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Copper Based Nanoparticles-Catalyzed Organic Transformations

S. Ganesh Babu · R. Karvembu

Abstract Copper (Cu) based nanoparticles mediated organic transformations have been focused worldwide because these methodologies afford industrially important fine chemicals under mild conditions. Moreover, Cu is environment friendly and relatively inexpensive. This review highlights the important developments of Cu based nanocatalysts for organic transformations.

Keywords Nano copper · Copper(I) oxide · Copper(II) oxide · Nano copper salt · Supported nano copper · Organic conversions

1 Introduction

Catalysis is one of the fascinating fields in chemistry. Approximately 90 % of the industrial and pharmaceutical products are achieved by catalytic processes. For the past few decades the field of catalysis is found to be an emerging one. In recent years many Noble laureates are from the field of catalysis, which showed the importance of this topic. There are two types of catalysis, one is homogeneous (in which the reactants and catalyst are in the same phase) and the other is heterogeneous (in which the reactants and catalyst are in different phases). Both the systems have their own merits as well as demerits.

Homogeneous catalysis is the most active one, with many attractive properties such as high chemo- and regioselectivity and high activities. However, engineering processes involving homogeneous catalysis suffer various difficulties like cumbersome product purification and difficulty in catalyst recovery. Because of these drawbacks many efficient systems cannot be commercialized. So the homogeneous catalysis is really difficult to handle.

Heterogeneous catalysis is one of the best options to overcome the drawbacks of homogenous catalysis. They have excellent stability, easy accessibility and most importantly, they can be easily separable from the reaction mixture. However, they do have some drawbacks such as inferior catalytic performance relative to their homogeneous counterparts, because of reduced contact between catalyst and substrate and it requires more reaction time.

So, we need a new catalytic system, which should be active like homogeneous catalysis, and should also be easily recoverable like heterogeneous catalyst. At this point of time, nanocatalysis comes into the picture, which combines the advantages of both the catalytic systems. Because of nano size, i.e. high surface area, the contact between reactants and catalyst increases dramatically (this phenomenon is close to homogeneous catalysis). Insolubility in the reaction solvent made the catalyst heterogeneous and hence can be separated out easily from the reaction mixture (this phenomenon is close to heterogeneous catalysis).

Nanomaterials can combine the advantages of both the systems, and can offer unique activity with high selectivity. Due to these significances, nanocatalysis finds more attention in recent years. The development of nanomaterials-catalyzed organic transformations is in progress worldwide. Still a lot has to be explored in the field of nanocatalysis. This motivates many to develop a simple, mild, efficient, environmentally benign, ligand free, heterogeneous and reusable nanocatalytic systems for organic transformations.

Transition metals and their complexes have been used as an active catalyst for many organic transformations.

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Especially, ruthenium, palladium, platinum, gold and iridium are the frequently used transition metals in catalysis. But to make the catalytic system cost effective, copper (Cu) has been used instead of the above said metals with comparable efficiency. Very recently, nanoparticles (NPs) find much importance in catalysis because of its high surface area and high activity. Many researchers have reported nano Cu in the form of metal, metal oxides or compounds as potential catalysts under ligand free condition for various organic reactions.

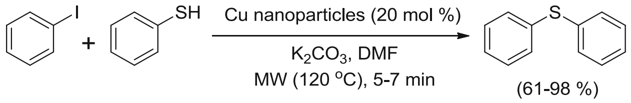
2 Cu Based Nanocatalysts

2.1 Cu NPs as a Catalyst

Using nano-Cu as a catalyst, Zhikun et al. [1], have prepared a new kind of elastic nano-conductive fibers by the polymerization reaction of acetylene and found that it has more conductivity and elasticity. Nano-conductive fibers were separated in alcohol one by one. Nano-Cu was prepared by using H_2 and Ar thermal arc plasma method. Then bulk Cu was melted and evaporated into Cu atom vapor from the liquid metal surface. Then it was condensed as nano-Cu particles on the vacuum chamber and cooled by liquid nitrogen. Polyhedron structure of the nano-Cu particles were confirmed by TEM analysis. DTA studies inferred that the melting point of the formed NPs is 750 °C which is 300 °C lower than that of bulk Cu.

Cu NPs have been used as an effective catalyst for the production of graphene with uniform thickness by chemical vapour deposition technique. Bhaviripudi et al. [2], have studied the kinetics and the interaction between the graphene nanofeatures and Cu NPs. They also studied the kinetics of the growth phenomenon of graphene under different conditions like atmospheric pressure (AP), low pressure, LP (0.1–1 torr) or under ultrahigh vacuum in presence of Cu nanocatalyst. In addition to that, nanoribbons and nanostrips with widths ranging from 20 to 100 nm were also observed on the APCVD grown graphene. Morphology of the formed graphene monolayer was studied using TEM analysis. Furthermore, the interaction of Cu with graphene nanosheet was studied by Raman spectra.

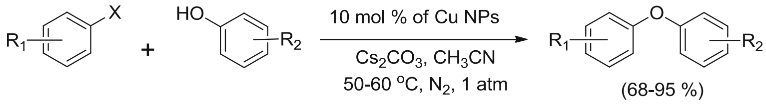
A new protocol for the coupling of aryl iodides with thiophenols and alkanethiols catalyzed by Cu NPs under ligand-free condition has been developed by Ranu et al. [3]. Varieties of aryl sulfides were prepared under microwave irradiation with excellent yield (Scheme 1). All the reactions were completed within 5–7 min. They have suggested plausible radical mechanism for Cu NPs-catalyzed coupling of aryl iodides with thiophenols. Among the conventional bases (Na_2CO_3, K_2CO_3, K_3PO_4, NaOH), K_2CO_3 was chosen as it gave better results in terms of yields. Different substituted aryliodides reacted with a variety of substituted thiophenols, benzylmercaptan, butane- and dodecanethiols to form the corresponding diaryl/aryl–alkyl sulfides. The catalytic products were isolated and characterized by infrared (IR), ^1H and ^{13}C NMR spectroscopic methods. The yields were ranging from 61 to 98 %.



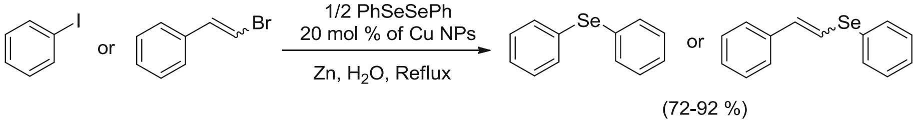
Scheme 1 Nano copper-catalyzed S-arylation of thiols

It was found that metallic nano-Cu could be used as an efficient catalyst for the conversion of formaldehyde into hydrogen and formic acid under room temperature and AP [4]. Effect of different reagents such as methanol, formic acid, acetone, formaldehyde, acetaldehyde, propionaldehyde and benzaldehyde was studied and found that formaldehyde produces high rate of hydrogen (140 mL min^{-1} g^{-1} catalyst) over nano-Cu catalyst at room temperature. Cu NPs were synthesized from polyvinyl pyrrolidone (PVP) and $Cu(NO_3)_2$. Cu^{2+} was reduced with $NaBH_4$ solution and the resultant black solids were washed with distilled water and ethanol to remove PVP and finally dried at room temperature. Hydrogen was generated from HCHO by using Cu nanocatalyst with NaOH. The increase in concentration of NaOH as well as HCHO resulted in Cannizzaro reaction which resulted in the retardation of hydrogen generation.

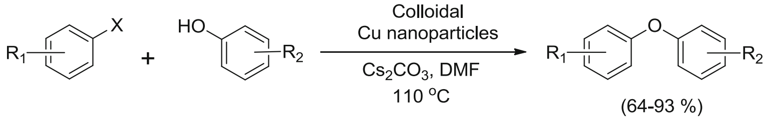
Because of the significant biological activity, diaryl ethers find more attention [5, 6]. Transition metal-catalyzed O-arylation of phenols using aryl halides is a good methodology to achieve diaryl ethers. Metallic Cu NPs have been used for O-arylation of phenols with aryl halides [7]. This catalytic system offered competitive advantages such as recyclability of the catalyst without further purification or without using additives or cofactors, low catalyst loading, broad substrate applicability, and high yields in short reaction times (Scheme 2). 91 % yield of diaryl ether was observed in 4 h in the presence of catalyst. But in the absence of catalyst, the ether was obtained in only 5 % yield in 42 h. Increase of catalyst amount to 50 mol% increases the formation of the product to 95 % in 1.5 h. Increase in the concentration of catalyst promotes the reaction as well as increases the yield of the product. However, very lower yields were observed at room temperature, even after long reaction times. Basicity of the base plays an important role in the reaction of phenols and aryl halides. The Cu-NP catalyzed reaction is much faster with Cs_2CO_3 than with K_2CO_3 or Na_2CO_3 due to the enhanced basicity of Cs_2CO_3. The yields of the product were ranging from 68 to 95 % under optimized condition.



Scheme 2 Nano copper-catalyzed O-arylation of phenols



Scheme 3 Phenyl-selenylation of aryl iodides and vinyl bromides

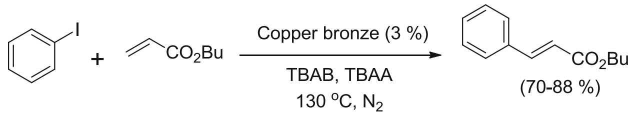


Scheme 4 Colloidal copper nanoparticles-catalyzed O-arylation of phenols

Synthesis of organoselenium compounds found special attention because of its biological activity especially as anticancer and antioxidant agents [8, 9]. Saha et al. [10], developed an efficient procedure for the preparation of aryl- and vinyl-selenides using Cu NPs catalyst from aryl iodide/vinyl bromide with diphenyl selenide in the presence of zinc and water. Stereoselective coupling was observed with (*E*)-vinyl bromides. The catalyst can be recovered from the reaction mixture and reused for four cycles without much decrease in the yield of the product (Scheme 3).

Surfactant-free, single nano-sized Cu NPs (2 nm) were prepared by the DMF reduction method. The prepared Cu NPs were found to be an attractive catalyst for Ullmann type cross-coupling of aryl halides with phenols under ligand-free conditions (Scheme 4). The catalyst showed high turnover number of up to 2.2×10^4. The chemical composition of the Cu NPs was examined by X-ray photoelectron spectroscopy (XPS). The major peak at 932.0 eV confirmed the formation of zero valent Cu. However, the minor shoulder peak with the smaller contribution at 934.4 eV is consistent with Cu oxide (CuO), suggesting the existence of a thin CuO layer around the particle surfaces [11]. The reaction conditions were optimized by using the reaction between iodobenzene and 3,5-dimethylphenol as the model reaction. In this reaction, Cs_2CO_3 was found to be a suitable base, whereas other bases such as Na_2CO_3, KOH, K_3PO_4, and NEt_3 totally inactivated the catalytic activity. Among the different solvents used DMF gave good yield. Therefore, DMF was considered to be the best solution as a solvent in this reaction.

