFs

Abstracts

(A) In 2019, Ki Yong Cho *et al.* used Zr-based MOFs as a catalyst for the hydrolysis reaction. In this report, they have shown that this category of metal-organic frameworks has a high catalytic performance. Zr-based MOFs have been used as Lewis acid, and in this regard, the catalytic activity has increased by reducing the volume of the solvent. Catalytic application of three different synthesized UiO-66 catalysts has been used to hydrolyze the nerve agent simulant methyl paraoxon (MPO). The hydrolysis efficiency has been increased by controlling the density of defects and the particle size of UiO-66. In addition to these cases, in this report, an acceptable reaction mechanism in the nucleophilic attack by the hydroxide group is proposed based on the computational simulation, which influences the catalytic performance of UiO-66 [27].



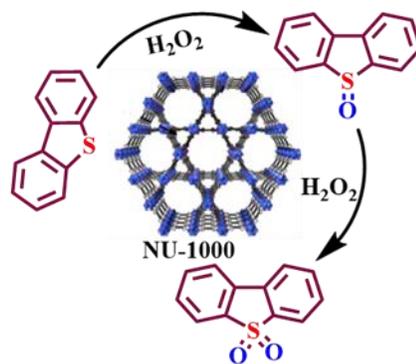
(B) In another report, in order to develop the advantages of Zr-based MOFs for other catalytic processes, in 2014, an Ir-Zr-MOF catalyst was designed and synthesized using the method of post-modification of metal-organic frameworks. In this catalyst, iridium is placed on Zr-based MOFs. The multifunctional iridium-Zr-based MOF heterogeneous catalyst can efficiently catalyze the hydrogenation of aromatic compounds in high yield under mild conditions. Among the advantages of this catalyst is its recyclability, which can be easily recycled with high conversion efficiency up to five cycles and has shown to be an attractive choice for green industrial and synthetic applications [28].



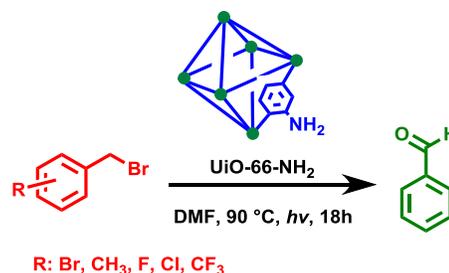
(C) In 2020, Seungsoo Kim and co-workers introduced a MOP-BPY-supported single Pd as a novel heterogeneous catalyst for the Suzuki-Miyaura cross-coupling reaction. These reactions were carried out under an aqueous solution. The results show that the coupling efficiency of the Suzuki-Miyaura cross-coupling reaction exhibited more than 90%, which is excellent compared to Pd molecular complex and metal-organic framework (MOF). Moreover, the Pd of MOP-BPY (Pd) has been successfully recovered and recycled without performance loss [29].



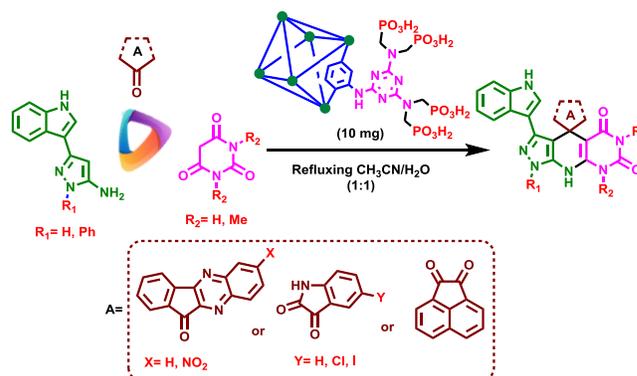
(D) One of the most important organic reactions is the oxidation reaction, for which many methods have been reported in recent years. In a report, a Zr-based MOF has been used as a catalyst in the oxidation reaction of sulfur compounds. The oxidants which have been used in this reaction are such as hydrogen peroxide and NU-1000. Zr-based MOFs are effective catalysts in oxidation reactions. Under optimal conditions, the conversion of dibenzothiophene has reached 100% in 180 minutes. In this report, the removal of other organic sulfur compounds, 4,6-dimethyl dibenzothiophene, 3-methyl benzothiophene, and benzothiophene is also investigated. It is known that the reactivity of compounds depends on their structure. NU-1000 has shown excellent stability in the oxidation performed and can be reused for four cycles without apparent loss of its corresponding activity [30].



