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Cr-Based Metal-Organic Framework: As a multipurpose catalyst

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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.

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Introduction

The MOFs word is the abbreviation of metal-organic frameworks and as it is clear from its name, it formed organic compounds as ligands and inorganic (metal) parts at the same time [1,2]. It means there is a central metal that forms a porous polymer network with organic ligands. This porous hybrid organic-inorganic polymer network with a feature such as indestructibility up to high temperatures and chemical flexibility by placing different functional groups on their surfaces can be modified [3]. This unique structure of MOFs has given their applications in various fields such as catalyst, photocatalyst, magnetic resonance imaging (MRI), gas separation and storage, absorption, desorption, purification, and drug delivery (**Fig. 1**) [4-9].

MOFs are a new class of porous materials and new-generation nanoreactors [10, 11]. Among the various applications of this category of porous compounds, their catalytic applications have attracted the attention of many scientists in recent years. Many groups have improved their catalytic properties by modifying these compounds [12, 13]. Catalytic MOFs have many capabilities, for example; increase efficiency, decrease reaction time, recoverability, etc. On the other hand, different applications for catalytic MOFs can be achieved by replacing different metals and ligands [14, 15]. This means that MOFs are very designable and various ligands and metals can be used to synthesize these porous compounds. Also, their diversity can be expanded via the post-modification method. Chromium (Cr) is one of the metals that have been used in the structure of various MOFs and it's suitable for MOF synthesis. Many MOFs have been synthesized based on the central metal Cr. MIL-100 (Cr) and MIL-101 (Cr) are the most important MOFs in the catalytic process due to the variety of ligands [16-17]. The use of different organic ligands gives different properties to these Cr-MOFs, which can be used according to the needs of catalysis [18, 19]. MOFs have distinctive features such as a large surface area, adjustable pore size, very diverse structure, and adjustable chemistry due to their two-dimensional and three-dimensional porous structure [20]. In this study, an attempt has been made to give a brief overview of the most important catalytic and photocatalytic applications of Cr-based MOFs. Moreover, various applications such as cross-coupling reactions, oxidation, reduction, synthesis of multicomponent reactions, ring-opening reactions, nitration, asymmetric reaction, isomerization, cyclization, and photocatalytic reactions have been reported for this MOF (**Fig. 2**).

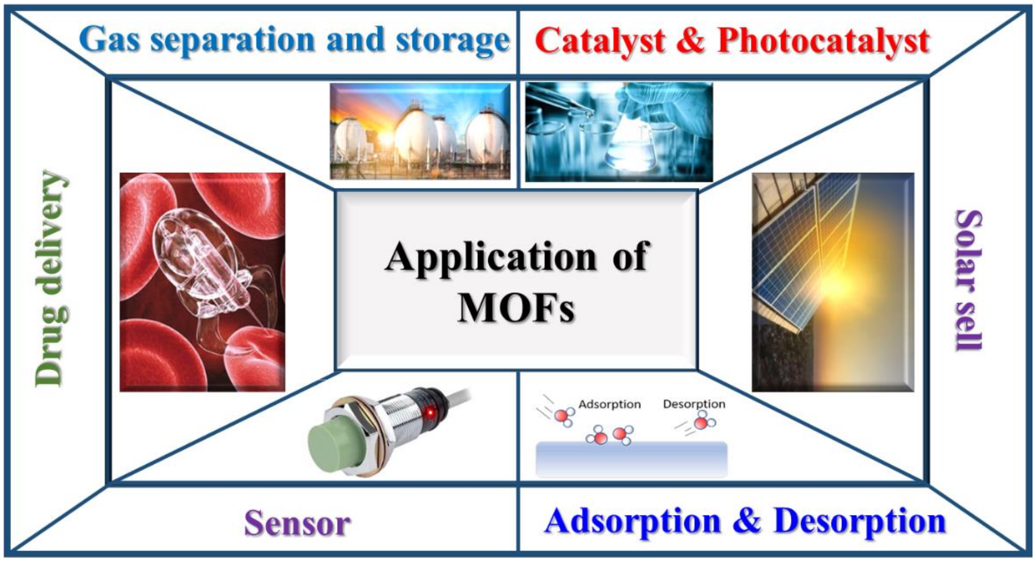


Fig. 1. Different applications of MOFs.