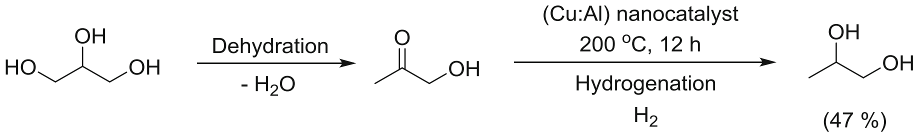
Calo et al. [12], have used nano Cu–bronze as a catalyst for Heck reaction in ionic liquid. Cu NPs-catalyzed Heck reaction has many advantages like inexpensive and eco-friendly alternative to noble metal catalysts [13–17]. The effective catalysts are Cu NPs which are derived from the reaction of iodobenzene with Cu–bronze (Scheme 5). Initially the ionic liquids and bases were screened and found that the presence of both tetra-*n*-butylammonium bromide as solvent and tetra-*n*-butylammonium acetate as base was found to be essential to promote the coupling. These NPs are very stable in tetraalkylammonium salts, easily recycled, and can be stored for months without a loss of catalytic efficiency.



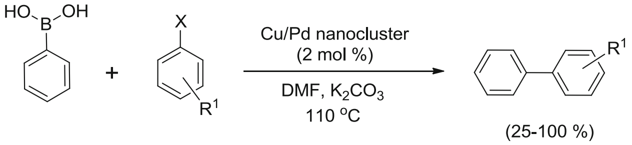
Scheme 5 Copper–bronze nanoparticles-catalyzed Heck reactions in ionic liquid

Production of industrially important compounds from biomass is an attractive green chemical path way [18]. Selective hydrogenolysis of glycerol is the easiest approach to generate 1,2-propanediol which is a major commodity chemical used in the production of antifreeze functional fluids, paints, humectants and polyester resins [19–21]. Mane et al. [22], prepared nanostructured Cu (Cu:Al) catalyst by co-precipitation method from $Cu(NO_3)_2 \cdot 3H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ and used for the selective hydrogenolysis reaction. Highest TOF of 10.2 h^{-1} was observed with Cu:Al nano (7–11 nm) catalyst for the hydrogenolysis of aqueous glycerol. This protocol gave 91 % of 1,2-propanediol selectively whereas only <5 % of degradation product (ethylene glycol, EG) was obtained (Scheme 6). The recycling ability of nano Cu:Al catalyst was also tested and found that it can be reused for three times without much decrease in the catalytic performance. This also provides the information regarding the stability of the nanocatalyst under the reaction conditions.

Suzuki–Miyaura reaction is a noble method to produce carbon–carbon (C–C) bonds via cross-coupling of aryl halides with arylboronic acids, which is a key synthetic step in the production of agrochemicals, polymers and pharmaceuticals [23]. The use of multi-metallic



Scheme 6 Cu:Al nanoparticles-catalyzed selective hydrogenolysis of glycerol



Scheme 7 Cu/Pd nanocluster-catalyzed Suzuki cross-coupling reaction

nanocluster as catalyst enhances its competence because incorporation of different metals can induce large changes in the structure. Thathagar et al. [24], reported that Cu/Pd nanoclusters are the superior catalyst for Suzuki cross-coupling of aryl halides with arylboronic acids (Scheme 7).

Cu in the form of oxides have found more attraction because of its high air and thermal stability. Both Cu(I) and Cu(II) oxides have been employed as effective catalysts for various organic transformations.

2.2 Cu(I) Oxide NPs as a Catalyst

Huang et al. [25], prepared Cu_2O NPs and microparticles by liquid phase chemical synthesis and compared their photocatalytic activity towards the degradation of methyl orange. Initially CuO NPs were prepared from $CuSO_4$ and NaOH. The black CuO precipitate was filtrated and washed with distilled water for three times, dried at 120 °C overnight and then grinded for use. The prepared CuO powders were converted to Cu_2O by using cetyltrimethylammonium (CTAB) in EG. Then its photocatalytic performance was checked for the degradation of methyl orange. But unfortunately, Cu_2O NPs are very easy to deactivate during the photocatalytic reaction because of its rapid photocorrosion. Cu_2O microparticles, whose photocorrosion rate is very slow, have a higher photocatalytic activity than Cu_2O NPs.

Kim et al. [26], have used thermal and air-stable uniform Cu_2O nanocubes for Ullmann cross-coupling reaction of aryl halides with phenols. Cu_2O NPs were synthesized from Cu(II) acetylacetonate by a one-pot polyol process in the presence of PVP as a surfactant and 1,5-pentanediol (PD) as both reductant and solvent (Scheme 8). Initially the reaction conditions were optimized. The scope of the present system was extended with different aryl halides with substituted phenols under optimized reaction condition. The reaction of substrates with electron-donating and electron-withdrawing groups on the phenol ring resulted in high yields of the cross-coupled products. In the case of methyl and methoxy substituents, the conversion yield was 100 %. Furthermore, the reaction of substrates with NO_2 was examined and was found to have high conversion yields (100 %). This protocol provided the advantages of recyclability of the catalyst, low catalyst loading, wide-ranging substrate applicability and high yields in short reaction times.

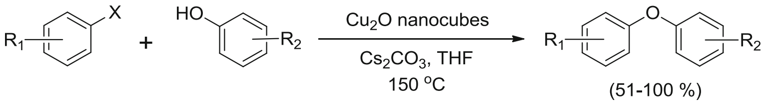
The Mizoroki–Heck cross-coupling reaction is an excellent chemist's toolbox to attain huge variety of different coupled substrates [27–33]. One of the benefits of the Mizoroki–Heck reaction is its outstanding *trans*-selectivity. Ligand free Cu-catalyzed Heck coupling was achieved by Peng et al. [34]. The model coupling reaction between iodobenzene and *n*-butyl acrylate was conducted to screen the optimal reaction conditions, including bases, solvents, and catalysts (Scheme 9). Among all the bases screened, tetramethyl ammonium bromide was superior to some others such as Et_3N, K_2CO_3, Cs_2CO_3, NaOAc, LiOH and LiF. The choice of solvent was also vital to the success of the catalytic reaction. DMF appeared to be the best choice among the common solvents such as DMSO, toluene, xylene, ethanol, acetonitrile, 1,4-dioxane, sulfolane and PEG-400. The present catalytic system has advantages like ligand-free as well as inexpensive catalyst, it has limitations that it can be applied effectively only to the coupling of aryl iodides and olefins.

2.3 Cu(II) Oxide NPs as a Catalyst

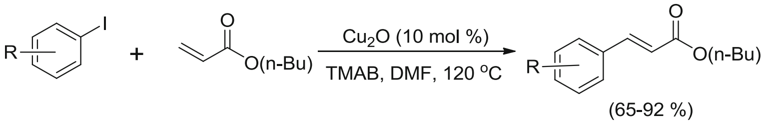
Multi-component domino coupling reactions are powerful synthetic tactics favored by organic chemists which allow the creation of several bonds in a single operation [35, 36]. 1,4-Dihydropyridines (1,4-DHPs) are important class of compounds in the field of drugs and pharmaceuticals which can be achieved by domino coupling [37]. Some of these 1,4-DHPs are useful for regeneration of the reduced form of nicotinamine adenine dinucleotide, an essential compound for living organisms [38, 39]. Nanocrystalline Cu(II) oxide catalyzed three-component coupling of aromatic amines, β-ketoesters and cinnamaldehyde afford the corresponding 1,4-DHPs in moderate to good yields under mild conditions (Scheme 10). The catalyst can be recovered and reused for four cycles with almost consistent activity [40].

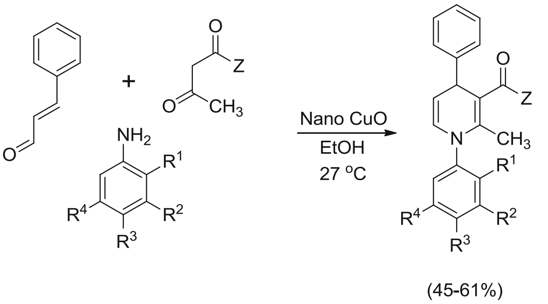
A^3 coupling is the one pot synthetic path way to produce propargylamines in which the coupling of aldehydes, amines and alkynes takes place. Cu(II) oxide was found to be an effectual catalyst for this coupling. Kantam et al.

Scheme 8 Cu_2O nanocubes-catalyzed O-arylation of phenols

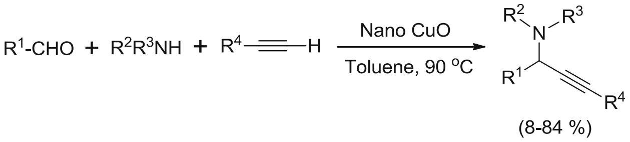


Scheme 9 Cu_2O nanoparticles-catalyzed Mizoroki–Heck reaction

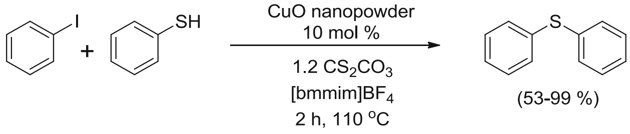




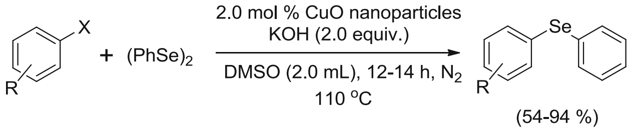
Scheme 10 Nano CuO-catalyzed synthesis of 1,4-dihydropyridines



Scheme 11 Nano CuO-catalyzed A^3 coupling



Scheme 12 CuO nanopowder-catalyzed S-arylation of thiols



Scheme 13 CuO nanoparticles-catalyzed diaryl selenides synthesis

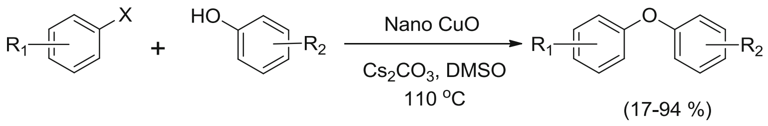
[41], prepared nanocrystalline CuO, tested its catalytic activity (Scheme 11). A series of experiments were carried out in an effort to develop an improved catalytic system for the synthesis of propargylamines by A^3 coupling of benzaldehyde, piperidine and phenylacetylene. When the reaction was conducted with bulk CuO as well as Cu_2O, a poor yield of the product was obtained. When the nano CuO catalyzed A^3 coupling reaction was carried out in solvents other than toluene, such as dry THF, acetonitrile or DCM, a significant decrease in yield was noticed. Trace amount of product was observed when water was used as the solvent, even after a prolonged reaction time. The optimum ratio of aldehyde, amine and alkyne was found to be 1:1.3:1.5. A probable mechanism was proposed for A^3 coupling.