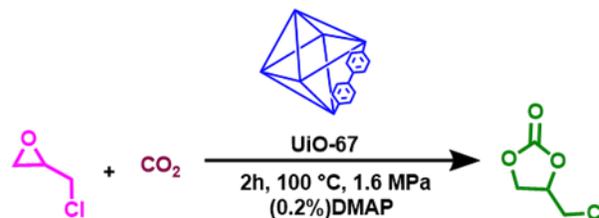
(E) In another discovery, the metal-organic framework based on zirconium (UiO-66-NH₂) has been used as an efficient heterogeneous photocatalyst for the conversion of benzyl halides to the corresponding aldehydes with high selectivity (about 80%) and conversion (up to 99%) in the presence of oxygen and DMF as solvent. In this transformation, the photoelectrons produced from UiO-66-NH₂ under visible light have caused the conversion of O₂ to [•]O₂⁻ radicals, which mediate the oxidation of benzyl bromides to create the corresponding benzaldehydes with high conversion and selectivity. This study provides a general, environmental, and highly selective method to prepare benzaldehydes and broadens the application fields of UiO-66-NH₂ [31].



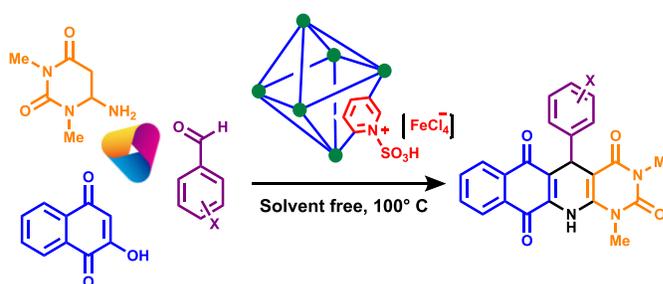
(F) Recently, Zolfigol *et al.* have introduced a novel metal-organic framework with phosphorous acid tags namely UiO-66-NH₂/Melamine/[N(CH₂PO₃H₂)₂]₂ as a porous and heterogeneous catalyst. The reported catalyst showed good catalytic efficiency in synthesizing novel spiro-oxindoles with pyrazole, indole, and uracil moieties as a biological structure. The special structure and morphology of the catalyst, such as the high surface area, prevented the formation of by-products. High efficiency of the obtained products and gentle green conditions are other features of this methodology using the described porous and heterogeneous catalyst [25].



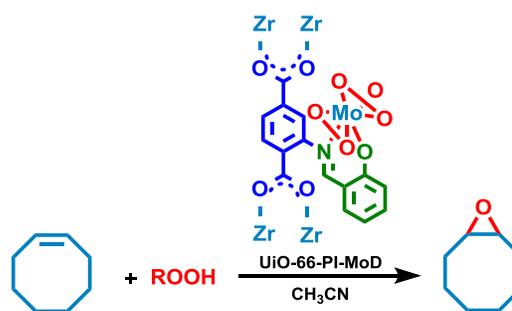
(G) Demir *et al.* have introduced UiO-type zirconium metal-organic frameworks (Zr-MOFs) to synthesize cyclic carbonates from CO₂ and epoxides under solvent-free conditions. In this report, the catalytic experiments have been well performed to prove the catalytic efficiency of Zr-MOF for using CO₂ in cycloaddition reactions. Zr-MOFs increase synergistically in catalytic activity. In addition, other features such as high activity, selectivity, and reusable performance of the catalyst have made this class of catalysts suitable for performing other organic and inorganic functional group transformations [32].



