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Article

Recent Advances in Polymer Supported Copper Catalyst – A Review

Saba Azim[1], Samridhi Dwivedi[2], B. S. V. Prakash[3], Alfred Lawrence[2]*

[1]Department of Chemistry, Baba Saheb Bhim Rao Ambedkar Central University, Lucknow, Uttar Pradesh, India, [2]Department of Chemistry, Isabella Thoburn College, Lucknow, Uttar Pradesh, India, [3]Department of Botany, Lucknow Christian Degree College, Lucknow, Uttar Pradesh, India

ABSTRACT

Polymers are a wide variety of compounds that provide a variety of compositions and properties useful in catalysis. Polymer supported copper catalyst is polymers possessing catalytically active moieties. Hence, its usage in polymer industry has been increased day by day and is still an innovative area for new research. This review illustrates the recent advances of polymer supported copper catalyst. It covers the classification along with various approach adopted for the synthesis of the same. Further the review will also deal with the existing applications of the Polymer supported Cu catalyst in different area which will help the professionals in field to have a better insight for the future research and applications.

Key words: Polymer, Copper catalyst, Transition metal.

1. INTRODUCTION

The industry of polymers is composite, in part because it encompasses many aspects that are of multidisciplinary nature [1]. Polymers have become a major part of essentially all industries, from food and beverage packaging to transportation to the medical industry [2]. Polymers sciences and technologies have advanced tremendously from the past years and the production of polymers and plastics produced has enlarged at an impressive place [3-5]. Likewise, polymer chemistry where the catalysts are anchored to the support is added, and the review summarizing this field is available [6,7]. Consequently, the profusion of literature on the topic of polymer supported catalyst, in specific copper containing catalyst, some limitations in the material covered [8]. As copper is a 3D transition metal and has some fascinating physical and chemical properties [9]. Copper-based catalyst can promote and undergoes a variety of reaction due to copper's wide range of oxidation states such as Cu(I) and Cu(II) [10]. Copper-based catalysts have found many advantages in nanoscience, organic synthesis, mechanical transformation, electrocatalysis, etc. [11]. The polymer supported copper catalyst has the potential to reuse the catalyst [12]. It is also important from the green chemistry point of view [13]. The development of current and more active heterogeneous stable copper catalysts is efficient for the application of the green and sustainable chemistry [14].

Highly focused in the area of polymer supported organometallic reagents, copper-based metal has an efficiency to recycle the catalyst [15]. Many copper-based metal such as inorganic solid supported Cu catalyst, biopolymer supported Cu catalyst and other polymers [16]. The use of polymer supported metal catalysts plays a major role for the preparation of various transformations reactions [17]. The nature of catalytic species (homogeneous vs. heterogeneous) is imprecise, supported metal catalyst, which is stated in the review as merely heterogeneous catalyst can shows a significant activity, reaction rate, and reusability much than the homogeneous catalyst [18]. The potential of heterogeneous supported metal catalyst has been reported so far, focused on some particular types of supports metal oxides, N-heterocycles, nanoparticles, or an specific classes of organic reactions such as Click reaction, Heck reaction, and Huisgen (3+2) copper catalyzed cycloaddition reaction [19].

Click chemistry is a conception that uses the most suitable and practical organic transformation for clicking reagents or makes the reactions faster with high yield and in an organized manner [20].

In 2001, Sharpless reported the synthesis of click reaction as a wide range in scope, a high yielding products and stereospecific [21]. Among all these clickable reaction, a very well-known Huisgen reaction (CuAAC) is usually accomplished at a higher temperature for a longer time and yields a high stability product [22]. Much of the recent view, the development of heterogeneous CuAAC procedures, mainly depends on the anchoring of the copper catalysts as an organic complexes or copper based nanoparticles on a wide range of supports, including polymers, biopolymers supported Cu catalyst, zeolites, Si supported Cu catalyst, and C-C- and C-N-based nanomaterials. [23].

