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# Taking organic reactions over metal-organic frameworks as heterogeneous catalysis

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## ABSTRACT

Metal-organic frameworks (MOFs) are crystalline solids formed by inorganic clusters or metal ions (generally transition metal) linked by bi- or multifunctional organic ligands. Exploiting the advantages of the MOFs including large surface area, high metal content, and flexibility in designing the active sites, would be an innovative idea to make novel catalysts. This review gives a useful overview on the catalytic applications of MOFs regarding their structural developments toward catalyst fabrication. The catalytic applications cited in this review include the condensation of organic reaction of two or more components involved in a verity of reactions. More specifically, the review has explored the catalytic applications of MOFs in C-C and C-X (S, N, O) bond formation reactions leading to the formation of a more complicated compounds. The emphasis has been made on discussing the stability of the MOFs, their reusability and in providing a comparison of the performance of MOFs with respect to other homogeneous and heterogeneous catalysts.

## 1. Introduction

In recent years, the subject of green and sustainable chemistry has been accompanied by introducing new heterogeneous catalysts, as a proper alternative for homogeneous ones. Accordingly, in the scope of catalysis science and technology, nanoporous silica materials such as MCM-41 and SBA-15 have increasingly gained attention in replacement of the conventional mineral amorphous silica materials because of their higher surface area, lower densities, higher thermal and mechanical stability during reaction processes [1–4]. Organic part of the organic-inorganic hybrid nanoporous silica materials supported on the surface of pore walls can regulate many mechano-chemical features including thermal stability, hydrophobic and reactivity of the surface leading to the improved catalytic properties in reaction conditions [5–8].

Since the advent of metal-organic frameworks (MOFs) as a promising novel organic-inorganic hybrid nanoporous solid materials, their applications have been steadily increased. Nowadays, MOF-based catalysts are widely used not only in research and development (R&D) activities, but also in large scale of industrial products [9–19]. Within two last decades, MOFs have been widely employed in gas storage and separation, catalysis and chemical sensing. These coordinative polymeric networks consist of nodes from metal ions or metal clusters and bridges, so called organic “strut” or “linker”, which can be either negatively charged or neutral species taken from organic ligands; finally called metal-organic frameworks [20–27]. Unlike mesoporous silica materials and likewise zeolites, MOFs contain crystalline structures wherein metal cations or clusters (nodes) are connected by bi/multidendate ligands with repeated and order pattern [28]. Furthermore, the post-modification ability of the linkers gives rise to more flexible and compatible MOFs [29,30]. The nanoscale features of MOFs can be decorated with functional organic groups for specific

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interactions with biomolecules makes them appealing to stabilize enzymes for catalytic applications [31–33]. Moreover, the large internal surface area, intensive porosity, and high crystalline degree of MOFs are often compared to zeolites. In most cases, MOFs and zeolites have been utilized for many of the same applications, however their chemical structures are totally different [34,35].

The catalytic activity of MOFs in cases such as oxidation reactions has been already reviewed. Garcia et al. discussed and reviewed the importance and applications of MOFs in oxidation reactions [36]. They documented that MOFs are as the green heterogeneous part of catalysts in the oxidation of cycloalkanes, benzylic positions, cycloalkenes, and alcohols. Garcia's team also applied MOFs as the reusable and efficient catalysts for the synthesis of *N*-contained heterocycles including pyrimidines, N-substituted piperidines, quinolines, indoles, N-substituted imidazoles, triazoles and heterocyclic amides [37,38]. Excellence of MOFs originates from their reaction conditions, low metal leaching and reusability [38]. Su and coworkers regarded MOFs as the supramolecular structures and reviewed some of their catalytic applications as the heterogeneous supramolecular catalysts [39].

C-C bond formation reactions are of pivotal importance in synthetic organic chemistry as well as the modern chemical synthesis [40]. The first report of C-C bond formation came from Knoevenagel and aldol, in the early twentieth century, showing that nucleophilic addition of carbanions to electrophilic carbons could be effective [41]. In the next years, Grignard reaction was proposed based on the addition of organometallic reagents. This idea was further developed by introducing palladium-catalyzed coupling reaction of some stable derivatives such as olefins [42] and acetylenes [43], boronic acids/esters [44,45], and tin or zinc compounds [46]. At the same time, some other methods were proposed to produce complex carbon frameworks such as metathesis of olefins [47–49]. Additionally, tertiary amine catalysts were employed to produce allylic alcohols from aldehydes and $\alpha,\beta$-unsaturated electron-withdrawing (EW) groups. These methods offered much greater flexibility and tolerance to produce a wide range of sensitive functional groups in single molecule enabling the construction of more complicated and densely functionalized carbon frameworks. Attempts made to explore simpler and more efficient techniques for C-C bond formation paved the way for remarkable advances in synthesis of more efficacious drugs and natural compounds. Additionally, many developments including asymmetric synthesis, and green synthesis have been theorized these reactions. Catalytic nature of these reactions is of particular importance in eligibility and quality of the products and reaction process. So, much effort has been devoted to characterize the catalytic properties of the reactions involved in C-C bond formation.