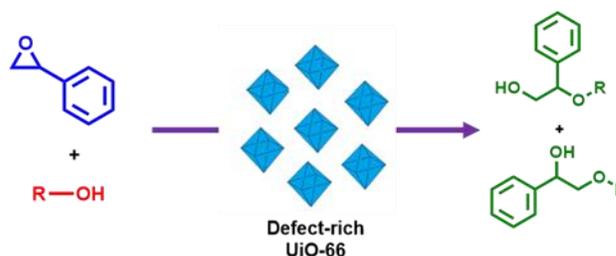
(H) In another report, Zolfigol and his co-workers designed and synthesized [ZrUiO-66-PDC-SO₃H]FeCl₄ as a novel porous heterogeneous catalyst to demonstrate the catalytic applications of Zr-MOFs. In this report, the post-modification method has been used to synthesize the catalyst. At first, [ZrUiO-66-PDC-SO₃H]Cl has synthesized, and in the next step, [ZrUiO-66-PDC-SO₃H]FeCl₄ is synthesized by applying the anion exchange method. This catalyst has a dual role as a Brønsted-Lewis acidic catalyst for the preparation of biological compounds, which has increased the yield of the products reported in this article [33].



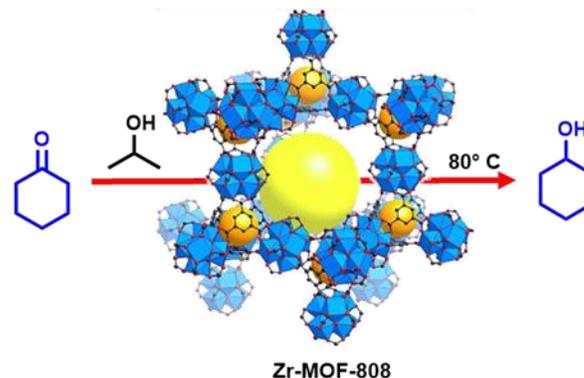
(I) To the best of our knowledge, ring formation is very important in chemical reactions. One of the important rings in these reactions is epoxide rings which are synthesized differently. In 2014, a report on synthesizing epoxide rings by oxygen source in the presence of a Zr-based metal-organic framework catalyst was reported. In the trial method, Zr-MOF and porous (UiO-66(NH₂)) with salicyl aldehyde, pyridine-2- aldehyde or 2-pyridine chloride is modified by PSM correction and then molybdenum loaded on it [34].



(J) In 2021, the ring opening of epoxides was investigated. In this report, ring opening of epoxides in the presence of alcohols nucleophile has been performed using a metal-organic framework catalyst based on Zr. In this report, it is shown that perfect crystals do not exist for the synthesized catalyst and it has crystal defects. Defects in metal-organic frameworks (MOFs) can tune the physical and chemical properties of materials and play a role in many applications, including catalysis, gas separation, and energy storage. This property in the ring opening of epoxides has been done by this type of catalyst [35].



(K) In many MOFs synthesis, creating defects in its corresponding structure is important. In a report using various combinations of crystal-engineered defects, Zr-trimesate MOF-808 (DE-MOF-808) is prepared by mixing tricarboxylate ligands with dicarboxylate ligands. The crystal structure of the synthesized compounds is very similar to the unmodified MOF 808. The catalytic application of these MOFs in reducing carbonyl groups has been investigated. In this catalytic application, modified MOFs have shown better catalytic efficiency than unmodified samples, which is the reason for their better performance due to defects in the structure of MOF. A further improvement in the catalytic activity of MOF-808-IP and MOF-808-Pydc with the engineered defect has been observed, which may be related to less crowded Zr⁴⁺ sites in DE-MOF-808 [36].



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