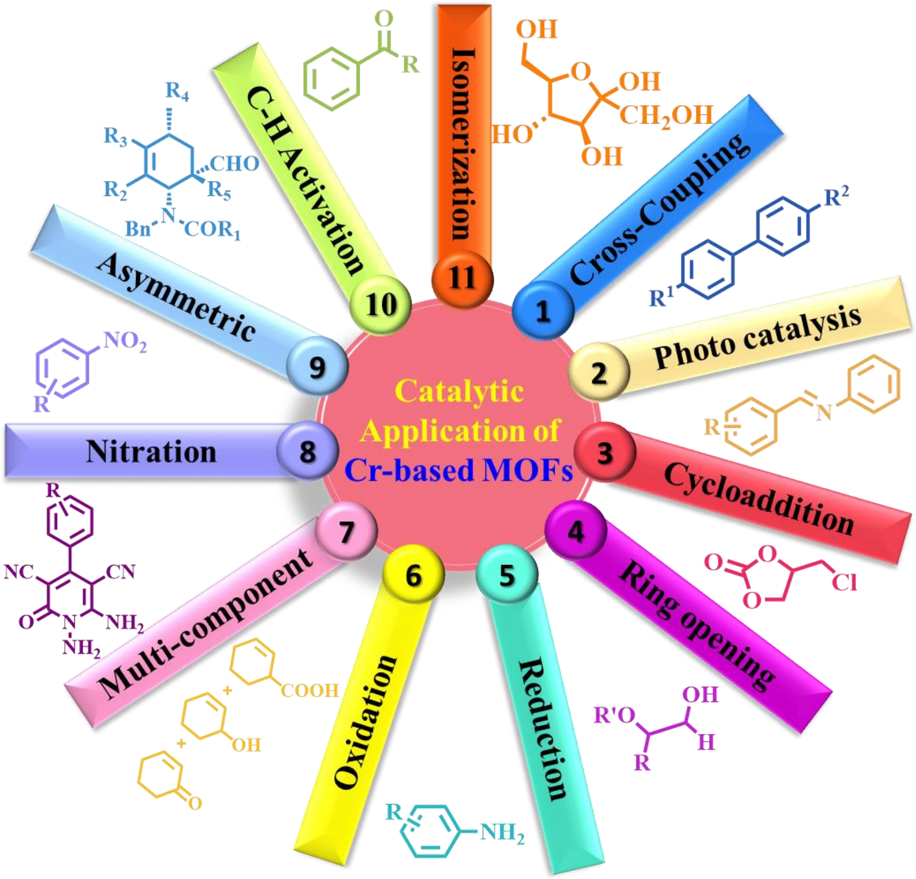
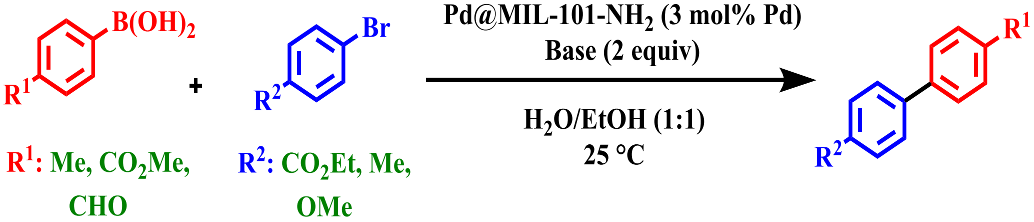


