

A Study on Some Cu(II)-Phenanthroline Complexes and CuO-based Nanocatalysts for Alcohol Oxidation, C-C, C-N Bond Formation Reactions

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CHAPTER 6

Conclusion and Future Scopes

6.1. Conclusion

Copper (Cu) is an essential redox-active transition metal, shows crucial role in catalytic reactions, which enable efficient electron transfer during chemical reaction. Moreover, Cu is a fundamental component of numerous metalloenzymes within biological systems, actively participating in diverse metabolic reactions. Looking into different aspects of Cu-containing catalysts this thesis focuses on investigating the catalytic capabilities of four distinct Cu-based catalyst systems. The designed catalysts were employed for aromatic and primary alcohol oxidation, Henry reaction, benzimidazole synthesis, amide synthesis and imination of toluene & p-xylene reactions. Thorough characterization using various physicochemical and spectroscopic analyses provided insights into the composition, morphology, and electronic structures of the synthesized catalytic systems. Moreover, an intriguing finding emerged from the study, where the synthesized Cu-complexes mimic bio-enzyme and Cu-oxide nanocatalyst showed superior catalytic efficiency for above-mentioned reaction. However, a crucial dimension of catalysis lies in comprehending the mechanisms underlying to the catalytic reactions. To delve into this aspect, an array of analytical techniques, including PXRD, Raman spectroscopy, FTIR, cyclic voltammetry (CV), electron spin resonance (ESR), nuclear magnetic resonance (NMR), and computational analysis, were employed. These tools helped in understanding the details of the reaction mechanisms.

The overall findings in this thesis work are summarized below-

Four Cu(II) complexes *viz* acetato diphenanthroline copper (II) complex (CuPhenAc), chlorido diphenanthroline copper (II) complex (CuPhenCl), diacetate dimethoxytetraphenanthroline dicopper(II) complex (CuPhenMAc), Imidazolate diphenanthroline dicopper (II) complex (CuPhenIm) were well synthesized and characterized by different physicochemical, spectroscopical technique. The mononuclear Cu(II) phenanthroline complexes of Cl⁻, acetate (CH₃COO⁻) ligand and dinuclear Cu(II) bridged complex of imidazole, acetate well studied for benzyl alcohol (BA) oxidation and catechol oxidation reaction. The single site Cu(II) catalyst showed much superior activity in the selective oxidation of benzyl alcohol compared to the binuclear. The mononuclear Cu(II) complex showed highest conversion for BA oxidation upto 96 %. The reaction was attributed to the notable instability of the Cl⁻ and ⁻OOCH₃ groups present in the mononuclear complexes. This inherent instability facilitated interactions between the active Cu center and various components such as the incoming oxidant, substrate, and the solvent

(acetonitrile, CH₃CN) molecules. Consequently, this interaction played a pivotal role in promoting the oxidation of benzyl alcohol. The dinuclear complexes showed good results in catechol oxidation. The catechol oxidation was then studied by CuPhenIm complex with H₂O₂ at room temperature in presence of 5 mL methanol (CH₃OH) solvent for 20 min. Under this condition, the catechol conversion to o-benzoquinone was found to be good and highly selective upto 98 %. The catechol oxidation reaction was thereafter optimized under different reaction parameters. The reaction took place very well with both the complexes at room temperature, giving 85-88% conversion and 100 % selectivity to benzoquinone. The oxidation of catechol into o-benzoquinone exhibited a higher preference for catalysis within the di-nuclear systems.

