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Recent Advances on Copper Based Metal Organic Framework as Heterogenous Catalyst Inorganic Coupling Reaction: A Review

Eliza Ahmed[1,a], Basappa C. Yallur[2,b], Vinayak Adimule[3,c], Sheetal Batakurki[1,d*]

[1]Department of Chemistry, M. S. Ramaiah University of Applied Sciences, Bangalore-560054, Karnataka, India.

[2]Department of Chemistry, M.S. Ramaiah Institute of Technology (Affiliated to VTU), Bangalore-560054, Karnataka, India.

[3]Angadi Institute of Technology and Management (AITM), Savagaon Road, Belagavi 591108. Karnataka, India.

[a]elizahmed66@gmail.com, ORCiD: https://orcid.org/0000-0003-0426-3652
[b]yallurbc@gmail.com, ORCiD: https://orcid.org/0000-0002-9099-7056
[c]adimulevinayak@yahoo.in, ORCiD: https://orcid.org/0000-0002-2198-6601
[d*]sheetalrb@gmail.com,ORCiD:https://orcid.org/0000-0001-6363-173X

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Abstract. In synthetic organic chemistry, use of catalyst to accelerate the rate of reaction leading to high yield product is a common approach practiced by chemists. Numerous homogenous and heterogenous catalyst are widely used in chemical reactions, particularly metal based catalyst are widely used. The properties of metals and their oxides are fine-tuned by size reduction method bringing down to nano scale. Further hybrid materials are used for more specific applications among which metal organic frame works are listed in more number in last ten years. Herein this review focuses on use of metal organic framework in particular Copper metal based organic framework (Cu-MOF). Cu-MOF synthesis, properties and their applications are discussed. A detailed discussion on the use of Cu-MOF as a heterogeneous catalyst in various organic reactions.

Introduction

Transition elements are the most abundant elements that are boon to mankind from mother nature [1]. Transition metals and their alloys are widely used in various industrial applications such as production of parts and engines of various transportation system, in construction of buildings, industrial manufacturing units, used as fertilizers, paints and dyes, medicines, electronic devices, and most importantly many are micro and micronutrients that are required for survival of living organisms [2]. There are about 38 elements in the d- block. These elements have varied valences due to which they can be combined in numerous combination results in compounds with unique chemical and physical properties that re widely used in various industries [3]. In the past few decades use of metal oxides have gained lot of importance microelectronics, gas sensing, biomedical, thermal materials, energy, storage, environmental decontaminations and as catalyst. Various metal oxides [4-8] such as titanium oxide doped with gadolinium copper and zinc oxides [9-16], zirconium [17], chromium [18-20], strontium [21-22], cobalt [23], tin [24], titanium [25], gadolinium [26-29], magnesium [30-31], Tantalum [32], soft magnetic Fe80 doped with cobalt [33], terelium [34], yttrium [35], strontium doped with titanate [36], strontium doped with samarium [37], etc., are widely used in energy materials for semiconductor , solar, photovoltaic, Capacitors, supercapacitors, sensors, bio-sensors, metal additives, photoluminescence [38-40], high performance energy storage device [41], dielectric properties [42]. Metal based catalysts are commonly used by petroleum refining industries, pharmaceutical industries, food industries, and many other chemical manufacturing industries [43]. Out of these application, use of metal oxides as homogenous and heterogenous catalyst in various chemical transformation have become a greener route sustaining the green chemistry requirements at the same have reduce the cost and time required for completion of reaction with high yield product reducing the laborious work of separation of byproduct which are the major advantages of use of catalyst in industries [44]. However, the cost of manufacturing these catalysts, defect-free, lesser surface area, recyclability and reusability, and most important is poisonous of this catalyst after reaction completion hinders the usage of metal catalyst in reaction [45-46]. In recent years application of nanoscience reports breakthrough research in all aspects of science so do in chemistry, many materials are prepared in nanoscale to enhance their properties such as larger surface area, good conductivity, uniform size and shaped adsorbents to adsorb pollutants or hazardous substances from the environment, nano polymeric materials with high degrees of stiffness, strength, low to high density materials used for specific application in various industries. Further, use of nano catalyst have favored the rate of reaction, remedial to require huge temperature during conversion, high yield of product etc [47-49]. Adimule et al, [50] have reported the use Samarium (Sm) (1–12 wt %) doped $CuCo_2O_4$ nanohybrid photocatalyst in degradation of methylene blue and carbon-di-oxide. Basappa et., al [51] have synthesized Zr/Cu-(H2BDC-BPD) [44] MOF for mineralization of pollutants and hydrogen evolution from water. SmxGd(1−x): SrO were prepared by Vinayak Et., al and studied their photoluminescent properties which can be good candidature for high-luminescent devices [52]. CuO:CoO decorated with Sm2O3 nanostructure have synthesized by co-precipitation method [47] and studied for their electrical and super capacitive applications. CuO:CoO decorated with 1%, 5%, 10%, and 12% of Sm2O3 [53-54] were synthesized by co precipitation method. The results indicated that the conductivity of $Sm_{10\%}$CuO:CoO exhibited better electrochemical response than other two samples. Due to change in high dipole moment specially by the 10% samarium a strong local electric field was formed exhibiting maximum specific capacitance of 67.4 F/g at 0.1 A/g.