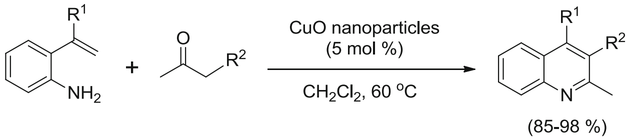
Aryl sulfides and their derivatives have been found in numerous biologically and pharmaceutically active compounds [42, 43]. Schwab et al. [44], have developed a recyclable Cu nanopowder catalytic system for the cross-coupling reaction of various thiols with aryl iodides in ionic liquid under ligand-free conditions (Scheme 12). [bmmim]BF_4 exhibited higher performance with the advantage of being able to be reused for up to four successive runs. A variety of inorganic and organic bases were used to afford aryl sulfides. Despite that the respective sulfide could be detected employing the related bases screened, Cs_2CO_3 showed the best performance. Using the optimized conditions, the present reaction was further expanded to a broader range of aryl thiols and aryl iodides in order to evaluate the scope and limitations of the method. The yields of diarylsulphides were ranging from 53 to 99 %. Reusability of both catalyst and solvent makes the system more interesting in green chemistry point of view.

Diaryl selenides are significant compounds in organic chemistry and catalysis [45–52]. Selenium and organo selenium compounds have antioxidant, antitumor, antimicrobial, anticancer, and antiviral properties; hence their biological and medicinal activities are increasingly appreciated [53–56]. Reddy et al. [57], developed a novel, efficient and ligand-free catalytic system for the cross-coupling of aryl halides with diaryl diselenides using a catalytic amount of nanocrystalline CuO as a recyclable catalyst with KOH as a base in DMSO at 110 °C (Scheme 13). This protocol has been utilized for the synthesis of a variety of aryl selenides in excellent yields from the readily available aryl halides and diaryl diselenides. Plausible reaction pathway for the CuO NP-catalyzed C–Se cross-coupling of aryl halides with diphenyl diselenide in the presence of KOH was proposed. The catalyst can be easily recovered and reused.

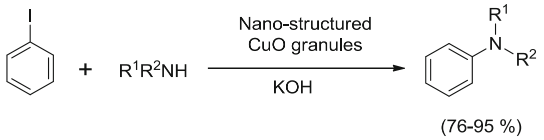
Diaryl ethers are important structural motifs in numerous natural biologically active compounds, for example, K13, perrottetin and vancomycin, as well as in many polymers such as poly(aryl ethers) [58]. CuO NPs have been employed as an effective catalyst for organic

Scheme 14 Nano CuO-catalyzed O-arylation of phenols





Scheme 15 Nano CuO-catalyzed Friedlander quinoline synthesis



Scheme 16 Nanostructured CuO granules-catalyzed synthesis of *N*-arylamines

reactions such as Ullmann coupling of phenols with aryl halides under ligand free condition [59] (Scheme 14). Common solvents, such as DMSO, DMF, dioxane, toluene and NMP, were tested; DMSO gave the highest yield. Following these results, different bases, such as KOH, K_2CO_3 and K_3PO_4 were screened. Temperature also had a large effect on the reaction. Below 100 °C the reaction produced the desired products in low yields, but when the reaction was performed above 110 °C, there was no obvious improvement in yield. The catalyst can be reused at least five times without loss in catalytic activity. TEM images showed that the shape and size of the CuO NPs have undergone almost no change even after the fifth cycle.

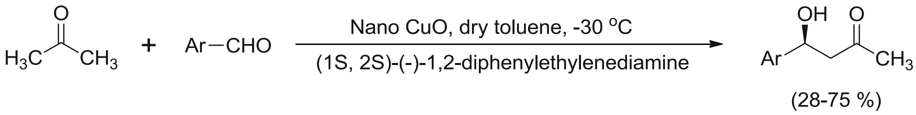
The quinoline moiety is present in a number of natural and synthetic products [60, 61]. Similarly its derivatives are utilized as antimalarial, antitumor and antibacterial agents [62]. Nezhad et al. [63], reported CuO NPs as an efficient and reusable catalyst for the one-pot Friedlander quinoline synthesis (Scheme 15). The CuO catalyst is prepared by PEG assisted method with a few modification. The size of the prepared catalyst is found to be 25–27 nm and surface area is about 214 $m^2\ g^{-1}$. The prepared CuO NPs were characterized by X-ray diffraction (XRD) and SEM. It was observed that solvent-free condition gave the excellent yield of product than that in the presence of solvents. The major advantages of performing the Friedlander reaction in the presence of nano CuO as catalyst are use of a safe, nonvolatile, noncorrosive catalyst; recovery of catalyst at the end of the reactions by simple filtration; the target products are obtained generally in excellent yields under easy and mild reaction conditions; and the reactions are carried out under solvent free conditions with economic benefits.

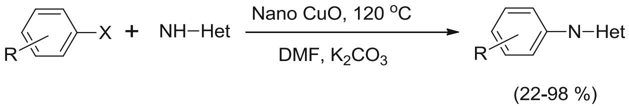
Synthesis of *N*-arylamines is an active area in organic synthesis because of the occurrence of these moieties in biologically important natural products, pharmaceuticals, and their applications in materials research [64]. Ahmadi et al. [65], prepared granulated Cu(II) oxide NPs by hydrothermal decomposition of Cu nitrate under supercritical water conditions. The nano-structured CuO granules-catalyzed reaction has the advantages in terms of easy product purification, efficient recycling of the catalyst (for at least five consecutive trials without a decrease in their activity) and minimization of metal oxide traces in the product. The scope of the Cu-catalyzed aryl amination reaction was explored by using CuO granules as the Cu source and KOH as the base under solvent-free conditions. The coupling reaction of iodobenzene with various amines was carried out using this catalyst system, and the desired amination products were obtained in good to high yields. Furthermore, various aryl, alkyl, and *N*-heterocyclic amines can be utilized to produce *N*-arylamines (Scheme 16).

Discharge of hazardous organic pollutants such as pesticides, polychlorinated biphenyls, halogenated organic solvents and polycyclic aromatic hydrocarbons (HCs) from industrial and waste water treatment plants are the major environmental issue in recent years. Oxidative mineralization by heterogeneous photocatalysis is one of the hopeful techniques to eliminate the organic pollutants [66]. Catalytic activity of Cu(II) oxide NPs was investigated for the removal of organic pollutants in aqueous solutions, using hydrogen peroxide as an oxidant by Moshe et al. [67]. The effects of several factors such as irradiation, oxidant concentration, ionic strength and pH on the reaction were also investigated. Degradation was achieved for both alachlor and phenanthrene cases after 20 min. Nano CuO was found to be an efficient catalyst for the degradation of alachlor and phenanthrene. This catalytic system does not require any type of irradiation. The kinetics of the reaction was confirmed as pseudo-first-order with respect to the degraded organic compound. However a high concentration of NaCl increases the rate of the reaction dramatically.

Optically active β-hydroxy carbonyl compounds were traditionally achieved by transition metal catalyzed direct asymmetric aldol reactions [68, 69]. Kantam et al. [70], has reported Cu(II) oxide NPs-catalyzed aldol reaction with good yields and good to moderate enantioselectivities in the presence of (1*S*,2*S*)-(−)-1,2-diphenylethylenediamine at −30 °C (Scheme 17). In the process of optimization of

Scheme 17 Nano CuO-catalyzed aldol reactions





Scheme 18 CuO nanoparticles-catalyzed *N*-arylation of heterocycles

the reaction conditions, reaction was carried out with different solvents and temperatures. It is evident that toluene is the best solvent in terms of both yield and ee. A significant increase in ee was observed by decreasing the reaction temperature. The use of toluene at −30 °C resulted in optimum enantioselectivity. The nano-CuO catalyst could be reused for four cycles without loss of activity and selectivity. No reaction occurred when the reaction was conducted with the filtrate obtained after removal of the catalyst. The absence of Cu in the filtrate was also confirmed by AAS studies. The XRD patterns of fresh and used nano-CuO were compared and the results confirmed the fact that the structure and morphology of the catalyst remained the same during the course of the reaction.

The formation of C–N bonds by cross coupling reactions finds much attention because of its importance in biological, pharmaceutical and material sciences. The traditional methods suffer often with the requirement of stoichiometric amounts of Cu reagents, which, on scale-up, leads to the problem of waste disposal [71, 72]. CuO NPs found to be an effective catalyst for the C–N cross coupling of amines with iodobenzene in excellent yields (Scheme 18). The procedure reported for C–N cross coupling reaction is simple and efficient. CuO NPs are marked as cheap and air stable catalyst [73]. Rout et al., have found that the Cu(II) salts such as $CuSO_4{\cdot}5H_2O$ and $Cu(OAc)_2{\cdot}H_2O$ afforded diphenylamine in low yield whereas CuO NPs were superior in catalytic performance. Similarly, among the different solvents studied, DMSO, toluene, dioxane, and DMF, the solvent DMF gave good yield. They also reported that the reaction with KOH was more effective in comparison to that with K_2CO_3. The catalyst has been reused three times without much decrease in the yield of the product. Finally possible mechanism was proposed for this catalytic system.

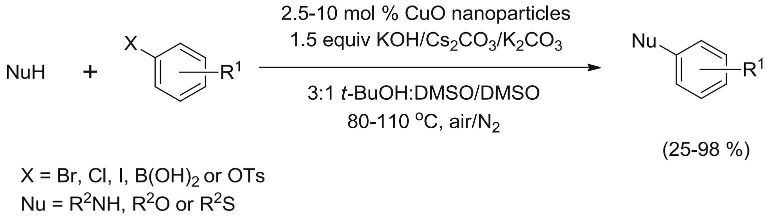
CuO NPs have been studied for C–N, C–O, and C–S bond formations via cross-coupling reactions of nitrogen, oxygen, and sulfur nucleophiles with aryl halides [74]. Amides, amines, imidazoles, phenols, alcohols and thiols undergo reactions with aryl iodides in the presence of a base such as KOH, Cs_2CO_3, and K_2CO_3 at moderate temperature (Scheme 19). The procedure is simple, general, ligand-free, and efficient to afford the cross-coupled products in high yield. The CuO NPs are recyclable without loss of activity. After completion of the C–O cross-coupling of phenol with iodobenzene, the reaction mixture was treated with water and EtOAc. The CuO NPs were recovered from the aqueous solution by centrifugation. It was reused for the fresh C–O cross-coupling of phenol with iodobenzene for three times, and no loss of activity was observed.

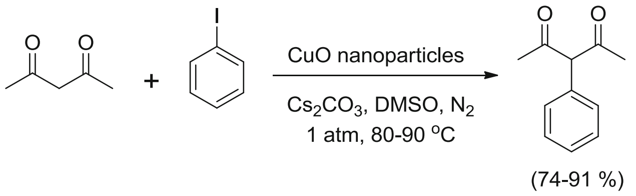
C–C bond formations play a vital role in organic synthesis because the final products are found to be valuable synthons in organic synthesis [75–78]. However, C-arylation of active methylene compounds has not been investigated to the same extent as other C–C bond forming reactions. Kidwai et al. [79], found that CuO NPs to be an excellent heterogeneous catalyst for C-arylation of active methylene compounds using various aryl halides (Scheme 20). Other Cu salts such as $Cu(OAc)_2$ and CuO were found to be inferior to CuO-NPs and gave low yields of 3-phenylpentane-2,4-dione. The catalyst can be recovered from the reaction mixture and used for four consecutive cycles without decrease in its activity. A possible reaction pathway for the CuO-NPs catalyzed C–C coupling reaction was proposed.