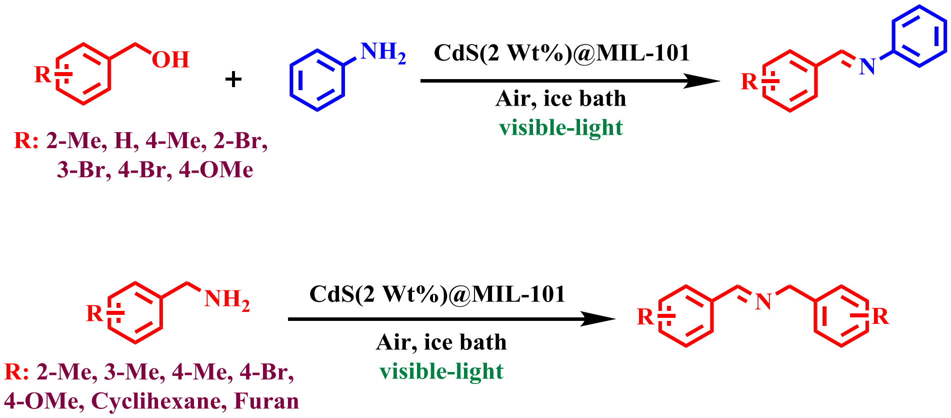
Fig. 2. Different catalytic applications of Cr-based MOFs

Abstracts

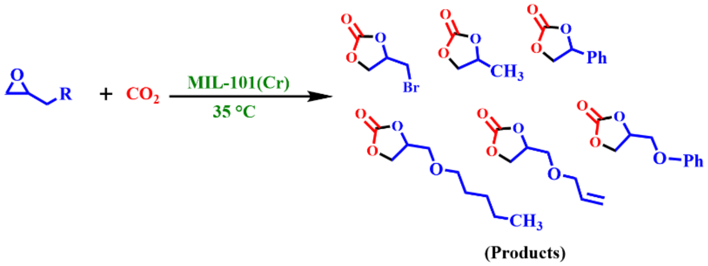
(A) (Cross-Coupling) Carson *et al.* have been designed and build a Cr-based MOF that catalyzes Suzuki-Miyaura Cross-Coupling without catalyst destruction in 2015. They designed Pd@MIL-101(Cr)-NH_2 based on the loading of Pd nanoparticles (NPs) on MIL-101(Cr)-NH_2. Four different types of bases have been used to evaluate their effect in the Suzuki-Miyaura cross-coupling reactions. Fluorides and carbonates have been as bases and observed that carbonates lead to the degradation of Cr-based MOF, and the use of fluoride is more desirable [21].



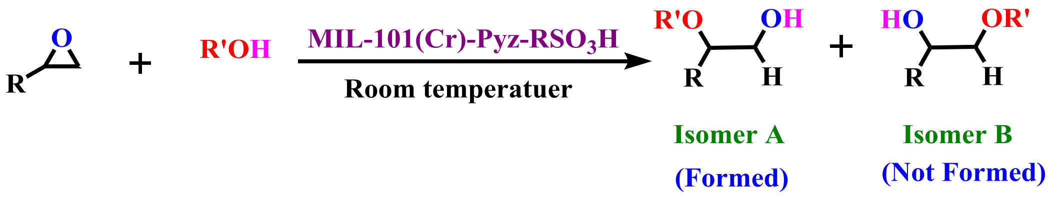
(B) (Photocatalysis) The photocatalytic application of Cr-based MOF is also very important. It should be noted that imine compound synthesis is important in the chemical and pharmaceutical industries, which mediates the construction of *N*-heterocyclic compounds. These compounds were mostly based on noble metal-based catalysts, which do not have adequate efficiency. In 2019, Wu *et al* have been fabricating MIL-101(Cr) with CdS quantum dots support, which catalyzes the photocatalytic reaction of the synthesis of imines through the coupling of amine and alcohol in the air/N_2 atmosphere. Also, the use of this catalyst in oxidative self-coupling of benzylamine derivatives for the synthesis of imines with air as a photo-oxidant has been investigated. The CdS quantum dots revealed an enhanced photocatalytic nature [22].



(C) (Cycloaddition) In another investigation, Akimana *et al* have been used MIL101(Cr) with acidic tags in cyclization with CO_2. Their aim has been epoxides cyclization reaction by CO_2 under acidic conditions. MIL101(Cr) catalyst contains strong acid sites that accelerate epoxide ring opening. Also, the catalyst has the possibility of absorbing more CO_2 by using its high surface area, which increases efficiency. The recovery capability of the catalyst has been investigated and the results indicate that this catalyst can be recovered 5 times without reducing the yield of the desired product [23].