In this context, researchers are working on hybrid nano materials such as metal organic frame works (MOF) [55], covalent organic frame works (CMOF) [56], polymer metal organic frame works (PolyMOF) [57], amorphous porous organic framework (APOF) [58] and nano porous ionic organic networks (NPION) [59]. Structural improvement, increased porosity, high surface size, tunable topological, electrical, and chemical properties have made these resources as excellent choice of advanced materials for vast applications [60].

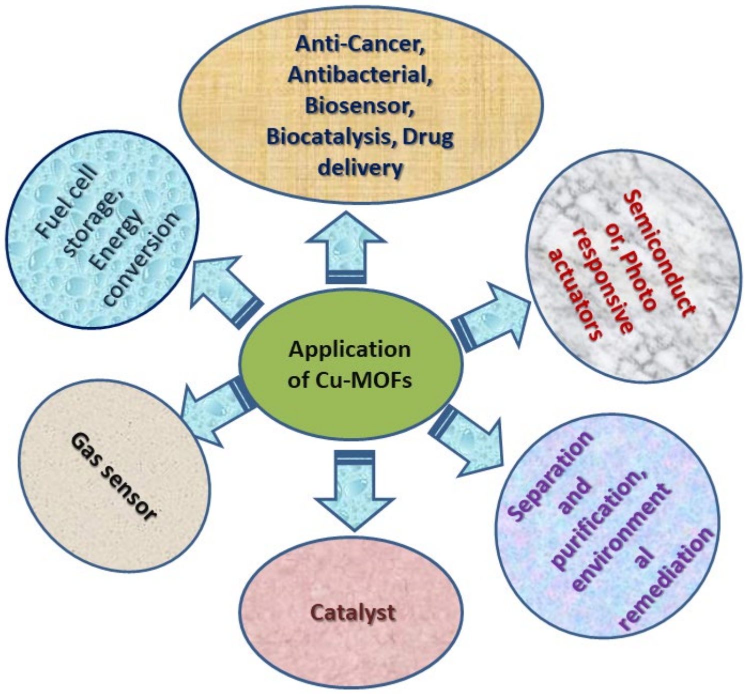


Figure 1: Various applications of metal organic frameworks

Metal organic frame are porous materials composed of organic linker with metal oxide and have attracted by several investigators for their exceptional properties like physico-chemical, tunable electrical, flexible thermal, heterogenous catalytic and mechanical characteristics [61-63]. Poly (3-octyl Thiophene) synthesized with Nickel- strontium titanium trioxide [64] has been found to possess excellent properties required for solar cell applications and also in medical applications such as DNA binding [65]. MOFs have been explored for various applications such as energy storage capacity, semiconducting nature, magnetism, luminescence, sensor technology, gas storage, molecular separation, and catalysis [66] etc. In several studies, fabrication of MOF's nanocomposites like Ag NPs onto UiO-66(Zr) has been done by the impregnation method where in Mahugo et al. prepared Ag@MIL-100(Fe) nanocomposites by employing a different procedure [67-68]. Further, the amalgamation of MOFs and metal oxide like zeolite, AgO, ZnO, graphene, carbon nano tubes etc. made a composite material. Metals such as copper, iron, zinc, vanadium, titanium, samarium, are widely used metals with carboxylic acid, amines as organic linkers. These MOFS are prepared by various methods such as co-precipitation method, thermal method, solvothermal method, ultrasound, microwave, and conventional methods [69-70].