Next, the synthesis and characterization of CuO nanoparticles (CuO-NPs) loaded onto the external surface of zeolite-Y were conducted. The synthesized material was well characterised by XRD, XPS, EPR, SEM, TEM, and AFM analyses. In the CuO-Y composite, CuO-NPs existed in both Cu(I) and Cu(II) oxidation states. Utilizing a solid-phase grinding approach, the composite catalyst facilitated diverse organic transformations. Specifically, the solvent-free and liquid-assisted grinding approaches successfully yielded benzimidazoles, benzaldehydes, and nitro-aldol products. All the reactions obtained with high yield and selectivity in solvent-free condition. The yield of benzimidazole, benzaldehydes, nitro-aldol products were 99-91%, 99-75%, and 99-80% respectively. This was an environmentally friendly approaches or methods because it carried out in mechanochemical process without the use of a solvent. The catalyst CuO-Y demonstrated reusability across several cycles, albeit with diminishing catalytic activity attributed to Cu-metal leaching and CuO-NPs agglomeration. The introduction of benzimidazole resulted in enhanced catalytic reactions, benefiting conversion, selectivity, and product yield. A comparative study encompassing bare CuO-NPs, zeolite-Y, as well as CuO-NPs supported on various other zeolites like beta-zeolite, zeolite X, and ZSM-5 was undertaken. Remarkably, the catalytic performance of CuO-Y zeolite significantly outperformed the other prepared catalysts. While the nature of zeolite support demonstrated minimal influence on CuO-NPs' activity, both the zeolite support and the presence of benzimidazole proved essential for achieving superior catalytic activity.

After the success with the CuO-catalyst, the CuO nanoparticles supported on Fe-exchanged zeolite-Y exhibited characteristics of a reusable heterogeneous catalyst for dehydrogenation benzyl alcohols, followed by their coupling with amines to give amides. This reaction exhibited remarkable selectivity, with no detection of minor by-products. The reaction was performed under milder condition by using ^tBuOOH as an oxidising agent at 60 °C. By using this reaction pathway, obtained eighteen amide product with highest yield of 85 %. The mechanism of the amide bond formation reaction was examined by Raman and cyclic voltametric studies. The reaction conditions were notably milder compared to expensive metallic catalysts, and it proceeded without necessitating appropriate ligand systems, operating under base-free external conditions. Nonetheless, the formation of amides was influenced by the substrate's characteristics. For instance, when 2-chloro-5-nitrobenzyl alcohol was subjected to different amines, the outcome was a C-N bond coupling rather than the anticipated amide bond formation.

In the last chapter, a cost-effective catalyst composed of copper oxide in layered tin oxide (CuO/SnO₂) was produced and examined using various analytical techniques. This catalyst, possessing a layered structure, demonstrated remarkable efficacy in selectively transforming toluene and p-xylene into different derivatives of N-benzylideneaniline *via* in-situ oxidation of toluene, xylene. Thirteen different imines were synthesized with good yield 70-92% in 12h of reaction time by using 7 mg of catalyst. Theoretical investigations of this reaction pathway indicated that non-covalent interactions such as cation- π interactions and hydrogen bonding played a pivotal role in stabilizing potential intermediate species within the reaction. Such approach of generating imines using toluene and p-xylene can open new avenues for addressing both environmental and health concerns associated with volatile organic compounds (VOCs) like toluene and p-xylene.

6.2. Future Scope of the Thesis Work

In the preceding Chapters (2-5), an array of Cu-based catalysts has undergone thorough examination through various experimental and mechanistic analysis. As a result, we hold a strong belief in the potential of these synthesized material to pave the way for novel research directions within the domain of catalysis. By looking this conviction of work, the present thesis lays the foundation for future explorations, primarily focusing on the subsequent area:

- Cu phenanthroline complex possessing good redox behaviour can be explored for water splitting reaction and also to mimic other Cu metalloenzyme catalyst reaction.
- As CuO nanocatalyst supported on zeolite-Y showed significant activity in different solid-state transformation reaction, So, such catalyst can be modified for solvent-free Sonogashira coupling, Ullmann coupling reaction.
- In this thesis, we have monitored the impact of other metal like Fe, Sn on the catalytic activity of Cu. So, in near future the influence of other metals in modulating the activity of Cu catalyst provides a new insight in exploring similar reaction.
- Density functional theory calculation using some high level calculations by considering larger model system would provide more understanding of the reaction mechanism.
- The use of costly spectroscopic tools like EXAFS, XANES would provide more information about the location of Cu-sites in zeolite framework which will in turn facilitate in understanding the reaction mechanism