Many researchers are attracted towards the development of effective catalytic system for the *N*-arylation of heterocycles because the final products, *N*-arylheterocycles play an important role in a wide range of pharmaceuticals industries, agrochemical industries, natural products synthesis and synthesis of biologically active compounds [80–83]. They can be exploited as precursors of versatile *N*-heterocyclic carbenes and also can be used as efficient ligands for transition-metal catalysis. Kantam et al. [84], developed nanocrystalline Cu(II) oxide-catalyzed *N*-arylation of heterocycles with activated chloro- and fluoroarenes using potassium carbonate as a base. Particularly noteworthy is that fluoroarenes containing several *ortho*- or *para*-electron withdrawing groups are also coupled with imidazole to afford the corresponding *N*-arylated products in excellent yields. This catalytic system was not restricted to imidazole but extended to various *N*-heterocycles such as pyrrole, benzimidazole, pyrazole and indole. The yields were ranging from 76 to 94 %. The catalyst can be used for five cycles with almost consistent activity (Scheme 21).

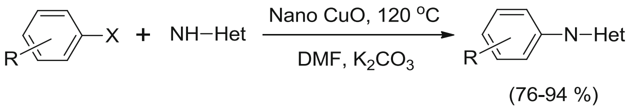
S-arylation of thiols is an important organic transformation because the final products have more biological and pharmaceutical impact, and also used as molecular precursors for the development of materials [72, 85–91]. C–S

Scheme 19 CuO nanoparticles-catalyzed C–N, C–O and C–S cross coupling





Scheme 20 CuO nanoparticles-catalyzed α-arylation of β-diketones



Scheme 21 Nano CuO-catalyzed *N*-arylation of heterocycles

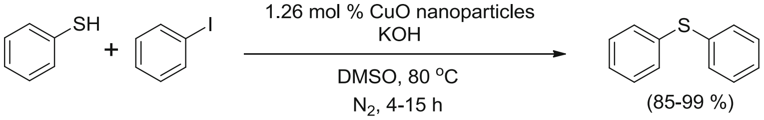
cross-coupling of thiols with iodobenzene was achieved by nano CuO catalyst. Rout et al. [92], have proposed the reaction pathway for the CuO NPs-catalyzed C–S cross-coupling of iodobenzene with thiols in the presence of KOH (Scheme 22). The solvents i-PrOH, DMF, 1,4-dioxane, and toluene were less effective than DMSO. Of the bases tested, KOH gave the best results. The product was formed in lower yield with K_2CO_3. The Cu(II) salts $CuSO_4 \cdot 5H_2O$, $Cu(OAc)_2 \cdot 2H_2O$, and CuO were found to be inferior to CuO NPs as catalysts for the C–S coupling reaction. Furthermore, iodobenzene was a more reactive substrate than chlorobenzene or bromobenzene. 4-Methyl-, 4-methoxy-, 4-nitro-, 4-bromo-, and 2-bromobenzenethiol underwent the C–S cross-coupling reaction with iodobenzene to afford the corresponding products in 88–99 % yield. Substrates with electron-donating groups were more reactive than those with electron-withdrawing groups. Similar reactivity was observed for 2-naphthalenethiol. After the completion of the reaction, the catalyst was recovered from the reaction mixture by centrifugation and reused up to three times. Only a slight decrease in catalytic activity was observed after the third cycle.

This catalytic system was also tested with butane-1,4-dithiol and found that both the –SH groups underwent the cross-coupling reaction to give the corresponding bisarylated product in high yield (Scheme 23).

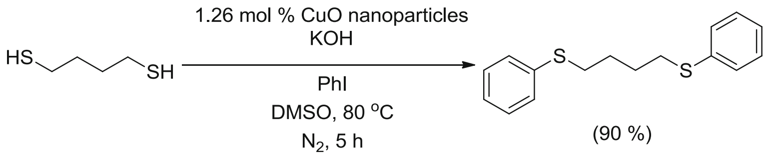
Huisgen 1,3-dipolar cycloaddition reaction of azides and terminal alkynes has made a great impact on biological, industrial and synthetic applications and provides synthetically and biologically useful 1,2,3-triazole type products with high regioselectivity [93–98]. Song et al. [99], demonstrated the excellent catalytic activity of CuO NPs in the Huisgen cycloaddition reaction of azides and acetylenes (Scheme 24). To explore the scope of the substrates, various alkynes and azides were subjected to the standard CuO NPs-catalyzed cycloaddition reactions. Since the functional groups on the substrates are known to play a significant role in terms of the yield and selectivity, initially, alkynes possessing different groups were examined. This method provided tolerant to a wide range of functional groups and reaction conditions involving air and water. Catalytic activity of Cu species is remarkably improved by controlling the particle size. Furthermore, the system has advantages like, the use of cheap, stable and recyclable heterogeneous CuO NPs.

Aryl sulfides are structural motifs found in many biological and pharmaceutically active compounds and have been used as important intermediates in several organic transformations [100, 101]. Bhong et al. [102], have reported CuO NPs-catalyzed C–S cross-coupling and concomitant oxidative aromatization of 4-aryl-3,4-dihydropyrimidin-2(1*H*)-thione with diaryliodonium salts under ligand free condition (Scheme 25). The optimum conditions for the S-arylation of 4-phenyl-3,4-dihydropyrimidine-2(1*H*)-thione were investigated by screening of appropriate arylating agents and Cu catalysts in DMF using K_2CO_3 as the base. Poor results were observed with various Cu catalysts such as $Cu(OAc)_2$, $CuCl_2$ and CuI. But nano CuO offered good yield and hence the scope was extended with nano CuO catalyst. The yields are ranging from 63 to 88 % with nano CuO catalyst. This method offered significant advantages such as operational simplicity with a recyclable catalytic system.

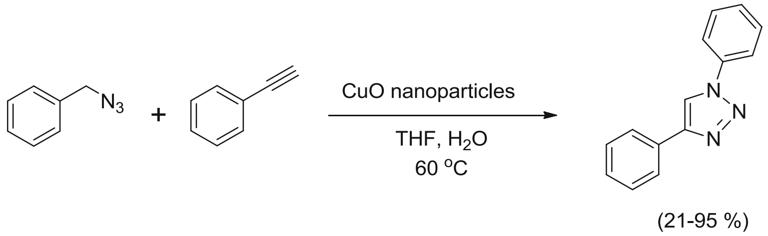
Scheme 22 CuO nanoparticles-catalyzed S-arylation of thiols



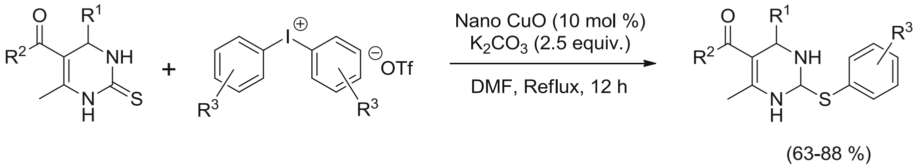
Scheme 23 Nano CuO-catalyzed synthesis of butane-1,4-dithiol



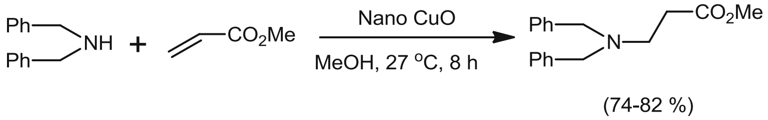
Scheme 24 CuO nanoparticles-catalyzed Huisgen cycloaddition reaction

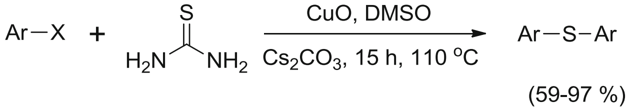


Scheme 25 CuO nanoparticles-catalyzed C–S cross-coupling and concomitant oxidative aromatization

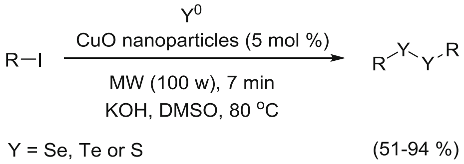


Scheme 26 CuO nanoparticles-catalyzed synthesis of β-amino carbonyl compounds





Scheme 27 CuO nanoparticles-catalyzed synthesis of diaryl sulfides



Scheme 28 CuO nanoparticles-catalyzed synthesis of organochalcogen

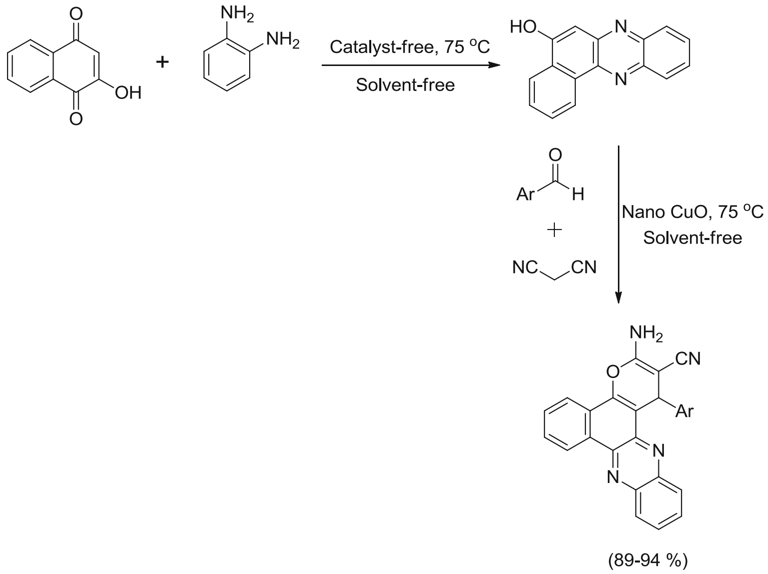
β-Amino carbonyl compounds are important intermediates in the synthesis of various complex natural products, antibiotics, β-amino alcohols, and chiral auxillaries [103–106]. Nanocrystalline Cu(II) oxide-catalyzed aza-Michael reaction and insertion of α-diazo compounds into N–H bonds of amines was reported by Kantam et al. [107]. This methodology has also been used to produce glycine esters in good yields (Scheme 26). The catalyst was used for three cycles with minimal loss of activity.

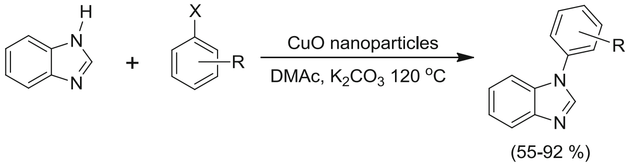
During the last few decades, aryl sulfides and their derivatives are found in numerous biological, pharmaceutical, and material science applications [86, 108–112]. Reddy et al. [113], has developed recyclable CuO NPs-catalyzed simple and highly efficient protocol for the synthesis of symmetrical aryl sulfides by the cross-coupling of aromatic halides with inexpensive and commercially available thiourea (Scheme 27). The reaction employs a very simple catalyst system, having functional group tolerance, and resulting in good to excellent yields.