The systematic approach of the supported catalyst has been classified in three parts –

1.1. Copper Supported Catalyst on Inorganic Matrices

The polymer supported copper catalyst based on inorganic matrices is for the synthesis of Nitrogen containing heterocycles compound (Nitrogen-heterocycles) [24]. The development of reusable metal supported copper catalyst, the inorganic matrices such as silica-based supported Cu catalyst, carbon-based Cu supported catalyst, anchoring

***Corresponding author:**
Alfred Lawrence,
Email: alfred__lawrence@yahoo.com

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on metal-based oxides, minerals and magnetic ore, plays a significant role and broadly used as a metal support [25]. Due to low cost, giving high yield stability at high temperature and pressure, showing outstanding mechanical properties and longtime duration stability, these metals materials are easily commercially obtainable [26]. The possible recovery of the catalyst from the medium of the reaction by simple filtration is only allowed because the inorganic matrices are generally insoluble in organic solvent [27].

1.2. Copper Supported Catalyst on Organic Matrices

In the view of the development of supported catalyst for reusable copper catalyst, organic matrices represent a more wide and more convenient alternative in inorganic metals materials [28].

Organic matrices have been further divided into two category –

1.2.1. Synthetic organic based matrices

This category includes the polymer and polymers supported copper catalyst anchored on ligands. These metals materials can be simply achieved with their physical, chemical, and morphological structure [29].

1.2.2. Natural organic matrices

This category includes biopolymers that are easily available at low cost and have the efficacy of a chemical modification. The further advantage of organic supported copper catalyst is that they give less hindrance in the whole catalytic process [30].

1.2.3. Copper catalyst supported on carbon

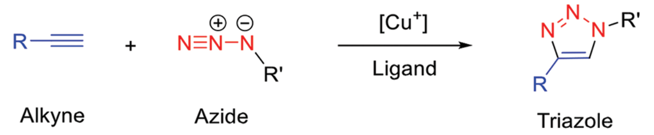
Djakovitch *et al*. reported the first synthetic application of copper supported catalyst on carbon. In several reactions, palladium on activated carbon was favorably applied that include [31].

Keeping in mind the above fact, this review will be focused and evaluate on the area of highly efficient heterogeneous catalyst based on copper complexes immobilized on polymer carriers [32].

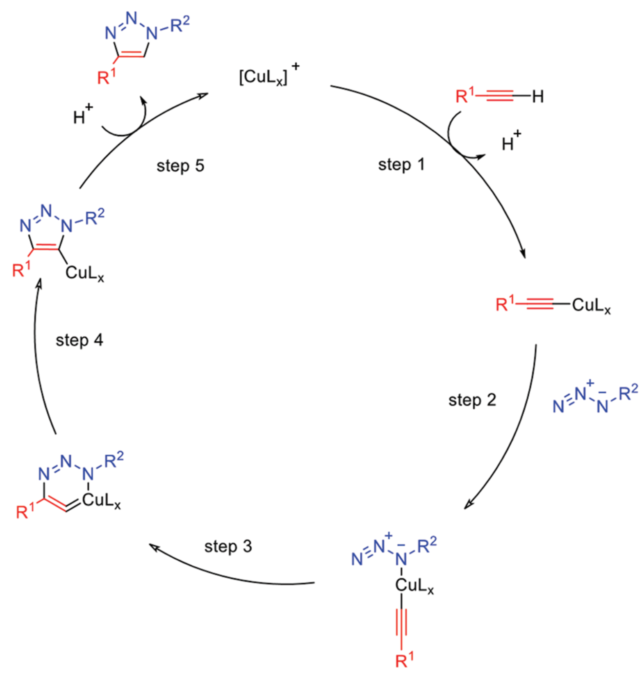
Click reaction has an efficient property to connect two potential stable complex building blocks under mild conditions. It was developed by Huisgen, the cycloaddition reaction between a terminal alkyne and an azide to give 1,4 or 1,5 -disubstituted 1,2,3 –triazole [33]. The major drawbacks of the reaction are the lack of regioselectivity and conditions of high temperature [34].