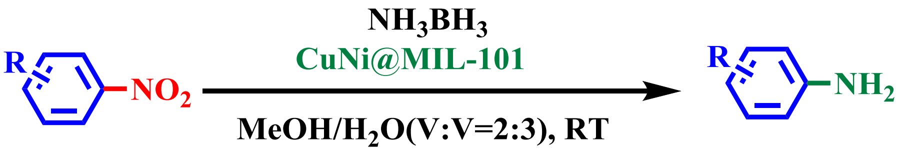


(D) (**Ring-Opening**) In another discovery, research on the design of a new heterogeneous solid Brønsted acidic catalyst has been carried out by post-modification of MIL-101(Cr). For this purpose, MIL-101(Cr) has been functionalized with pyrazine to obtain MIL-101(Cr)-Pyz. After that, the nucleophilic reaction of MIL-101(Cr)-Pyz has been carried out with 1,3-propane-sultone and its corresponding solid acid catalyst MIL-101(Cr)-Pyz-RSO$_3$H has been prepared. The catalytic application of MIL-101(Cr)-Pyz-RSO$_3$H has been evaluated for the esterification of acetic acid and the alkalization of epoxides in solvent-free conditions. The synthesized catalyst revealed high activity compared to unmodified MIL-101(Cr) in the alkalization of epoxides. These results indicate that tandem post-functionalization is a good way to incorporate acidic functional groups into the MOF structure for upgrading the catalytic activity [24].



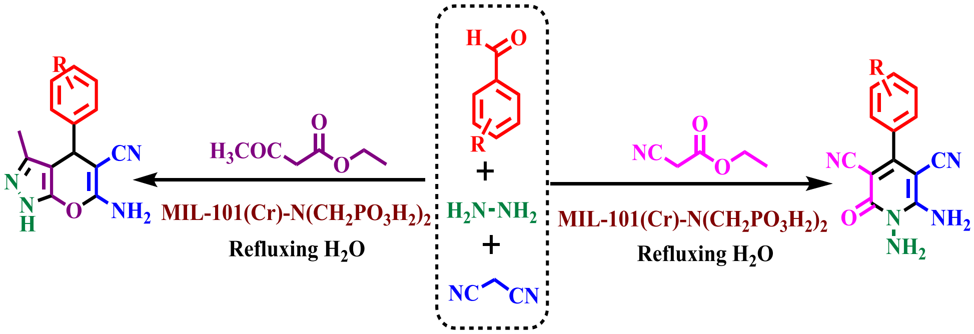
Alcohol: MeOH, EtOH, 2-Propanol, 2-Butanol, *tert*-Butanol, *n*-Hexanol

(E) (**Reduction**) In 2022, Zhou *et al.* introduced a novel Cr-based MOF catalyst for the reduction reaction. This report is based on low-cost bimetallic CuNi NPs rationally encapsulated within MIL-101(Cr) to provide CuNi@MIL-101(Cr). This strategy has been used for the hydrogenation of nitroarene under mild conditions. Furthermore, this methodology has been used in the borane dehydrogenation of ammonia with high efficiency and good recoveries. The excellent catalytic activity has been attributed to the fact that the hydrogen produced from NH_3BH_3 acted appropriately due to sufficient contact with the catalyst substrate, thereby accelerating the reduction of the nitroarene [25].