Over the past few decades organochalcogen compounds have attracted considerable attention due to their importance as reagents and synthetic intermediates in organic synthesis [114–116]. Botteselle et al. [117], developed microwave assisted one-pot synthesis of symmetrical diselenides, ditellurides and disulfides from organoyl iodides and elemental chalcogen. CuO NPs were found to be an efficient catalyst for C–Se, C–Te, and C–S bond formation under microwave irradiation (Scheme 28).

Phenazines are present in natural and synthetic products showing a variety of biological functions, including antimalarial, trypanocidal, fungicidal, antitumor, and antiplatelet activities [118]. An efficient one-pot quantitative procedure for the preparation of functionalized benzo[*a*]pyrano[2,3-*c*]phenazine derivatives from four-component reaction of 2-hydroxynaphthalene-1,4-dione, *o*-phenylenediamine, aldehyde and malononitrile in the presence of nano CuO as the catalyst has been developed (Scheme 29) [119]. The Cu(II) oxide NPs can be recovered and reused several times without loss of its activity.

Scheme 29 CuO nanoparticles-catalyzed synthesis of phenazines





Scheme 30 Nano CuO-catalyzed *N*-arylation of benzimidazole

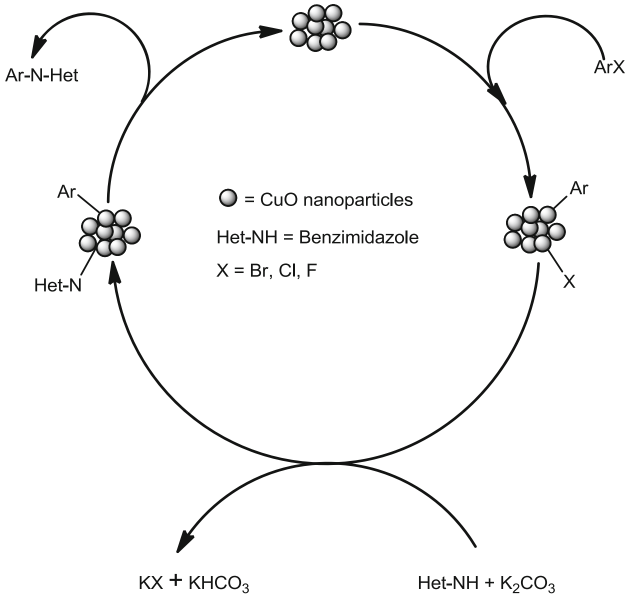


Fig. 1 Proposed mechanism for CuO nanoparticles-catalyzed *N*-arylation of benzimidazole with aryl halides

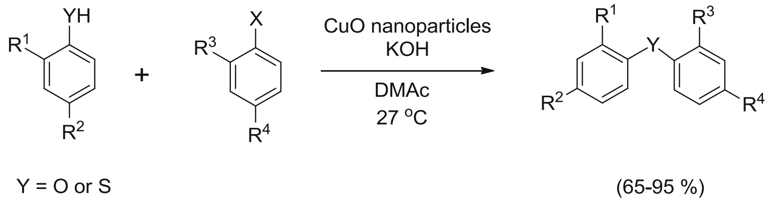
C(aryl)–N(heterocycle) bond formation is an important organic reaction since the resultant *N*-arylated heterocyclic product play an important role in a wide range of pharmaceuticals, natural products and biologically active compounds [120–125]. CuO NPs were found to be a cheap, air stable and efficient catalyst for *N*-arylation of benzimidazole with variety of aryl halides (Scheme 30). The procedure is simple, general, ligand-free and efficient to afford the cross-coupled products in high yield. Since nanocrystalline CuO is a heterogeneous catalyst, it can be easily separated from the reaction mixture as well [126].

A plausible mechanism has been proposed for this catalytic system (Fig. 1).

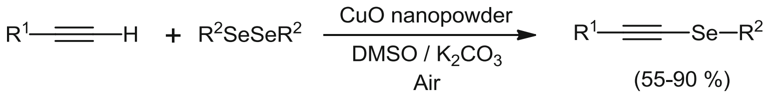
Diaryl ethers and diaryl thioethers syntheses have absorbed more attention in recent years because it is found in subunits of many synthetically challenging and medicinally important natural products [86, 127–129]. Simple, efficient, regio- and chemoselective, reusable and heterogeneous nano CuO-catalyzed Ullmann type C–O/C–S cross coupling of aryl halide with phenol/thiophenol has been demonstrated at room temperature (Scheme 31). The reaction condition was optimized and scope was explored with various aryl halides and phenol/substituted phenol/thiophenol [130].

Alkynyl selenides have been used as precursors in hydrohalogenation, hydrosulfonation, hydroboration, hydrostannylation, etc. [131–135]. More recently, acetylene selenides have been employed as a powerful building block in supramolecular chemistry as well as for the synthesis of several heterocycles via cyclization reactions [136, 137]. Godoi et al. [138], report an efficient method for the synthesis of alkynyl selenides and tellurides from terminal alkynes and diorganyl diselenides or ditellurides using CuO nanopowder as a recyclable catalyst (Scheme 32).

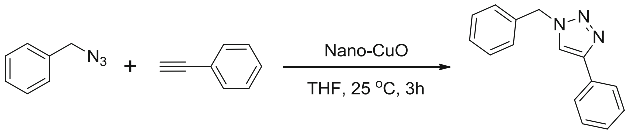
Alkyne–azide cycloaddition is one of the important transformations as far as organic chemistry is concerned. CuO NPs showed good catalytic activity to form 1,4-disubstituted 1,2,3-triazoles in the absence of reductants in THF as well as in water (Scheme 33) [139].



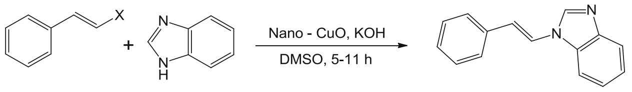
Scheme 31 Nano CuO-catalyzed C–O/C–S cross coupling



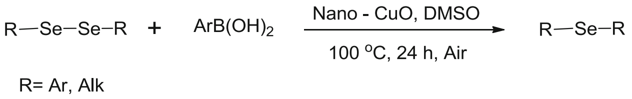
Scheme 32 Synthesis of alkynyl selenides catalyzed by CuO nanopowder



Scheme 33 CuO nanoparticles-catalyzed alkyne–azide cycloaddition



Scheme 34 CuO nanoparticles-catalyzed vinylation of imidazoles



Scheme 35 CuO nanoparticles-catalyzed coupling of diselenides with aryl boronic acids

Vinylation of imidazoles is an important protocol because the final product plays an important role in pharmaceutical and agrochemical industries. Rao et al., reported a straightforward methodology for the vinylation of imidazoles under ligand-free conditions catalyzed by recyclable CuO NPs. Various imidazoles were cross-coupled with different substituted vinyl halides to obtain the corresponding products in excellent yields (Scheme 34) [140].

Cross coupling of diselenides with aryl boronic acids is a general cross-coupling which is performed with organic diselenides and aryl boronic acids to afford the corresponding selenides. CuO NPs have been found to be an efficient catalyst for the coupling of organic diselenides with aryl boronic acids bearing electron-withdrawing and -donating groups in good to excellent yields (Scheme 35) [141].

2.4 Cu Salt NPs as a Catalyst

Cu salts with ligand lead to in situ formation of Cu complex which can be used as an effective homogeneous catalyst for many industrially important organic transformations. Based on this idea, in some cases, nano Cu salts have been used as a heterogeneous and reusable catalyst under ligand free condition. For example, Sreedhar et al. [142], have used CuI NPs for the C–N and C–O cross coupling of heterocyclic amines and phenols with chlorobenzenes (Schemes 36, 37). Less basic K_2CO_3 led to an efficient *N*-arylation of imidazole. Of all the solvents screened, DMF served as the prime solvent; DMSO and NMP were fair solvents but were not as good as DMF. Variety of products including *N*-arylimidazoles and aryl ethers were synthesized in good to excellent yields. The yields of the product were ranging from 33 to 99 %. Furthermore, the nanocatalytic system can be reused for several cycles without loss of its activity.

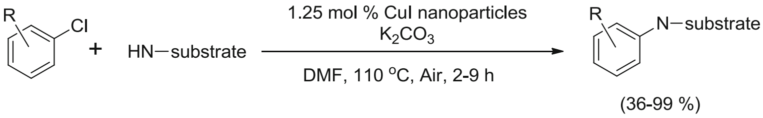
Nanosized metal and metal oxides have shown interesting features in catalysis. Even then, they have some limitations such as recovery of catalyst from the reaction mixture and aggregation during the course of the reaction. This reduces the reusable capability of the NPs. To prevent the aggregation, NPs have to be stabilized. One strategy to stabilize NPs against their tendency to grow is to support them on a solid surface. The surface of solids can interact with NPs through van der Waals, hydrogen bond and electrostatic forces and restrict the mobility of the NPs, making their aggregation more difficult.

2.5 Cu NPs Decorated over Solid Supports as a Catalyst

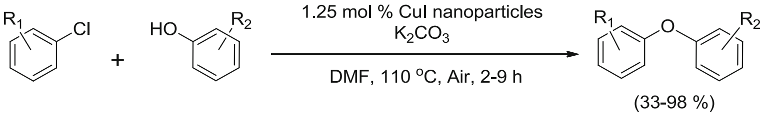
Air pollution is one of the major issues in environmental point of view. The main pollutants in air are carbon monoxide (CO), HC and nitrogen oxide (NO_x). One of the best ways to reduce these pollutants is to convert them into harmless materials by catalytic process. Lin et al. [143], prepared Cu NPs by arc or thermal plasma method and were supported on γ-Al_2O_3 by mechanical means and approached this problem. The catalyst was characterized by SEM, TEM and XRD. They concluded that supported nano-Cu particles have huge catalytic activity towards the oxidation of CO at room temperature.

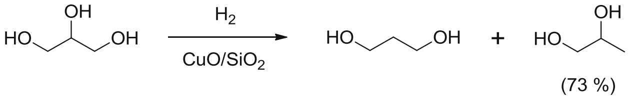
CO oxidation reaction is an important process from environmental point of view. Many researchers try to develop efficient catalytic systems for this conversion. Noble metals such as palladium, platinum and gold

Scheme 36 CuI nanoparticles-catalyzed *N*-arylation of heterocycles



Scheme 37 CuI nanoparticles-catalyzed O-arylation of phenols





Scheme 38 CuO/SiO_2-catalyzed hydrogenolysis of glycerol

supported on oxides are the most active catalysts for CO oxidation reaction [144–146]. Sundar and Deevi [147], synthesized ceria supported Cu(II) oxide (CuO/CeO_2) nanocomposite catalyst by laser vaporization and controlled condensation method and tested its catalytic activity for the complete oxidation of CO. Ceria supported Cu catalysts were characterized by XRD, TEM, EDAX and TPR. The catalytic activity of the nanopowders for CO oxidation reaction was tested in a fixed bed flow tube reactor in Ar: 20 %, O_2: 4 % and CO mixture. The nanocatalysts are active towards oxidation of CO, and irrespective of the Cu content, the light-off temperature for CO oxidation in the initial test run is around 120 °C.

