National Conference on "Recent Trends in Mathematical Modeling, Simulation Methods, Computations, and Physical Sciences"
(MMSCP-2019), Organised by Hislop College, Nagpur, Maharashtra, India
International Journal of Scientific Research in Computer Science, Engineering and Information Technology
© 2019 IJSRCSEIT | Volume 4 | Issue 4 | ISSN : 2456-3307

Copper and Copper Oxide Nanoparticles : Applications in Catalysis

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ABSTRACT

Copper and Copper oxide nanoparticles (Cu NPs) have attracted considerable interest because of their catalytic, optical, mechanical and electrical conducting properties. The earth-abundant and inexpensive copper metal, have generated a great deal of interest specially in the field of catalysis. This paper discusses the uses of Cu and Cu-oxide NPs as catalysts for Ullmann type reactions and Gas Phase Reactions. We believe that this article will provide the necessary background information for further study and applications of Cu-based nanoparticles in catalysis.

Keywords : Copper, Nanoparticles, Ullmann reaction, Gas Phase Reaction

I. INTRODUCTION

Metal and metal oxide nanoparticles exhibit special properties and potential applications. Nanoparticles offer high surface to volume ratio and its size, dispersal, and morphology are the main reason for the novel and enriched properties.[1] Among various metal nanoparticles, inexpensive copper nanoparticles have attracted considerable interest because of their catalytic, optical, mechanical and electrical conducting properties.[2] Cu is relatively non-toxic to human beings, but is toxic towards many micro-organisms and hence can be used for antimicrobial treatments.[3] Because of their variable oxidation states (Cu^0, Cu^I, Cu^{II}, and Cu^{III}), it has a great scope in photo catalytic degradation of organic pollutants and catalytic organic transformations.[4]

Cu nanoparticles are initially formed and subsequently oxidized to form highly crystalline and stable Cu_2O. Copper (I) oxide (Cu_2O) also called cuprous oxide is a *p*-type metal oxide semiconductor with promising applications in solar energy conversion and catalysis.[5] In addition to this copper has high melting and boiling point which makes it thermally stable. Hence, Cu is compatible with high temperature and high pressure chemical reactions, like vaporphase reactions, microwave-assisted reactions, continuous flow reactions, and various organic transformations.[6]

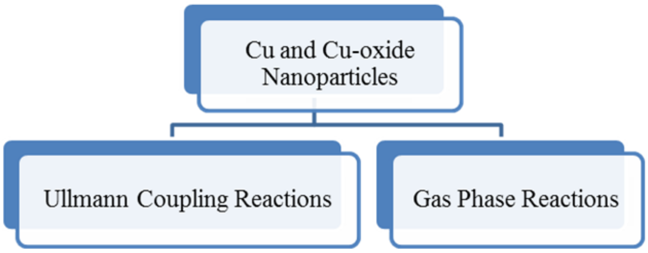
II. METHOD OF PREPARATION of Cu-NPs

Preparation of highly active, selective, stable, robust, and inexpensive Cu nanoparticles is always a challenge in the field of research. The technique for the synthesis of Cu NPs are rely on the same methods that have been used to prepare other metal NPs,[7] which mainly include either "bottom-up" or "top-down" approach. In bottom-up approach atomic level precursors are used to synthesize nanoparticles sized materials, whereas in top-down method a bulk solid is broken down into nanosized materials. NPs are highly structure sensitive and their catalytic efficiency and selectivity mainly depend on the shape, size, and composition of the nanoparticle. While both approaches have their pros and cons, the bottom-up approach has become more prominent as it offers greater scope for controlling the shape and size of the resulting nanomaterial.[8]

Generally physical and chemical methods have been used to synthesize copper nanoparticles. The most common approach for synthesizing Cu NPs is by creating microemulsions. However, this method requires large amounts of surfactants and organic solvents which increases the cost of production.[9] Microwave irradiation,[10] aerosol techniques, laser ablation, and radiolysis are common physical methods to synthesize nanoparticles but the use of expensive instruments and excessive energy consumption limits their application.[11] Chemical treatment for the synthesis of Cu NPs involves wet chemical, reverse micelle, biosynthesis and ionic liquid assisted methods.[12] In comparison to above methods, green synthesis of the Cu NPs is more safer and environmental friendly technique. Existing literature reports the use of *Terminalia arjuna* bark,[10] leaf broth of *Azadirachta indica*,[13] *Capparious zeylanica*[14] and *vitis vinifera*[15] as well as various other plant extract, were used as reducing and capping agent for the successful synthesis of Cu NPs. The uses of microorganism like *Pseudomonas stutzeri* bacteria and *Aspergillus* fugi have also been reported in the literature for the Cu NPs synthesis.[16]