First developed by Iyer and coworkers, a very well-known Heck type reaction of aryl and vinyl halides with olefins is catalyzed by copper [35]. However, only confined reports are obtainable on the copper catalyzed Heck type reaction and are usually performed under high temperature and longer reaction time [36]. A narrative polymer supported copper complex is prepared by immobilising (CuI) on amidoxime modified Polyacrylonitrile (mmPAN) [37-39]. The copper catalyst used in the reaction offers easy preparation, excellent stability, and efficient catalytic stability and reusability [40]. The polyacrylonitrile supported Cu catalyst has an approach toward environmental and heterogeneous Heck reaction [41].

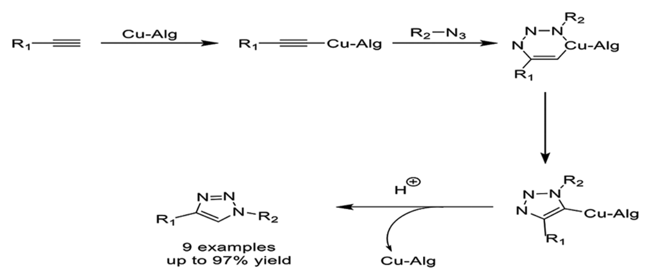
In this review, we immersed on Cu (1) and Cu(II) complexes immobilized on polymer supported catalysis. Many prepared copper-based heterogeneous catalyst was effectively used for oxidative homocoupling of terminal alkynes, synthesis of propargylamines, azide alkyne cycloaddition, nitroaldolization reaction, Heck coupling reaction, and aza -Michael addition assymetric friedel crafts reactions. The asset of discussed heterogeneous catalysts consisted in their simple preparation, isolation, and the possibility of reuse [42]. Huisgen cycloaddition, Heck coupling reaction, the above mentioned reactions possesses high probability of industry usage; hence, the copper-based catalyst presented in this review significantly contributes to further advancement of ecologically sustainable and organic or chemical transformations and technologies.



Scheme 1: Synthesis of Triazole Copper catalyst.[18]



Scheme 2: Plausible mechanism of the reaction.[25]



Scheme 3: Synthesis of Triazole by sodium alginate with $CuCl_2$.[44]

2. SYNTHESIS OF POLYMER SUPPORTED CU CATALYSTS

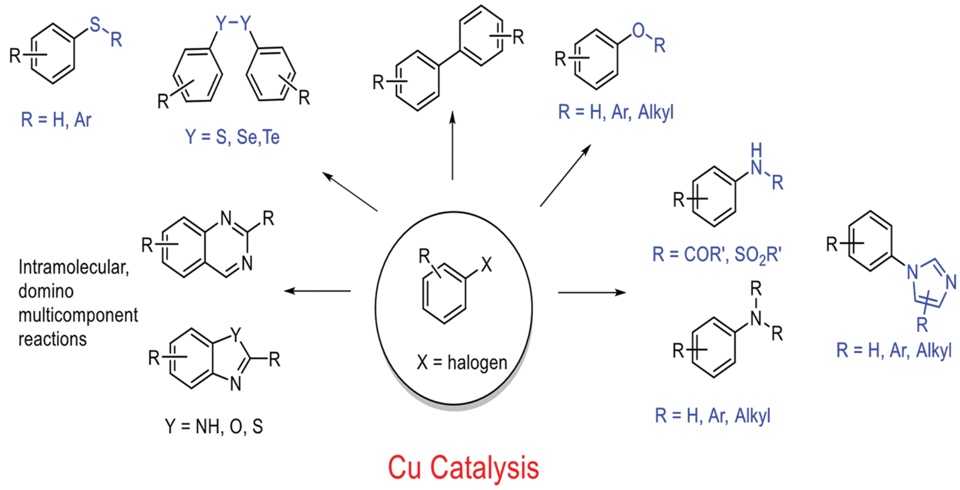
2.1. Experimental Preparation of Polymer Supported Cu (Copper) Catalyst