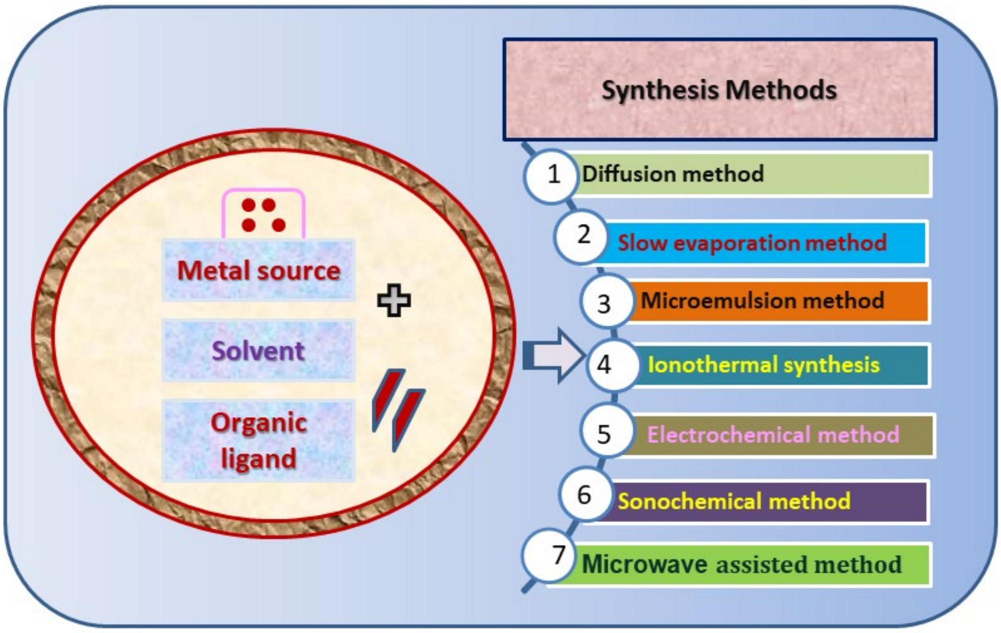


Figure 2: Synthetic Methods of metal organic frameworks.

Among, various metals copper metal organic framework has been widely used for photocatalyst, heterogenous catalytic applications by synthetic organic chemist. Here in this review presents the synthesis and applications of copper metalorganic frameworks particularly for the organic functional group transformations.

Synthesis of Cu-MOF's Long et al., have synthesized Cu-TDPAT with 2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine (H_6TDPAT) by solvothermal process. The FESEM image revels the formation of 0–40 µm sized polyhedral shaped with 1855 m^2/g surface area, stable up to 250 °C. These Cu-TDPAT was used as heterogenous catalyst (0.05 mmol) in the Goldberg-type C–N coupling reaction in which of iodobenzene coupled with 5-methyl-2-(1*H*)-pyridoneat120 °C were coupled in DMSO solvent and base K_2CO_3.The reaction conditions were optimized by varying solvent, temperature, base. It was observed that polar solvent DMSO was best suitable for N-arylation and enhanced catalyst activity of MOF. The catalyst was recycled and reused for N-arylation upto four cycles with being at 81% [71].

Figure 3: Goldberg-type C–N coupling reaction of iodobenzene coupled with 5-methyl-2-(1*H*)-pyridone at 120 °C in presence of Cu-TDPAT

Sagarmani et., al have synthesized with two N-methylimidazoles and Benzenedicarboxylic acid resulting in Cu-1D MOF which was used as heterogeneous catalyst (BDC) 1D MOF acts as a solid heterogeneous catalyst and exhibits efficient catalytic activity in intermolecular and intramolecular cross-coupling reactions aziridine derivatives with aryl, amines, thiols and phenols resulting in 75 – 90 % yield [72].