Highly dispersed Cu supported over silica (CuO/SiO_2) catalyst was prepared by a simple and convenient precipitation-gel method. The prepared nanocatalyst was characterized by FT-IR, BET, dissociative N_2O adsorption, TEM, TPR, XRD and XPS techniques. It was used for the selective hydrogenolysis of glycerol to propanediols (Scheme 38). The present protocol showed high selectivity (>98 %) toward 1,2-propanediol in glycerol hydrogenolysis [148]. The catalytic behavior of calcined and reduced samples and the structure changes of these samples after reaction allow the understanding of the stability toward sintering as well as the possible mechanism of the reaction.

Transition metal has been doped over solid support usually by sol–gel, wet impregnation and co-precipitation methods. But Zhang et al., preferred magnetron sputtering technology for doping Cu NPs over TiO_2 surface, which is an interesting method because it can be applicable to large-area deposition, and high quality TiO_2 films can be achieved even at low substrate temperatures. Cu-doped TiO_2 film catalyst has been characterized by XPS analysis to confirm the formation of Cu(II) oxide [149]. 1.45 wt% of Cu doped over TiO_2 film showed the most effective photocatalytic activity towards the degradation of methyl orange.

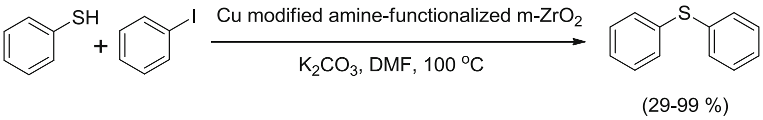
Water–gas shift reaction (WGSR) is one of the pioneer methods to generate pure hydrogen. Cu-based catalysts are well known low temperature WGSR catalysts. Boccuzzi et al. [150], prepared gold, silver and Cu particles supported on TiO_2 and tested their catalytic activity towards the WGSR. They observed the silver catalyst did not have any catalytic activity, whereas Cu and gold catalysts showed moderate and good activity respectively. This variation in activity is due to the difference in catalysts behavior towards the CO adsorption at −183 °C and on the effect of co-adsorbed species.

Synthesis of methanol at LP condition is a challenging task. Cu–Zn and Cu–Zn–Al are the most common catalysts for methanol synthesis [151]. Cu/ZnO catalyst was synthesized by a simple co-precipitation method. Its catalytic activity was studied towards the methanol synthesis from H_2, CO and CO_2 in a continuous circulated flow reactor at 0.1 MPa and 220 °C. The major advantage of this catalytic system is that no by-product was detected [152].

Ceria is well known for its high oxygen storage capacity and hence it can be used as a promoter in many oxidation reactions. So, highly dispersed Cu particles stabilized over La-doped CeO_2 and Y-doped ZrO_2 were synthesized and their catalytic activity was studied on methane oxidation reaction. Cu is more stabilized when dispersed in Ce(La)O_2 than in Zr(Y)O_2 matrix, so that reduction of CuO species requires lower temperatures on the Zr(Y)O_2-based catalysts. Kundakovic and Stephanopoulos [153], concluded that strongly associated Cu (ions) and large Cu particles were both found to be less active than Cu nano clusters dispersed on the support.

Oxidation of CO in the H_2-rich stream has been recognized as one of the most straightforward and cost-effective methods to achieve acceptable CO concentrations. A catalyst with 5 wt% of CuO supported on ceria (CuO/CeO_2) was prepared by incipient wetness impregnation of Cu nitrate on a nanocrystalline CeO_2 support. This prepared catalyst was found to be effective for the selective CO oxidation [154].

WGSR and CO oxidation processes are critical to get pure hydrogen for fuel cells and other industrial applications. Heterogeneous catalysts are frequently used to accelerate them. Wang et al. [155], synthesized Cu/CeO_2



Scheme 39 Nano Cu/ZrO_2-catalyzed S-arylation of thiols

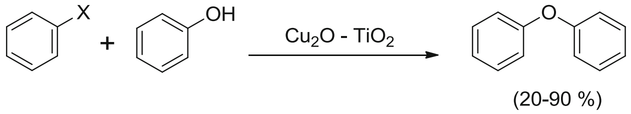
NPs by a reversed microemulsion method. The behavior of CuO/CeO_2 catalyst for the WGSR was investigated by time-resolved XRD (TR-XRD), TR X-ray absorption spectroscopy and IR spectroscopy to illustrate the active sites of Cu–CeO_2 catalyst for the WGSR. This study clearly revealed the importance of in situ structural studies for heterogeneous catalytic reactions.

Kameoka et al. [156], designed a new form of Cu catalyst (Cu–Cr_2O_3) with high thermal stability and activity. Delafossite ($CuCrO_2$) was reduced to fine dispersion of Cu and Cr_2O_3 particles with porous structure by the treatment with H_2 at 600 °C, which exhibited much higher activity and thermal stability for steam reforming of methanol (SRM). The structure consisting of fine dispersion of Cu NPs within the porous chromium oxides was the main reason for high surface area and huge catalytic activity for SRM.

Kameoka et al., demonstrated that spinel $CuFe_2O_4$ as a precursor for a highly active Cu catalyst. $CuFe_2O_4$ on the SiO_2 was reduced to fine dispersion of Cu and Fe_3O_4 particles by the H_2 reduction at 240 °C [157]. The $CuFe_2O_4/SiO_2$ catalyst exhibited much higher activity and thermal stability for SRM compared with the Cu/SiO_2 and Fe/SiO_2 catalysts. High activity and thermal stability are due to homogenous dispersion of Cu NPs within Fe_3O_4.

A facile method was developed for C–S coupling reaction catalyzed by Cu modified with amine-functionalized mesoporous zirconia [158]. Cu modified amine functionalized zirconia has been synthesized by a co-condensation method using zirconium butoxide and aminopropyl-triethoxy-silane in the presence of a cationic surfactant (CTAB) followed by impregnation of Cu. XRD, FT-IR, ^{13}C NMR, SEM, TEM, TG–DTA, XPS and UV–Vis DRS techniques were used to characterize the catalyst. This Cu-anchored mesoporous material has been found to be an efficient and reusable catalyst for aryl-sulfur coupling reaction between aryl iodide and thiophenol (Scheme 39). The bond energies of different C–halogen bonds are 548.1, 340.2, 281.4 and 222.6 kJ mol^{-1} for C–F, C–Cl, C–Br and C–I bonds, respectively. So the expected order of reactivity of different halobenzenes are iodobenzene > bromobenzene > chlorobenzene > fluorobenzene, which is observed in our case. Plausible reaction path way was proposed for C–S cross coupling reaction.

An in situ method has been used to load Cu_2O NPs on the surface of a hydroxyl group rich TiO_2 precursor. Excellent catalytic performance was observed for Cu_2O NPs decorated over TiO_2 for Ullmann type cross coupling reactions of aryl halides with phenol [159]. The composite catalyst also showed good stability under the reaction conditions (Scheme 40). In order to test the effect of Cu_2O loading on catalytic activity, four samples with loadings of 3.46, 7.76, 14.4 and 29.7 wt% of Cu_2O were tested in the time dependent cross coupling reaction between iodobenzene and phenol. The reaction conditions were kept the same in all the four cases. After reaction for a specific time, aliquots of the reaction mixture were collected and analyzed by GC. The TiO_2 precursor–Cu_2O composite with 3.46 wt% of Cu_2O showed the highest activity, while the sample with 29.7 wt% of Cu_2O exhibited the lowest reaction rate. The yield decreased as the Cu_2O loading increased. The catalyst showed high activity even after the five consecutive runs.



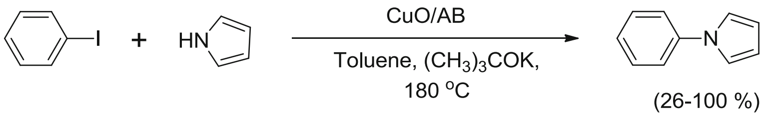
Scheme 40 TiO_2–Cu_2O-catalyzed O-arylation of phenols

An environmentally benign process for *N*-arylation of nitrogen-containing heterocycles with aryl halides has been developed [160]. The catalyst Cu(II) oxide on acetylene C black (CuO/AB) was characterized by TEM, XRD and ICP AES analyses. Increasing the reaction time and changing the base to KOH, K_2CO_3, and KO^tBu, gave respective, varied yields of 9, 71 and 72 %. In order to exploit the thermal stability of the CuO/AB catalyst, reaction temperature was increased. Placing the reaction in a closed system (stainless steel reactor) at 180 °C for 18 h achieved a 92 % conversion. The catalyst CuO/AB was readily separated by centrifugation and could be reused ten times under the mentioned reaction conditions without any loss of catalytic activity (Scheme 41).

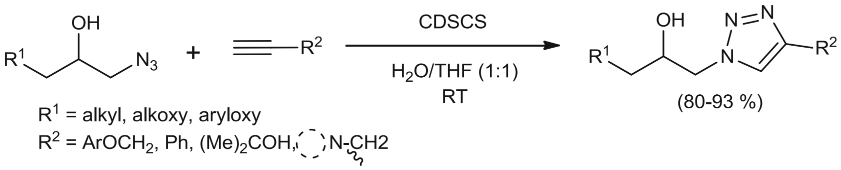
1,2,3-Triazole derivatives are important bioactive compounds especially as antiviral anticancer, anti-HIV, antibiotic, antibacterial, and antimicrobial [161–164]. These derivatives are also used for the preparation of dyes, agrochemicals, corrosion inhibitors, photo stabilizers and photographic materials [165, 166]. Rad et al. [167], have synthesized and characterized the Cu-doped silica cuprous sulfate (CDSCS) catalyst and found to be an effective catalyst for Huisgen cycloaddition to produce 1,2,3-triazole (Scheme 42).

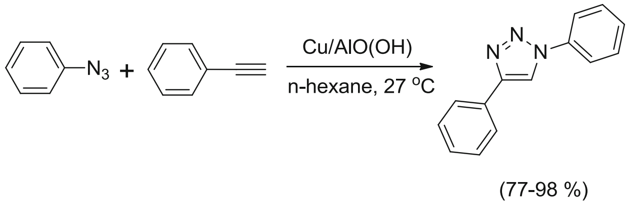
The Huisgen cycloaddition [168] using azides and alkynes is an important method for the synthesis of 1,2,3-triazoles. Park et al. [169], achieved heterogeneous

Scheme 41 CuO/AB-catalyzed *N*-arylation of heterocycles

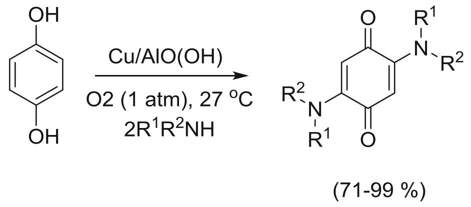


Scheme 42 CDSCS-catalyzed Huisgen cycloaddition





Scheme 43 Cu/AlO(OH)-catalyzed Huisgen cycloaddition



Scheme 44 Cu/AlO(OH)-catalyzed synthesis of 2,5-diamino-1,4-benzoquinones

Cu/AlO(OH)-catalyzed cycloaddition of azides with alkynes without additives under ambient condition (Scheme 43). Various terminal alkynes react readily with aliphatic azides as well as aromatic ones at room temperature in the presence of Cu catalyst.