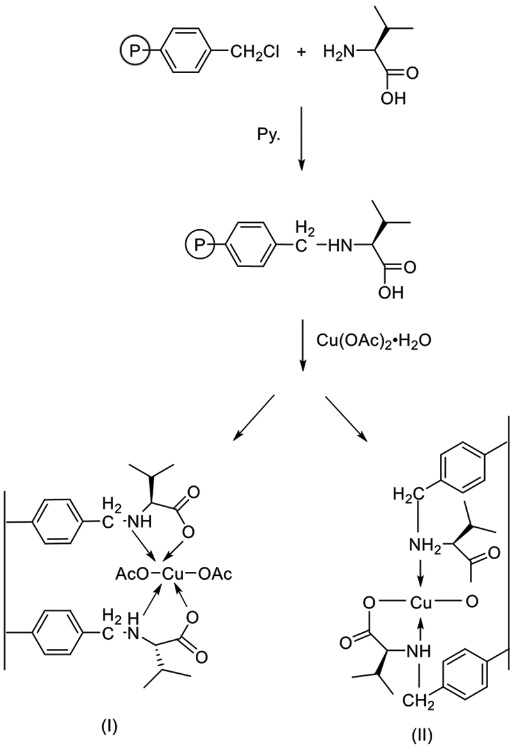
1. Bahsis *et al*. reported the synthesis of Cu(II) alginate based superporous hydrogel catalyst by the reaction of sodium alginate with $CuCl_2$ [43]. They applied this catalyst for the synthesis of triazole by click reaction as shown in Scheme 1 [44].

2.2. Application

Triazole has many useful properties and has the ability to bind hydrogen.

2. Valodkar *et al*. reported the synthesis of polymeric ligand by the reaction of Chloromethylated styrene-divinyl benzene





Scheme 4: Synthesis of poly (S-DVB) supported Cu (II)-amino acid complex.[45]

with L-Valine [45]. This polymeric ligand was further reacted with cupric acetate to give Cu(II) catalyst (polymer supported Cu(II) L–valine complex)[45] as shown in following scheme [46].

2.3. Characterization

The synthesized polymer supported copper catalyst is well characterized by many spectroscopic techniques such as-

1. Fourier transform infrared spectroscopy (FTIR)
2. UV-VIS DRS
3. Scanning electron microscopy
4. Transmission electron microscopy
5. X-ray diffraction
6. Thermogravimetric analysis
7. Energy dispersive X-ray.

2.4. FTIR Analysis

FTIR more commonly known as FT-IR is the preferred method for infrared spectroscopy.

Khan *et al*. reported the FTIR spectra of CuO-MOO$_3$, NPs on the surface of PEG6000. The FTIR spectrum of PEG-6000 shows its characteristic vibrations which are as follows in table.

1.	3453 cm 1404 cm	OH	Stretching and bending vibration
2.	2886 cm	C-H	Stretching vibration
3.	1460 cm	C-H	Bending and scissoring vibration
4.	1353 cm	O-H	Bending vibration
5.	1284 cm	C-O	Stretching vibration
6.	1251 cm 643 cm	C-O-C	Stretching vibration
7.	482 cm	Cu-O	Stretching vibration
8.	799 cm	Vo-MO$_2$	Stretching vibration
9	985 cm	MO=O	Stretching vibration
	990 cm		

3. APPLICATIONS OF POLYMER SUPPORTED COPPER CATALYST

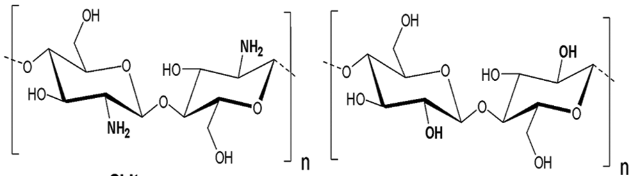
The applications of polymer supported copper catalyst play a significant role in enhancing and developing a new major criteria for the degradation of organic pollutants, waste water management, air purification, antibacterial agents, sensing and biosensing, etc., and in organic reactions [47].

3.1. Waste-Water Treatment

For the degradation of organic pollutants, we used Copper as a catalyst to remove the pollutant [48]. The various biopolymers and polymer supported copper catalyst play a wide and major role in the degradation of organic pollutants [49].

