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Research Collaboration

16. Dr. Jayantha K. Nath, Assistant Professor, Department of Chemistry, S. B. Deorah College, has Research Collaboration with Dr. Kusum K. Bania, Professor, Dept. of Chemical Science, Tezpur University.

Applied Catalysis A, General 644 (2022) 118816



Single and multiple site Cu(II) catalysts for benzyl alcohol and catechol oxidation reactions

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ARTICLE INFO

Keywords:
Cu(II) complex
CuO-nanocatalyst
Benzyl alcohol
Catechol
Oxidation
Reaction mechanism

ABSTRACT

Cu(II) catalysts both in homogeneous and heterogeneous form were synthesized to bring the distinction between the single and multiple site catalysis. The single site mononuclear complexes with axial occupancy of Cl⁻ and CH₃COO⁻ ligand and the acetate, imidazole bridged dinuclear Cu(II) complexes were tested for selective oxidation of benzyl alcohol and catechol oxidation. The reactivity of the complexes was compared with the multiple site copper oxide (CuO) nanocatalyst derived from the metal complex precursor. The single site Cu(II) catalyst showed much superior activity in the selective oxidation of BA compared to the dinuclear and the CuO-nanocatalyst. The oxidation of catechol to o-benzoquinone was however found to be catalyzed more preferably by the di-nuclear systems. The high lability of Cl⁻ and ⁻OOCH₃ groups in the mononuclear complexes allowed the incoming oxidant, substrate as well as the solvent (acetonitrile, CH₃CN) molecules to interact with the active Cu-centre and thereby favoured the benzyl alcohol oxidation. Both the experimental and theoretical studies provided a conclusive idea about the reaction mechanism of benzyl alcohol and catechol oxidation. UV-vis, cyclic voltammetric study and density functional theory (DFT) calculations provided the strong evidence for the formation of Cu-CH₃CN complex during benzyl alcohol oxidation. FTIR and Raman study substantiated by the theoretical calculations indicated for the formation of Cu-hydroperoxo species during the catalytic studies. The kinetics study revealed for the 1st order kinetic for the catechol oxidation and the DFT study predicted for the exothermic nature of the catechol oxidation process.

1. Introduction

Copper is known to be one of the trace elements in the biological system [1]. A good number of metalloenzymes like plastocyanin, hemocyanin involving copper as active centre are known to catalyse different enzymatic reactions [2]. Intrigued by the bioactive copper systems, different copper complexes are synthesized to mimic the bio-system [3,4]. The concept of single site catalyst is also derived from the naturally occurring catalytic reaction involving metalloenzymes [5]. The single site catalysts are known to provide good selectivity for which the catalytic reactions taking place in our biological process are highly selective [6]. In this respect the Cu (II) Phenanthroline complexes (Cu-Phen) and such Cu-nitrogen co-ordinated complexes are well studied for DNA interaction and for anti-cancer activity [3,7–9]. However,

the Cu-Phen complexes in mono, binuclear form are not well explored for benzyl alcohol (BA) oxidation reaction [10]. The oxidation of BA is one of the important reactions that is known to catalyse by different metal catalysts [11–13]. Due to the involvement of challenges and difficulties such as over oxidation, free radical mechanism, the BA oxidation reaction still remains as a reaction of research interest [14–16]. So far different Cu-based metal catalysts either in homogeneous or heterogeneous form have been studied for the BA oxidation [17–20]. For example, Das et al. performed such reaction with Cu phenanthroline complex using molecular oxygen and TEMPO as a promoter [21]. Recently, Zand et al. developed a new approach of BA oxidation via Cu-acetonitrile coordinated phenanthroline complex [22]. Ranjan et al. introduced mannich base ligand to form complex with Cu to do photocatalytic oxidation of such alcohol under visible light [23]. Paine et al.