III. APPLICATIONS OF Cu-NPs IN CATALYSIS

The catalytic activity of Cu NPs depends on composition of the nanoparticles as either the pure copper or the oxides; copper oxide nanoparticles have lower catalytic activity as compared to pure Cu NPs.[5] The activity is also affected by the method and condition of its preparation and the size of nanoparticles, smaller the particle size, greater the catalytic activity.[17] They are quit striking for this purpose because they often allow reactions to be carried out under green and sustainable reaction conditions. This section primarily focused on catalytic applications in Ullmann coupling reaction and gas phase reactions.



IV. ULLMANN COUPLING REACTIONS

Coupling reactions such as Suzuki, Heck and Sonogashira reactions, and C–S, C–O, C–B, and C–Se bond formation reactions are some of the important coupling reactions in organic synthesis. Several transition metal catalysts have been developed and employed for these conversions. Cu and Cu-based NPs emerged as an efficient, cost-effective and reliable option for many reported methods, and can be used for green and sustainable chemistry.[18]

The classical Ullmann reaction involves the conversion of iodobenzene to biaryl compound using various Cu nanoparticles (C-C bond formation reaction) (Figure 1). In 1998, Gedanken pointing out that different particle size of Cu NPs led to different catalytic activity, which could be due to the different surface areas, which decreases with increasing the particle size.[19]

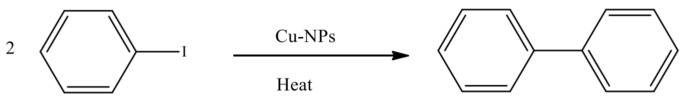


Figure 1. Classical Ullmann coupling reaction of iodobenzene

The development in the Ullmann cross coupling reaction is not limited to homo-coupling (C-C bond formation) of aryl iodide. Many protocols have been developed for Ullmann type *O*- and *N*-arylation reactions. Wang and Co-worker reported the use of Nano copper oxide catalyst for the C–O cross-coupling of phenols with aryl halides under ligand-free conditions (Figure 2). The catalyst can be reused for five times under DMSO as solvent and Cs_2CO_3 and KOH as a suitable bases for the cross coupling reactions with phenyl iodides and bromides, respectively.[20]

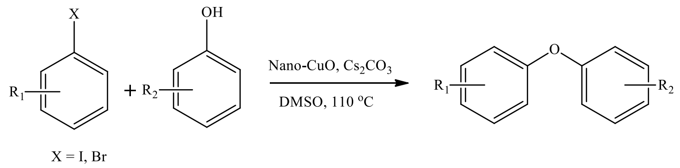


Figure 2. Ullmann C–O cross-coupling of phenols with aryl halides

Y. Kim et al. reported the Ullmann cross-coupling reaction of aryl halides and phenols with a catalytic amount of Cu_2O nanocubes as recyclable catalyst and Cs_2CO_3 as the base in THF at 150 °C.[21] They have examined a wide variety of substrates with C–I, C–Br, and C–Cl bonds, with various phenol to obtain their respective aryl ethers.

Ullmann-type *N*-arylation was recently explored by Pai and Chattopadhyay for arylation of *N*-heterocycles using Cu nanoparticles in the presence of K_3PO_4 as a base (Figure 3).[22] The arylation occurs under mild condition using Cu-NPs and can be used for synthesis of *N*-arylindole, *N*-arylimidazoles, *N*-arylpyrazole, *N*-arylindazole with aryl iodides in good to excellent yields.