Quinones are valuable and versatile compounds in nature and in organic synthesis [170]. One-pot protocol for Cu-catalyzed aerobic oxidation of hydroquinones and addition of amines was developed for the synthesis of 2,5-diaminoquinones. The catalyst can be reused five times without any decrease in the yield of the product (Scheme 44) [171].

Catalytic hydrogenolysis of glycerol to 1,2-propanediol is one of the fascinating transformation because this approach overcomes the dependency on fossil fuel and substantially alters the price of 1,2-propanediol [172–174]. Cu/boehmite catalyst showed the highest conversion and selectivity of 1,2-propanediol in the hydrogenolysis of glycerol as compared to Cu/γ-Al_2O_3, Cu/SiO_2 and Ru/C catalysts (Scheme 45) [175].

Selective oxidation of alcohols to carbonyl compounds is one of the most pivotal functional group transformations in organic synthesis [176–182]. Effective procedure was reported for the selective oxidation of alcohols to the corresponding carbonyl compounds catalyzed by Cu/AlO(OH) (Scheme 46) using H_5IO_6 as oxidant in water at room temperature [183]. The oxidation reaction was carried out four times under identical reaction conditions with the recycling of Cu/AlO(OH) catalyst without much decrease in the yield of the product. Mechanism has been proposed on the basis of spectroscopic studies.

Among 1,3-difunctionalized compounds, the β-amino acid unit is one of the most interesting target structures due to its pharmacology and its utility in several aspects of synthetic organic chemistry [184–188]. Solvent, ligand and base free, reusable, heterogeneous, environmentally benign and effective procedure was developed for the synthesis of β-ketoenamine from β-dicarbonyl compounds and primary amines using Cu/AlO(OH) catalyst (Scheme 47) [189].

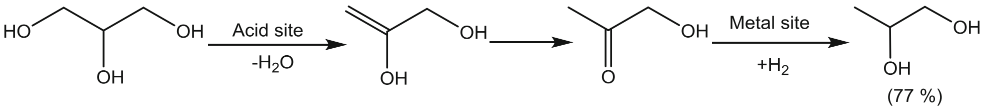
A mechanism was proposed for the nanocluster Cu-catalyzed formation of 4-(phenylamino)pent-3-en-2-one by the enamination of aniline with acetylacetone on the basis of DFT computational studies (Fig. 2).

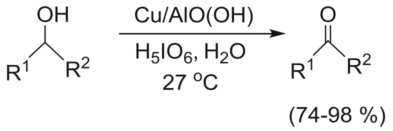
C–C bond formation can be achieved via various coupling reactions, one of which is the Heck reaction. Heck reactions yield stilbene derivatives by the coupling of styrene with aryl halides. These stilbene derivatives play a vital role in pharmaceutical, agrochemical and fine chemical industries. Reusable, heterogeneous and supported nano-CuO catalyst was reported for Heck coupling of styrene with aryl halides in water. The use of water as a solvent makes the system more interesting from the green chemistry point of view (Scheme 48) [190].

C–C coupled products find much attention because final products can be used in pharmaceutical and fine chemical industries [75–78, 191, 192]. The formation of C–C bond between β-diketones and aryl halides was achieved by using CuO/aluminosilicate catalyst [193]. This procedure is general, simple, ligand-free, air stable, efficient, high yielding and safe (Scheme 49). Both aryl bromides and chlorides gave good yield. Regioselectivity, chemoselectivity, heterogeneity and reusability of the catalyst have been tested. The results were found to be reasonable.

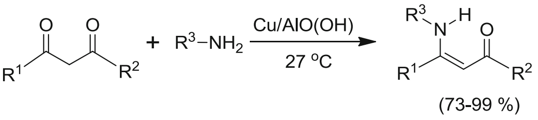
CuONPs were successfully decorated on acid treated multi walled C nanotubes (*f*-MWCNTs) using Cu acetate

Scheme 45 Cu/boehmite-catalyzed hydrogenolysis of glycerol to 1,2-propanediol





Scheme 46 Catalytic application of Cu/AlO(OH) for the oxidation of alcohols



Scheme 47 Cu/AlO(OH)-catalyzed synthesis of β-ketoenamines

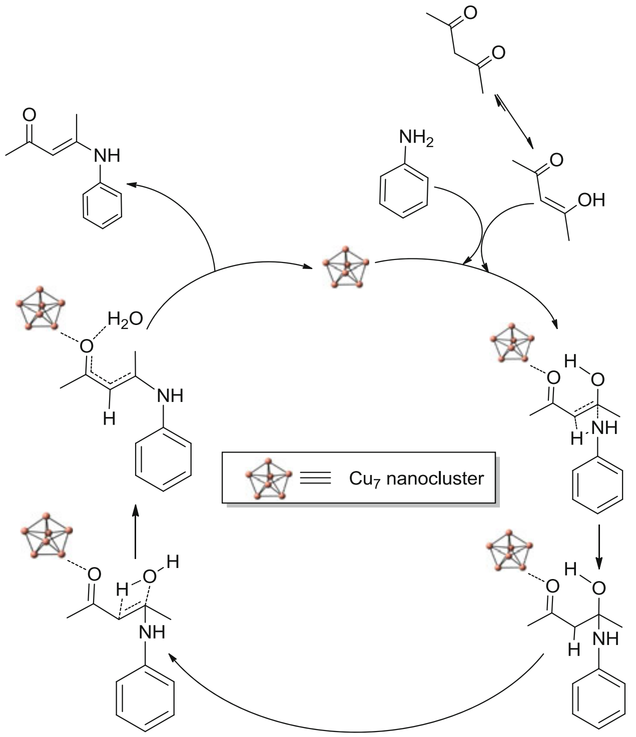


Fig. 2 Proposed mechanism for Cu_7 nanocluster-catalyzed formation of β-ketoenamines

$Cu(OAc)_2$ precursor by a very simple "mix and heat" method in an inert atmosphere, and was used as a heterogeneous nanocatalyst for the *N*-arylation of imidazole for the first time (Scheme 50). The catalysis is heterogeneous in nature and the catalyst is reusable. The nanocatalyst (MWCNTs–CuONPs) was also analyzed after the catalytic reaction, and no significant change was found in the morphology of the catalyst, and in the oxidation state and weight percentage of Cu. After the catalytic reaction, MWCNTs were successfully separated from the used MWCNTs–CuONPs [194].

A review article on Cu NPs-catalyzed C–C and C–heteroatom bond formation with a greener perspective was published by Ranu et al. [195].

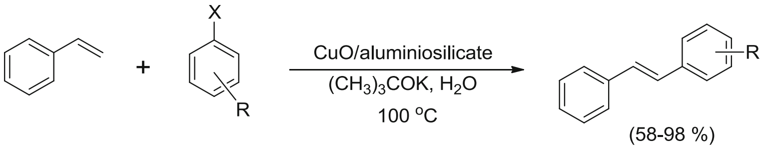
2.6 Magnetic Cu Based NPs as a Catalyst

In advance, some researchers have used magnetic material as a solid support which improves the recovering process of the catalyst.

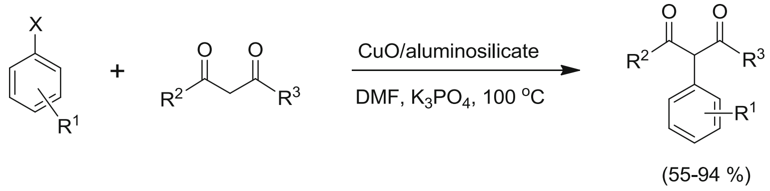
Very recently, nanoferrite–DOPA–Cu catalyst has been disclosed for the coupling of thiophenols with aryl halides at 120 °C under microwave irradiation. Baig and Varma [196], achieved C–S cross coupling using a magnetically recoverable heterogeneous Cu catalyst via one-pot multi component reaction (Scheme 51). In the context of optimization of solvent and base, the reaction in water did not proceed, and that in DMF, THF and CH_3CN gave coupled products in moderate yield. The use of K_2CO_3 or Cs_2CO_3 did not significantly affect the outcome of the reaction. This protocol has major compensation such as the use of MW irradiation, the use of isopropanol as a benign reaction medium, easy recovery of the catalyst using an external magnet, efficient recycling and the high stability of the catalyst. No Cu metal was detected in the reaction solvent after completion of the reaction which confirms the fact that dopamine provides enough binding sites on the surface of Fe_3O_4 NPs and serves as a pseudo-ligand by coordinating with Cu thus minimizing deterioration, preventing metal leaching, and enabling efficient catalyst recycling. All these benefits made the system economic and sustainable.

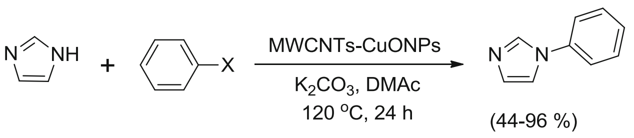
Nano $CuFe_2O_4$ can also be used as a magnetically separable catalyst. Swapna et al. [197], developed the magnetic nanocatalytic system for the synthesis of

Scheme 48 CuO/aluminosilicate-catalyzed Heck coupling of styrene with aryl halides in water

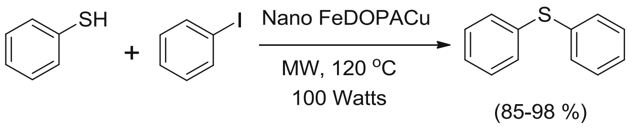


Scheme 49 CuO/aluminosilicate-catalyzed α-arylation of β-diketones

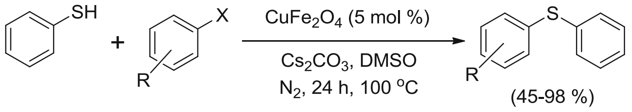




Scheme 50 MWCNTs–CuONPs catalyzed *N*-arylation of imidazole with various aryl halides



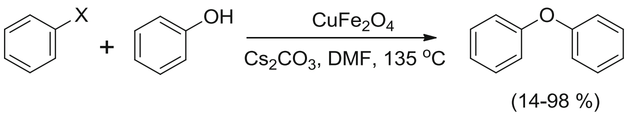
Scheme 51 Nano FeDOPACu-catalyzed S-arylation of thiophenols



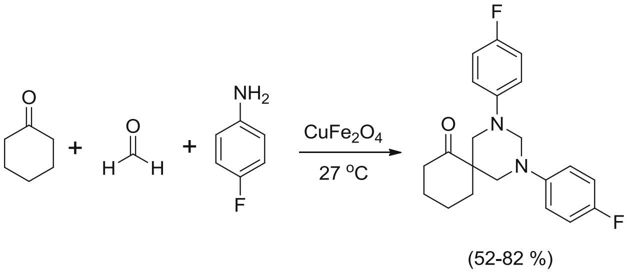
Scheme 52 $CuFe_2O_4$-catalyzed S-arylation of thiols

diaryl/aryl–alkyl sulfides via cross-coupling of aryl halides with thiols under ligand free condition (Scheme 52). This catalytic procedure can also be applied for the cross-coupling of aryl halides with diphenyl disulfides to produce C–S cross coupled product. In the course of optimization studies towards C–S bond formation, different metal oxide NPs, such as SnO_2, Y_2O_3, $NiFe_2O_4$, $ZnFe_2O_4$, $CuFe_2O_4$, YFe_2O_4 and Co_3O_4, were used as catalysts for the C–S cross-coupling process with aryl halides and thiols under ligand-free conditions. The possible mechanism was proposed for C–S cross coupling reaction. This is one of the convenient routes for synthesizing a variety of substituted organic sulfides. This system offered significant improvements with regard to operational simplicity, and worked efficiently by giving high yields of the corresponding products.