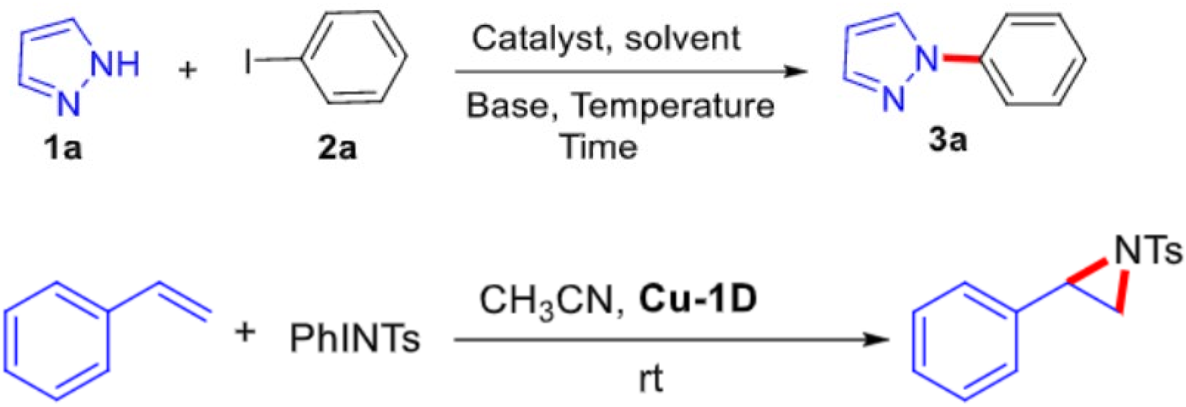


Figure 4: C-N, C-S, C-O coupling reaction in presence of in Cu-1D MOF

Rajendra Srivastava et. Al [73] have synthesized bimetallic Cu–Ce metal–organic framework (MOF) using Benzentricarboxylic acid (BTC) as organic linker with cerium nitrate and copper nitrate hexahydrate. The synthesized Cu_2O-CeO_2/CMOF was used as heterogenous catalyst in Sonogashira coupling reaction. 25 % of Cu_2O-CeO_2 /C MOF was used in coupling reaction offering 94.2% of 1,2-diphenylethyne carried out in presence of potassium carbonate and methanol: acetonitrile (1:1) in presence of 20W light-emitting diodes.

Nam T.S.Phan et., al [74] have synthesized $Cu_2(BPDC)_2(BPY)$using 4,4' -biphenyl dicarboxylic acid with 4,4' -bipyridine in DMF solvent maintained at 70 °C by a solvothermal method. This catalyst was used in coupling reaction between 2-hydroxybenzaldehyde and 1,4-dioxane to form 99% of 2-(1,4- dioxan-2-yloxy)benzaldehyde reaction was achieved at lower temperature 90 °C in presence of catalyst without any side products. Thus, $Cu_2(BPDC)_2(BPY)$ MOF was successfully used as heterogenous catalyst in cross-dehydrogenative coupling reaction.

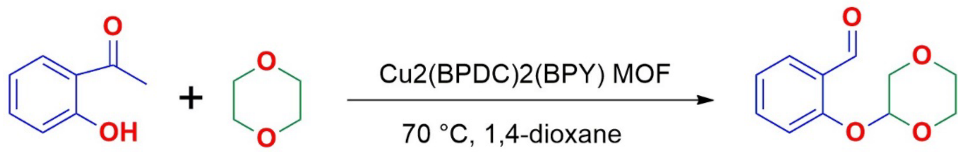


Figure 5: Cross-dehydrogenative coupling reaction of 2-hydroxybenzaldehyde in presence of $Cu_2(BPDC)_2(BPY)$ MOF

Liu et.,al. [75] have synthesized copper nanoparticles encapsulated in carboxy porphyrins organic frameworks. During the synthesis copper was encapsulated in different weight percentages and synthesized catalyst was screened for its catalytic activity in self coupling reaction of terminal alkynes. It was observed that 1.9 wt% of Cu NPs in Cu@PCN-222 (Cu) had excellent catalytic activity leading to highest 1,4-diphenylbuta-1,3-diyne and2,2,7,7-tetramethylocta-3,5-diyne as self-coupling products.