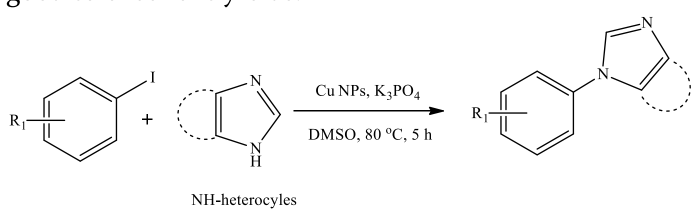


Figure 3. Ullmann-type *N*-arylation of NH-heterocycles with aryl halides

V. GAS PHASE REACTIONS

The best solvent from Green Chemistry point of view is no solvent i.e Solvent free reactions.[23] Consequently, reactions in the gas phase can be conducted in the complete absence of solvents. In this regards catalysts possessing nanostructured frameworks have major role in such gas-phase reactions by enabling the formation of high interfacial areas between the catalyst and reactants. Thus nanostructured support materials such as zeolites and mesoporous metal oxides extensively used as nanocatalytic species.[24] Mechanism wise the nanoporous materials allow reactants trapped in the pores and hence increased contact time with reacting molecules giving product without use of any solvent. In this context, the Cu-Nano and Cu-O Nano particles are widely used in gas phase reactions like NOx Reduction, CO Oxidation and Water gas Shift reaction.

a. NOx Reduction

NOx is one of the air pollutant generated from burning fuel. Thus its reduction (NOx to N_2) has gain considerable attention in recent past (Figure 4). Cu/zeolite nano structured materials prepared by inserting Cu ions into the zeolite structure using a simple ion-exchange reaction with conventional zeolites can serve as highly efficient catalysts for the selective catalytic reduction of NOx.[25]

$$\mathrm{NOx} \xrightarrow[\text{Reduction}]{\text{Cu-Zeolite}\ \ NH_3} N_2$$

Figure 4. NOx reduction reaction.

The porous structure of zeolite associated with its high surface area allows the absorption of NOx and the Cu ions activate NOx molecules through a redox cycle.

b. CO Oxidation

Carbon monoxide (CO) is also one of the very dangerous air pollutant. The Cu-based nanomaterials have been employed in the catalytic oxidation of CO to CO_2 (Figure 5).

$$CO \xrightarrow[\text{Oxidation}]{\text{Cu-Nano}} CO_2$$

Figure 5. CO oxidation reaction.

Zhou and Coworker have synthesized CuO nanocrystals with different shapes, including CuO NPs, nanobelts, and nanoplatelets, prepared by precipitation methods.[26] All forms of these CuO nanocrystals were tested as catalysts for the conversion of CO to CO_2, revealing a direct relationship between the catalytic reactivity of the CuO nanostructures and the exposed crystal planes, which vary with the crystal shape. The mesoporous CuO nanowalnut-shaped particles are also explored for the same reaction. Chung and group have reported CuO/CeO2 materials, prepared by co-precipitation of nitrates.[27]

c. Water-Gas Shift Reaction

H_2 is an important gas in the chemical industry and also used as fuel. The water-gas shift (WGS) reaction is an attractive approach for H_2 production.[28] This transformation could be performed using oxide-supported Cu nanomaterials, in which intense synergistic effects between Cu and the oxide support have been observed (Figure 6).

$$H_2O + CO \xrightarrow{\text{Cu-Nano}} H_2 + CO_2$$

Figure 6. General representation of Water gas shift reaction catalysed by Cu-Nano particles.

Tang et al. explored the WGS reaction over a binary model Cu/ZrO_2. Successively $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/ZrO_2/Al_2O_3$ catalysts were test for this attractive H_2 gas production reaction. The Cu NPs deposited on TiO_2 have been excellent catalysts for the WGS reaction.[29]

VI. CONCLUSION

This article has emphasized the use of Cu and Cu-oxide NPs in catalysis. The Cu-NPs are efficient and multipurpose catalysts that can be used to promote a wide range of organic transformation that go well beyond their traditional roles as metal catalysts. Various diaryl ethers and N-substituted heterocyclic compounds can be effectively prepared by Ullmann-type N-arylation and O-arylation respectively. We further discussed the role of Cu-NPs in gas phase reactions like NOx Reduction, CO Oxidation and Water gas Shift reaction. We believe that this review will serve to stimulate research in the field of Cu nanocatalysis and material science.

VII. REFERENCES

[1]. E. Roduner, Chem. Soc. Rev. 2006, 35, 583.

[2]. G. Evano, N. Blanchard, M. Toumi, Chem. Rev. 2008, 108, 3054–3131.