3.1.1. Water treatment using cellulose-MOFs

Cellulose-metal organic framework (Cellulose-MOFs) displayed an excellent performance using copper catalyst for the degradation of organic pollutants [50,51]. The various materials and their synthetic procedure are used for the water purification using Cellulose-MOFs as a copper catalyst species [52]. Cellulose materials are prominently utilized treatment of water. Properties of cellulose exhibits such as strength, hydrophilic characteristic makes it more efficient.



3.1.2. Cellulose-MOFs uses in adsorption

Adsorption of organic pollutants such as phenolic compound, antibiotics, volatile organic, and inorganic compounds, etc. can be done using cellulose-MOFs. All these composites were adsorbed using cellulose-MOFs compound [53].

3.1.3. Oil separation using copper-based cellulose-MOFs composites

Oils are considered to be one of the major and heavy pollutants. The separation of oils having copper ions present in the water can only be removed by different methods like adsorption [54].

4. CHITOSAN AS A BIOORGANIC

4.1. Chitosan

Chitosan is the most abundant biopolymer due to its renewability, biodegradability, biocompatibility, and adhesivity. A newly developed area, chitosan can provide recyclability and low yields which are essential and involve biomedicinal, bioengineering, waste water treatment, catalysis, etc. [55].

5. CHITOSAN AS AN ECOFRIENDLY BIOPOLYMER SUPPORTED CU CATALYST

Due to the fact that chitosan can be biocatalyzed, it is considered as a natural polymer. A Chitosan residue does not have toxicity and can be easily biomoulded by nature. Chitosan is a most and widely used bioreactivee material that can be degradated and used in many advantages.

Chitosan used as a sustainable production for the chitin extraction.

6. BIOMEDICAL APPLICATIONSOF POLYMER SUPPORTED COPPER CATALYST

Many nanomaterials such as Cello-MOFs and chitosan-MOFs have been used for biomedical applications such as antibacterial agents, drug delivery, cancer treatment, and biosensing applications [56]. High content of biomolecules and high stability under biological conditions must be showed by materials [57]. Many copper-based MOFs are efficient antibacterial materials such as Cu-BTC MOFs (also known as aka MOF-199 or HKUST-1) [58]. All the polymer supported copper catalyst-based exhibited high antibacterial activity [59].

6.1. Antibacterial Agents

Copper-based cellulose-metal organic framework exhibits high antibacterial activity. The antibacterial activities of cellulose could be due to intrinsic activity of the antibacterial of metal organic framework or due to the nanoparticles loaded on MOFs. Their activity can be modified by various methods. Antibacterial activity of copper based cellulose-MOFs can make more suitable by combining with the antibacterial agents.

7. CONCLUSION

In this review, we reported various methods for the development of polymer supported copper catalyst. These polymers supported copper catalyst are very useful in the synthesis of azide-alkyne cycloaddition reaction, Heck coupling reaction, friedel craft reaction, etc. There are other applications for these catalysts which observed in waste water management, in sensors and in biomedical. The review literature concerning the preparation and application of polymer supported copper catalyst in various organic synthesis. The synthetic route for preparing a metal complex immobilized on to a polymeric support Cu catalyst, Cu plays an efficient role in synthesizing the various base complexes. Copper-based catalyst promote the catalytic activity for the synthesis of various compounds.

Due to easy environmentally friendly, recyclability for such catalyst provides a major boost in organic reactions. Therefore, more research should be done on these topics.

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***Bibliographical Sketch**

Ms. Saba Azim did her Graduation from ISABELLA THOBURN COLLEGE and post-graduation from BABA SAHEB BHIM RAO AMBEDKAR CENTRAL UNIVERSITY.
She is currently working in a Research Laboratory as a Chemistry. She has a keen interest in research and wish to pursue for the lifetime.

B. S.V. Prakash is working as Associate Professor in Department of Botany, Lucknow Christian Degree College,Lucknow, U.P. India. He has a vast expertise in the field of Ecology of sand dunes and Plant adaptations.

Alfred Lawrence (Ph.D) is working as a faculty in Department of Chemistry, Isabella Thoburn College, Lucknow, India. He has done his Post-Doctoral from Purdue University, USA and has more than 52 International research publications.