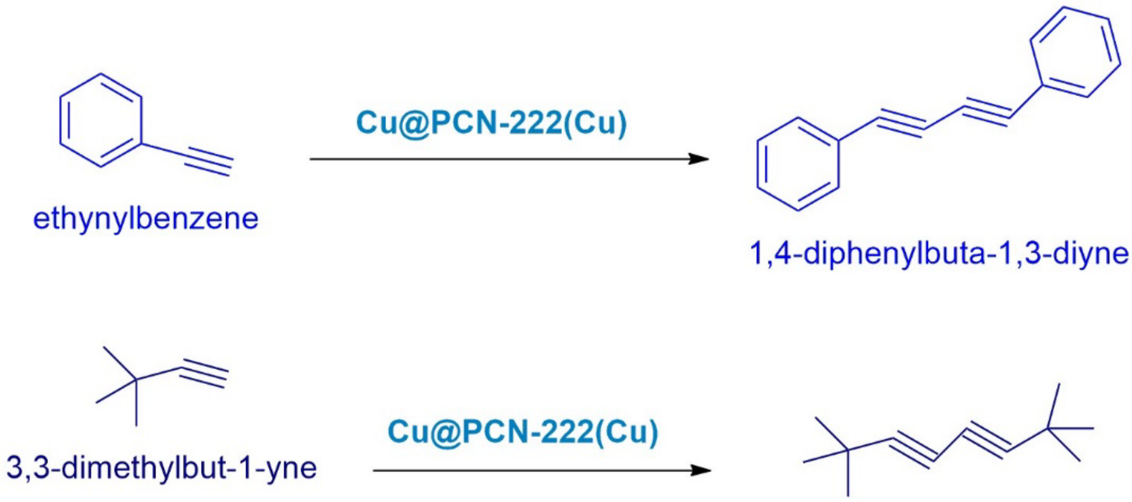


Figure 6 : Self coupling reaction in presence of Cu@PCN-222(Cu)

Qin et.,al [76] have synthesized 1,2,4,5-tetra(2H-tetrazole-5-yl)-benzene, with CuCN and NH4F in DMF and liquid NH3 maintained at 160 °C for 3 days in a steel bomb. The synthesized MOFs were labelled as (Cu^{I}-MOF-1) and ($Cu^{I}Cu^{II}$-MOF-2) and used as selective catalyst for selective ring opening reaction.

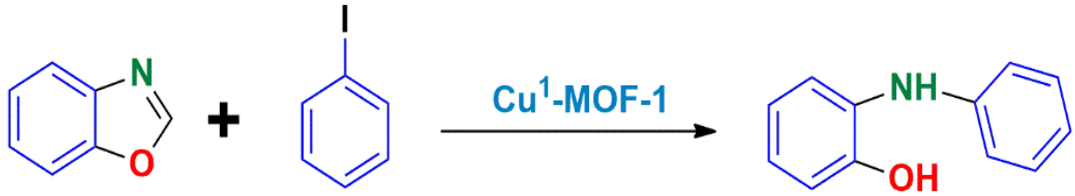
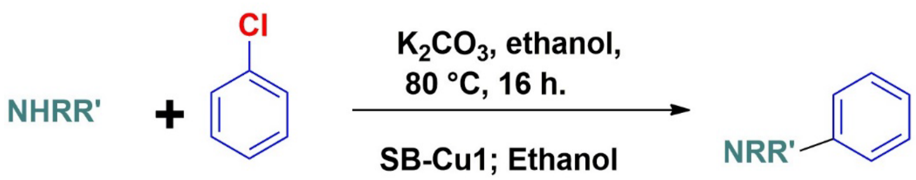


Figure 7: Selective ring opening reaction of 1,2,4,5-tetra(2H-tetrazole-5-yl)-benzene in presence of CuI-MOF-1

SB-Cu1 MOF can be successfully prepared by cooperative self-assembly between 1-benzimidazolyl-3,5-bis(4-pyridyl)benzene (bbp) and CuI 5-bis(4-pyridyl)benzoic acid, 1,2-diaminobenzene, phenylpropanolamine