When the subject of catalytic activities of MOFs is raised, active sites of MOFs and their corresponding interfaces become of utmost importance. Recent studies consider an intrinsic nature for MOFs' actives sites derived by the metal nodes or the organic linker. However, MOFs can be used as hosts to embed active species [50–53]. On the other hand, post-modification ability of MOFs is a powerful tool to manipulate and adjust the catalytic activity of MOFs enabling them to catalyze various sorts of reactions [30]. Therefore, MOFs have attained much attention as the catalyst in some C-C, C-N or C-X bond formation reactions. Accordingly, in this review, we try to overview some of the recent developments in producing materials through C-C and C-X bond formation reactions derived by different parts of various MOFs. However, in this regard, our glance is proceeding with different reaction types as sub-titles and then explain a series of MOFs that have applied for catalyzing them along with indicating advantages and disadvantages of each one.

## 2. Organic reactions catalyzed by MOFs

### 2.1. Knoevenagel condensation

Knoevenagel condensations reaction between carbonyl compounds and activated methylene groups produce various intermediates acting as the key components in the synthesis of several curative drugs and pharmacological products through C-C bond formation. The active methylene compounds are usually malononitrile (MN), ethyl cyanoacetate (ECA), diethyl malonate and malonic acid. The carbonyl compounds are benzaldehyde (BA) and its derivatives or aromatic ketones [51]. This reaction is often used as a benchmark reaction to evaluate the activity of a proposed catalyst [39–44]. Solid based catalysts, heterogeneous acid catalysts such as zeolites or mesopores and amorphous aluminosilica, are also known to catalyze Knoevenagel reaction. In addition, bifunctional catalysts are more effective than either of individually basic or acidic catalysts [45–47]. The acidic sites activate the carbonyl group of the acceptor molecule, while the basic sites deprotonate the methylene group to produce the corresponding enolate.

The MOF known as UiO-67 is among a series of zirconium MOFs based on $Zr_6$ clusters and dicarboxylates. An aldehyde-tagged Zr-MOFs, UiO-67-CHO, has been synthesized via the direct solvothermal reaction between $ZrCl_4$ and 2-formalbiphenyl-4,4′-dicarboxylic acid ($H_2$bpdc-CHO). Furthermore, amine functionality introduced into the MOF via postsynthetic modification (PSM) (Fig. 1) [54]. This basic MOF obtained by tandem Schiff-base condensation and reduction, UiO-67-diamine, was studied as a catalyst for Knoevenagel condensation. Using 6 mol% of amino-functionalized MOF, the reaction of BA with MN showed 81% yield in 30 min and was almost complete after 2 h in DMF at room temperature. In comparison, the reaction without any catalyst needed 24 h to reach 97% conversion, and the reaction over UiO-67-CHO gave a conversion of only 8% after 2 h. To confirm that the activity is not from any species leached into the liquid, the catalyst was filtered off after reacting for 5 min. The reaction in the filtrate was much slower, with the rate being similar to that of the blank reaction. Therefore, the active species is in the solid phase, and the catalysis is heterogeneous. The UiO-67-diamine framework showed no leaching and could be reused at least for two times without much loss in its activity. The powder XRD patterns of fresh and used catalyst showed no changes in the crystal structure.

Recently, a microporous negatively charged MOF based on cadmium(II) nods and TDPAT (2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine) ligand, FJI-C2, has reported. The presence of high density of uniformly distributed Lewis basic sites on its internal surface makes this MOF suitable to catalyze Knoevenagel reactions in a size-selective fashion [55]. In order to test the catalytic activity, the reaction of BA with MN was performed with 3 mol % of FJI-C2 catalyst at 35 °C in toluene, observing 81% conversion of aldehyde in 6 h. Control experiments revealed that blank experiment without any catalyst, and the ligands $H_6$TDPAT, $CdCl_2$, or residual solvent (DMF and water) show no product. In addition, the effect of electron-withdrawing (EW)/-donating (ED) groups on BA derivatives were tested for this reaction. Since the nucleophilic addition is the rate-determining step in the Knoevenagel condensation, the electron-deficient derivatives, such as 4-cyanobenzaldehyde, 4-nitrobenzaldehyde (NBA), and 4-chlorobenzaldehyde (CBA), gave the corresponding products with higher conversion (92%, 91% and 89%, respectively). On the contrary, the obtained yields were lower for the electron-rich derivatives, such as 4-methylbenzaldehyde (74%), 4-methoxybenzaldehyde (43%), and 4-phenylbenzaldehyde (75%). On the other hand, when the size of the active methylene substrates increased, the relative conversions of BA decreased. Under