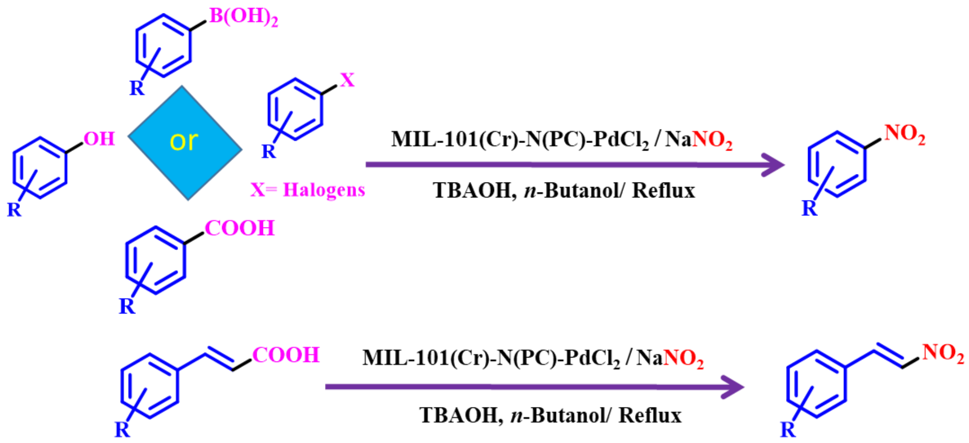


R: H, 4-Me, 3-Me, 2-Me, 4-OH, 2-NH_2, 3-NH_2, 4-NH_2,
4-Cl, 3-Cl, 2-Cl, 4-F, 3-NO_2, 3-$COCH_3$, 4-CN

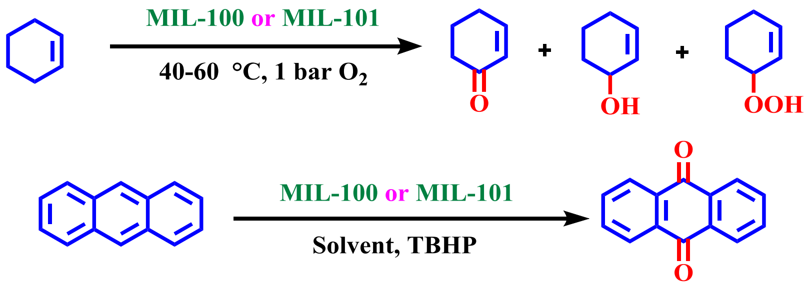
(F) (**Multi-Component Reaction**) Zolfigol *et al.* have succeeded in designing and synthesizing MOFs based on MIL-101(Cr)-NH_2 with phosphorus acid tags MIL-101(Cr)-N($CH_2PO_3H_2$)$_2$ which has been used as a heterogeneous and nanoporous catalyst for multicomponent synthesis. They reported the catalytic application of MIL-101(Cr)-N($CH_2PO_3H_2$)$_2$ for the synthesis of *N*-amino-2-pyridone and pyrano [2,3-*c*]pyrazole derivatives via condensation reaction of ethyl cyanoacetate or ethyl acetoacetate, hydrazine hydrate, malononitrile, and various aldehydes. The existence of a suitable substrate surface of MIL-101(Cr)-NH_2 with phosphorus acid agents has greatly contributed to the high yields of the target products [26].



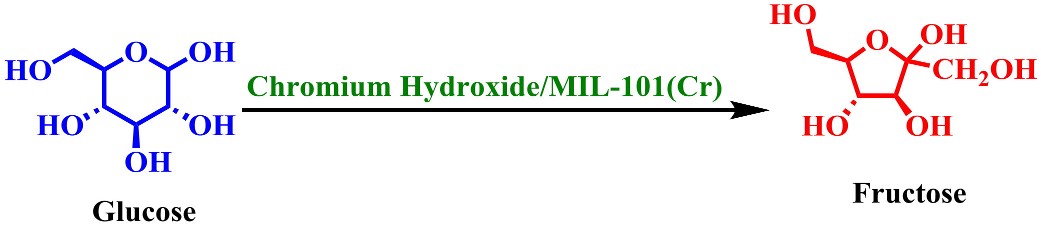
(G) (Ipso-Nitration) In recent years, ipso reactions have received much attention. One of the most famous ipso reactions is ipso-nitration, which are usually performed using various metals such as palladium as a catalyst. Zolfigol *et al*. have reported a new method of selective nitration, the catalyst of which was prepared by palladium (Pd) embedded into MIL-101(Cr)-NH_2 as porous metal-organic frameworks (MOFs). In this report, sodium nitrite salt is used as a source of NO_2. A series of compounds such as boronic acids, aryl halides, aryl trifluoromethane sulfonate, and aroyl chlorides have been subjected to an ipso-nitration reaction using the mentioned method [27].