Zhang et al. [198], used magnetic $CuFe_2O_4$ NPs for Ullmann type C–O cross-coupling of phenols with aryl halides (Scheme 53). DMF was found to be the best solvent for the reaction and, among several solvents tested, dioxane, toluene, DMA and DMSO were found to be less effective. Apparently, the outcome of the C–O cross-coupling reactions were also dependent on the selected bases. Consequently, a variety of bases were screened in DMF, the best results being those with Cs_2CO_3. A variety of phenols and aryl halides were transformed to diaryl ethers in good to excellent yields. Furthermore, the catalyst could



Scheme 53 $CuFe_2O_4$-catalyzed O-arylation of phenols



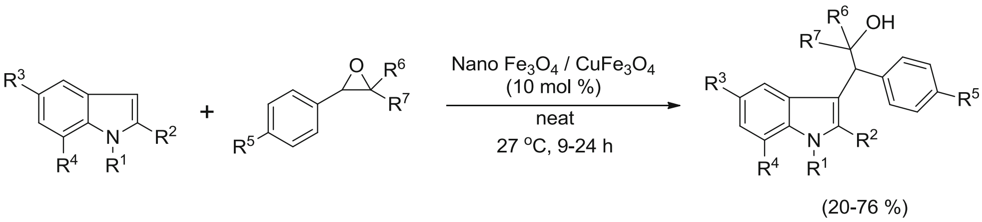
Scheme 54 $CuFe_2O_4$-catalyzed synthesis of spiropyrimidine

be separated and recovered easily by an external magnet and efficiently reused several times without significant loss of selectivity or activity.

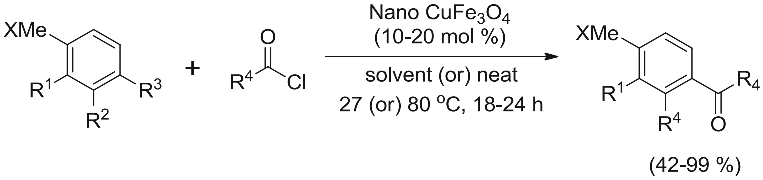
The hexahydropyrimidine skeleton is present in a number of alkaloids, tetraponerines, verbametrine and verbamethine. They form structural units in trypanothione reductase inhibiting ligands for the regulation of oxidative stress in parasite cells. Due to their significant biological activity, hexahydropyrimidines have received a great deal of attention in recent years. Dandia et al. [199], reported $CuFe_2O_4$ NPs as a highly efficient and magnetically recoverable catalyst for the synthesis of spiropyrimidine scaffolds (Scheme 54). Different solvents such as ethanol, acetonitrile, DMSO, DMF, dichloromethane, THF and dioxane, were explored. After optimization, they observed that ethanol was the most effective solvent for this three-component condensation reaction. They also reported that the reaction with a higher catalyst loading (20 mol%) had no significant effect on yield. However, if the amount of the catalyst was reduced to 5 and 1 mol%, the product yield was reduced to 62 and 26 %, respectively. Leaching out of metal from the catalyst was investigated by ICP AES studies and confirmed that no metal was present in the supernatant solution. The scope was extended and the yields were ranging from 52 to 82 %.

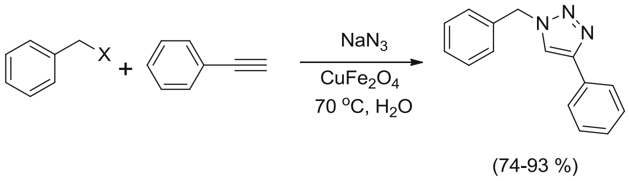
Stereo- and regioselective synthesis of C-alkylated indoles/pyrroles were achieved by the reaction of epoxides with indoles/pyrroles under solvent and ligand free condition (Scheme 55). Competent catalytic performance was

Scheme 55 $CuFe_2O_4$-catalyzed aza-Michael reaction



Scheme 56 $CuFe_2O_4$-catalyzed Friedel–Crafts acylation





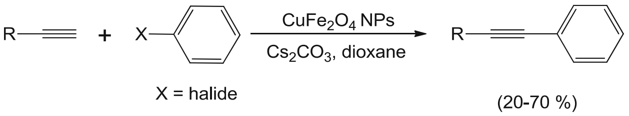
Scheme 57 Synthesis of triazoles using $CuFe_2O_4$ nanoparticles in water

observed with both nano Fe_3O_4 and $CuFe_2O_4$ heterogeneous catalysts. Chiral epoxides gave the alkylated indoles with a complete inversion of stereochemistry [200].

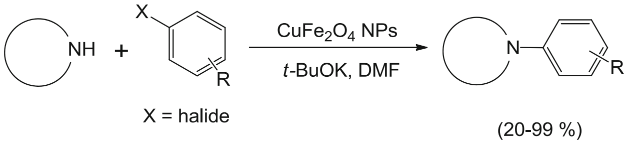
Numerous Friedel–Crafts acylation protocols based on homogenous or heterogeneous catalysts (e.g. metal oxides, zeolite, clays, heteropoly acids, sulfated zirconia and nafion) have been reported. Most of the existing methods suffer with the drawbacks such as pre activation of the catalyst and recovery of catalyst. New and improved catalytic protocols continue to attract the attention of industries/chemical laboratories due to very high importance of the aromatic ketones which are key intermediates in several fields including fine chemicals and pharmaceuticals. Parella et al. [201], developed regioselective Friedel–Crafts acylation of an array of anisoles/arenes with various acid chlorides using 5–20 mol% of magnetic nanopowder $CuFe_2O_4$ (Scheme 56).

1,2,3-Triazoles have attracted interest over the past few years as their moieties have been widely used in pharmaceuticals, agro chemicals, dyes, photographic materials, corrosion inhibition, etc. [202]. Kumar et al. [203], attempted the synthesis of 1,4-disubstituted 1,2,3-triazoles using magnetically separable and reusable Cu ferrite NPs in a one pot reaction, in tap water (Scheme 57).

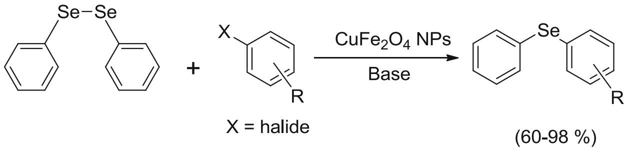
Coupling of terminal alkynes with aryl halides is a kind of biologically important C–C cross-coupling reactions. Panda et al. [204], compared the catalytic performance of $CuFe_2O_4$ with CuO and Fe_3O_4 NPs and found that neither CuO nor Fe_3O_4 NPs alone, could catalyze the transformation as efficient as $CuFe_2O_4$ (Scheme 58).



Scheme 58 $CuFe_2O_4$-catalyzed coupling of alkynes with aryl halides



Scheme 59 $CuFe_2O_4$-catalyzed coupling of *N*-heterocycles with aryl halides

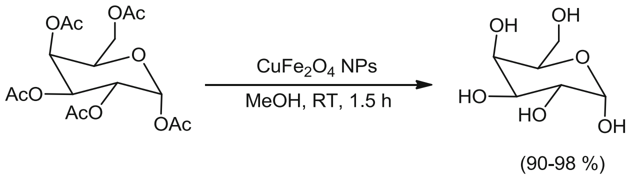


Scheme 60 $CuFe_2O_4$-catalyzed coupling of diaryl diselenides with aryl halides

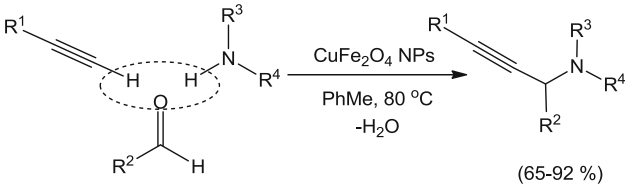
Panda et al. [205], have also studied the effect of Cu and iron towards C–N cross-coupling, and found that $CuFe_2O_4$ NPs effectively catalyze the coupling of *N*-heterocycles with aryl halides (Scheme 59).

Magnetically separable $CuFe_2O_4$ was found to be an efficient catalyst for the synthesis of various diaryl selenides by the coupling of aryl halides with diaryl diselenides [206]. This C–Se cross-coupling reaction was carried out at 120 °C (Scheme 60). The catalyst can be reused for consecutive cycles without much decrease in the efficacy of the catalyst.

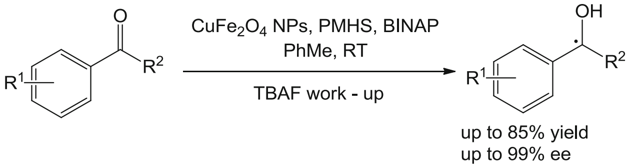
Deacylation of various protected sugars were carried out with $CuFe_2O_4$ NPs under mild conditions. Selective deacylation at the anomeric position could be achieved by changing the solvent and reducing the reaction time (Scheme 61) [207].



Scheme 61 CuFe$_2$O$_4$-catalyzed deacylation of sugars



Scheme 62 CuFe$_2$O$_4$-catalyzed A^3 coupling



Scheme 63 CuFe$_2$O$_4$-catalyzed asymmetric hydrosilylation of prochiral ketones

A^3 coupling is a one-pot coupling of aldehyde, alkyne, and amine, which was effectively achieved with CuFe$_2$O$_4$ NPs. A^3 coupling has already been reported for Fe$_3$O$_4$ NPs. But by substituting the Cu within the lattice made the reaction to proceed under milder conditions (Scheme 62) [208].

Asymmetric hydrosilylation of prochiral ketones was accomplished by CuFe$_2$O$_4$ NPs with the aid of a chiral BINAP ligand in tetra-*n*-butylammonium fluoride, which afforded the corresponding alcohols (Scheme 63) [209].

3 Conclusions

Cu is comparatively cheap and efficient metal as a catalyst for many industrially important reactions. Cu based NPs were found to be the most valuable catalysts for numerous catalytic systems. This review highlights the important developments of Cu based nanocatalysts for organic transformations.

Acknowledgments We acknowledge Department of Science and Technology, Government of India for financial support under the Nanomission Project (SR/NM/NS-27).

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