Bagheri et.,al. [77] have synthesized SB-Cu1 MOF by using 1-benzimidazolyl-3,5-bis(4-pyridyl)benzene (bbp) linker with diaminobenzene and copper iodide in presence of CH2Cl2/CH3OH solvent maintained at room temperature with continuous stirring for 48h. The synthesized SB-Cu 1 MOF was used as heterogenous catalyst in N- arylation of respective amine (imidazole, pyrrole and aniline) with various aryl halides respectively. Reaction was maintained at 80 °C for 16 h and in presence of K2CO3. The SB-Cu1 MOF was recovered and reused up to five cycles without loss of activity and leading to 80 % yield of coupling product.



where amine: aniline, pyrrole, imidazole,

Figure 8: N-arylation of N- arylation of respective amine (imidazole, pyrrole and aniline) with aryl halide in presence of SB-Cu1 MOF

Maya Pai et., al [78] have synthesized bimetallic MOF RIT 62-Cu/Pd by microwave process using 4-mercaptobenzoic acid, 2-bromomalonaldehyde and copper nitrate. Around 75% yield is reported through this process. The synthesized MOF RIT 62-Cu/Pd is used as heterogenous catalyst in Still polycondensation of thieno[2,3-b]pyrrol-5-one with three different thiophen donating groups. Polymerization reaction was optimized by varying base, solvent, and temperature. It was observed that polymerization took place at minimum temperature and time resulting in 98 % of polymerized product. The catalyst was recovered, recycled, and reused up to three cycles with good yield. However, for sixth cycle the polymerized product yield was moderate indicating that MOF RIT 62-Cu/Pd had good activity up to three cycles.

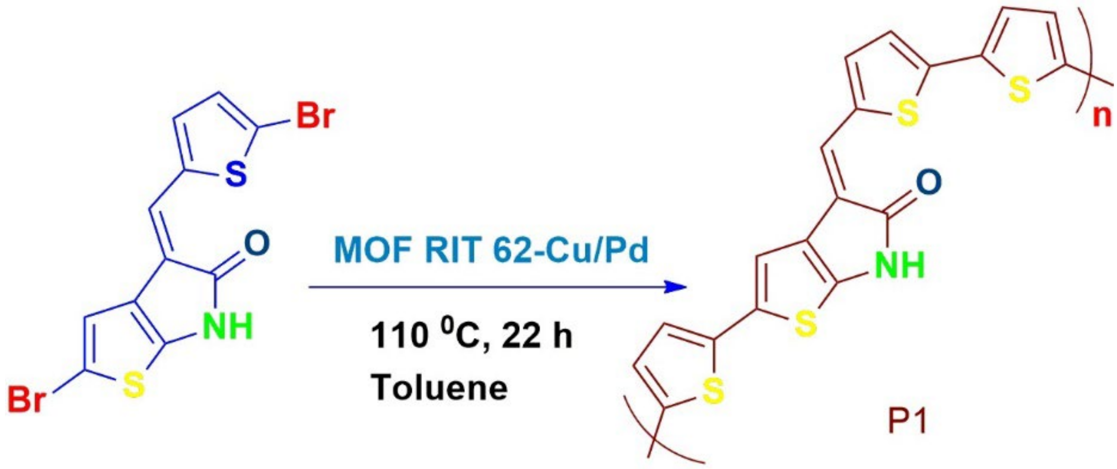


Figure 9 :Stille polycondensation of thieno[2,3-b] pyrrol-5-one in presence of MOF RIT 62-Cu/Pd, K2CO3, toluene

Conclusion

This review gives an insight on synthesis of Cu-MOF using various organic linkers by co-precipitation method, solvothermal, ultrasound, microvan method etc. The review suggests ways to fine tune the electrical properties of Cu-MOF by suitable dopants. Various applications in Cu-MOF are discussed. One of the most advanced applications of Cu-MOF is to behave as heterogenous catalyst. Cu-MOF based heterogenous catalyst are widely used in adsorption of toxic and hazardous chemicals present in the environment, used as economical catalyst in reforming process of petroleum refinery industries. Specifically, use of Cu-MOF in organic functional group transformation is explained. Novel hybrid bimetallic catalyst are used in various chemical reaction such as C-C coupling, N-alkylation, redox reaction, specific ring opening reaction, and condensation reactions. However, the choice of suitable organic linker, synthesis process to attain highly porous MOF materials are still a challenge and further the mechanism of these CU-MOFS in chemical transformation needs a detailed study.

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