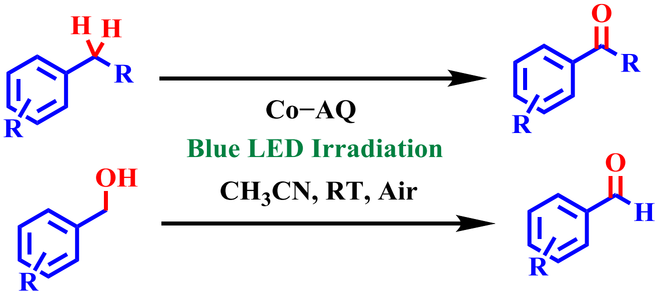
(H) (Oxidation) In another discovery, Kholdeeva *et al.* evaluated the catalytic properties of chromium- and iron-based MOF of MIL-100 and MIL-101 in two liquid-phase reactions in 2014. Solvent-free allylic oxidation of alkenes with molecular oxygen and oxidation of anthracene with *tert*-butyl hydroperoxide by catalyst has been investigated. Cr-based MOFs mainly have produced unsaturated ketones. In the oxidation of anthracene by using Cr-MOF, selectivity towards 9,10-anthraquinone has been achieved with conversion 92 up to 100% [28].



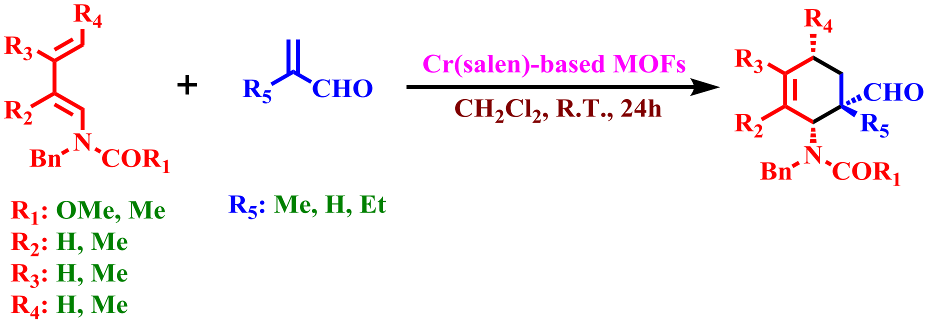
(I)(Isomerization) Isomerization reactions are very important in organic chemistry. Various catalysts and methods have been used to expand this category of organic reactions. In these studies, it has been shown that MOFs could also be effective in isomerization. In a report, a chromium hydroxide/MIL-101(Cr) composite catalyst was revealed for the selective isomerization of glucose to fructose. The designed and synthesized composite has performed highly selective conversion of glucose to fructose in ethanol as solvent. In this study, the isomerization of glucose to fructose on this catalyst has been investigated using isotopically labeled molecules, which are mainly through the proton transfer mechanism [29].



(J)(C–H Activation) MOFs have provided important insights into the C–H bonds activation. Zhao and co-workers have reported a bifunctional heterogeneous photocatalytic platform for C–H bond oxidation with MOF based on anthraquinone ligand and chromium metal. The excellent chemical stability and photocatalytic effects of bifunctional synergism through immobilization of anthraquinone in a MOF have been well demonstrated. This dual photocatalytic platform based on a heterogeneous MOF provides a stable catalytic pathway using oxygen as a strong oxidant [30].



(K)(Asymmetric Reaction) Asymmetric reactions are very useful in the synthesis of organic compounds. To the best of our knowledge, many special medicinal compounds can be made via asymmetric methodologies. In 2016, Xia and colleagues developed research on asymmetric reactions. They have well indicated the importance of porous compounds in asymmetric syntheses. This research group has performed a series of asymmetric reactions such as Diels-Alder using Cr(salen)-based MOF. M(salen)-based MOFs are one of the best catalysts for asymmetric synthesis. Heterogeneous Diels-Alder (HDA) reactions have been reported at 20 °C in CH_2Cl_2 [31].



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