[3]. N. M. Zain; A. G. F. Stapley; G. Shama, Carbohydrate Polymers, 112, 2014, 195-202.

[4]. M. B. Gawande, A. Goswami, F. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril, R. S. Varma, Chem. Rev. 2016, 116, 3722–3811.

[5]. M. Yin, C. Wu, Y. Lou, C. Burda, J. T. Koberstein, Y. Zhu, S. O'Brien, J. Am. Chem. Soc. 2005, 127, 9506-9511.

[6]. R. Rupanwal, A. Kulshrestha, N. Singh, N. Sahni, M. Shujauddin, R. Khare, J. Pandey, International Journal of Scientific & Engineering Research, 2017, 8, 1479-1496.

[7]. A. Umer, S. Naveed, N. Ramzan, M. S. Rafique, Selection of A Suitable Method for The Synthesis of Copper nanoparticles. Nano 2012, 07, 1230005.

[8]. D. Mijatovic, J. C. T. Eijkel, A. V. D. Berg, Technologies for Nanofluidic Systems: Top-Down vs Bottom-Up-A Review. Lab Chip 2005, 5, 492–500.

[9]. S. Pal, U. Jana, P. K. Manna, G. P. Mohanta, R. Manavalan, Journal of Applied Pharmaceutical Science, 2011, 01 (06), 228-234.

[10]. S. Yallappa, , J. Manjanna, M. A. Sindhe, N. D. Satyanarayan, S. N. Pramod, K. Nagaraja. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2013, 110, 108–15.

[11]. K. N. Thakkar, S. S. Mhatre, R. Y. Parikh. Nanomedicine: Nanotechnology, Biology and Medicine, 2010, 6 (2), 257–262.

[12]. N. Ojha, G. V. Zyryanov, A. Majee, V. N. Charushin, O. N. Chupakhin, S. Santra, Coordination Chemistry Reviews, 2017, 353, 1–57.

[13]. N. Nagar, V. Devra, Materials Chemistry and Physics, 2018, 213, 44-51.

[14]. K. Saranyaadevi, V. Subha, R.S.E. Ravindran, S. Renganathan, Int. J. Chem. Tech. Res. 2014, 6 (10) 4533-4541.

[15]. J.K.V.M. Angrasan, R. Subbaiya, Int. J. Curr. Microbiol. App. Sci. 2014, 3 (9) 768-774.

[16]. M. I. Din, R. Rehan, Analytical Letters, 2017, 50:1, 50-62.

[17]. M. Samim, N. K. Kaushik, A. Maitra, Bull. Mater. Sci., 2007, 30, 535–540.

[18]. C. Sambiagio, S. P. Marsden, A. J. Blackera, P. C. McGowan, Chem. Soc. Rev., 2014, 43, 3525-3550.

[19]. N. A. Dhas, C. P. Raj, A. Gedanken, Chem. Mater. 1998, 10, 1446-1452.

[20]. J. Zhang, Z. Zhang, Y. Wang, X. Zheng, Z. Wang, Eur. J. Org. Chem. 2008, 5112–5116.

[21]. J. Y. Kim, J. C. Park, A. Kim, A. Y. Kim, H. J. Lee, H. Song, K. H. Park, Eur. J. Inorg. Chem. 2009, 4219–4223.

[22]. G. Paia, A. P.Chattopadhyay, Tetrahedron Letters, 2016, 57, 140-3145.

[23]. G. G. Jernigan, G. A. Somorjai, J. Catal. 1994, 147, 567–577.

[24]. R. Silva, A. V. Biradar, L. Fabris, T. Asefa, J. Phys. Chem. C 2011, 115, 22810–22817.

[25]. S. Brandenberger, O. Krocher, A. Tissler, R. Althoff, Catal. Rev.: Sci. Eng. 2008, 50, 492–531.

[26]. K. B. Zhou, R. P. Wang, B. Q. Xu, Y. D. Li, Nanotechnology 2006, 17, 3939–3943.

[27]. L. C. Chung, C.T. Yeh, Catal. Commun. 2008, 9, 670–674.

[28]. C. Ratnasamy, J. P. Wagner, Catal. Rev.: Sci. Eng. 2009, 51, 325–440.

[29]. Q. L Tang, Z.P. Liu, J. Phys. Chem. C 2010, 114, 8423–8430.