



Immobilized magnetic nano catalyst for oxidation of alcohol



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ABSTRACT

Covalent attachment of Schiff base on magnetic nanoparticles yielded good selectivity for oxidation of alcohols. The ferromagnetic interaction in the complex added comprehensive advantage in enhancing the catalytic activity of the nanocatalyst. A greener approach for alcohol oxidation was achieved in solventless method with good yield (>78%). Leaching experiments confirmed a strong interaction between magnetic support and complex. The catalyst showed significant conversion even after 5 catalytic runs.

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1. Introduction

Metal(II) complexes coordinating with organic base ligands including Schiff bases are well-known to interact with molecular oxygen to form dioxygen adducts and have extensively been used as efficient and selective homogeneous catalysts for a variety of oxidation reactions in recent years [1,2]. However, the main drawback of these homogeneous catalysts is the necessity of their separation from the reaction mixture at the end of the reaction. Immobilization of Schiff base complexes to the magnetic nanoparticle support via covalent attachment provides facile separation of the catalyst during the reaction by external magnet [3]. The magnetic support offers high catalytic efficiency and better recycling without having the inherent problems of leaching of complex/ligand during the reaction.

In recent years, aromatic linkers have been extensively used to immobilize ligands on nanoparticle via click reaction [4,5]. The magnetic superexchange observed in the aromatic linkers such as *m*-phenylene, *p*-phenylene provides stable ferromagnetic interactions between immobilized ligands and the support [6,7]. Recent experimental and theoretical studies on dinuclear metal(II) complexes have shown higher amount of ferromagnetic interaction with bisidentate bridging ligands bearing *m*-phenylene linkers [8]. Phenylene spacers as linker groups provide aromatic bridging ligand and allow electron exchange between metal and ligand

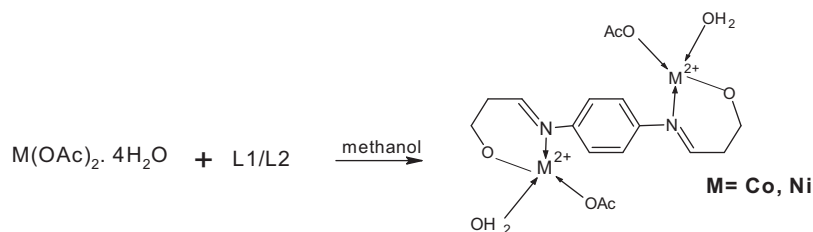
within the framework enhancing magnetic and catalytic activity of the immobilized catalyst.

Schiff base ligand framework forms stable complex depending on the flexibility of the linker group [9]. Schiff base ligands possess the ability to chelate many metal ions and form stable complexes. Researchers have proved that Co(II) and Ni(II) complexes binds with molecular oxygen and the resultant dioxygen–Co and Ni complexes exhibits efficient oxidation reaction [10]. The immobilized supports have shown better control on efficiency of the catalyst due to the microenvironment provided by the support. Hence, immobilized metal complexes have found its advantage in selective oxidation of alcohols with hydrogen peroxide oxidant without any organic solvent, phase transfer catalyst or additive. The redox potential of Co and Ni metal ions influences the decomposition of hydrogen peroxide by reducing its energy of activation and assists in enhancing the catalytic activity of the Schiff bases [11].

Immobilization of Schiff complexes by covalent attachment has proven to be the most effective method for anchoring the metal complexes. Hu et al. have recently reported that Schiff base molybdenum(VI) complexes immobilized onto zirconium poly(styrene-phenylvinylphosphonate)-phosphate showed comparable or even higher conversion and chemical selectivity for epoxidation of olefins compared with other heterogeneous catalysts [12]. The catalysts were easily recovered by simple filtration and were reused with little loss of activity. The potential use of the catalyst for oxidation was reported by Jiang et al. with increased catalytic activity by immobilizing Co salophen complex on montmorillonite [13]. Researchers have explored that higher catalytic activity is observed for oxidation of alcohols to carbonyls

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Scheme 1. Schematic representation of complex synthesis.

with efficient separation by immobilized complex on nanoparticle compared to their homogeneous counterparts [14–17].

The primary advantage of immobilization of Co(II) and Ni(II) catalysts is their facile magnetic recovery and the ease with which the reaction products can be separated from the catalysts. The other advantage of this catalyst is the possibility of not requiring solvent and the potential of increased catalytic stability. The geometric structure of the complexes can favour by altering the catalyst activity and selectivity. In recent years, many researchers have devoted on immobilization of the ligands on inert barrier such as silica [18], CNT [19], graphene oxide [20] etc. However, the reported complexes have the drawbacks of excessive loading of complex on magnetic support. Moreover, most of the reported methods are amendable for oxidation reactions by direct condensation of terminal group of the metal complex with chemically modified silane of magnetic support. The superparamagnetic nanoparticles are easily dispersible and have no tendency to aggregate in the solution. Hence, use of superparamagnetic support provides an exceptional behavior for catalytic reactions in solution with easy magnetic recovery. In addition, it would be beneficial if metal complexes are bound with stronger ferromagnetic interactions so as to avoid

aggregation of nanocatalyst during catalytic reactions. However, there are very few reports on magnetic interaction between support and immobilized ligands as a stable nanocatalyst for organic reactions. In this work, we have emphasized in studying the possible ferromagnetic interaction to enhance the magnetic and catalytic activity of the nanocatalyst.

2. Experimental

2.1. Materials

Ferrous chloride, ferric chloride, cobalt(II) acetate tetrahydrate and nickel(II) acetate tetrahydrate were purchased from Merck, India and used as received. 3-aminopropyltriethoxysilane was purchased from Sigma–Aldrich and used without further purification.

2.2. Characterization techniques

The FTIR spectra were measured on JASCO FTIR-4200 (KBr technique). ¹H NMR was recorded in Bruker instrument using TMS as internal standard. Thermal analysis was carried out (EXSTAR-6000)

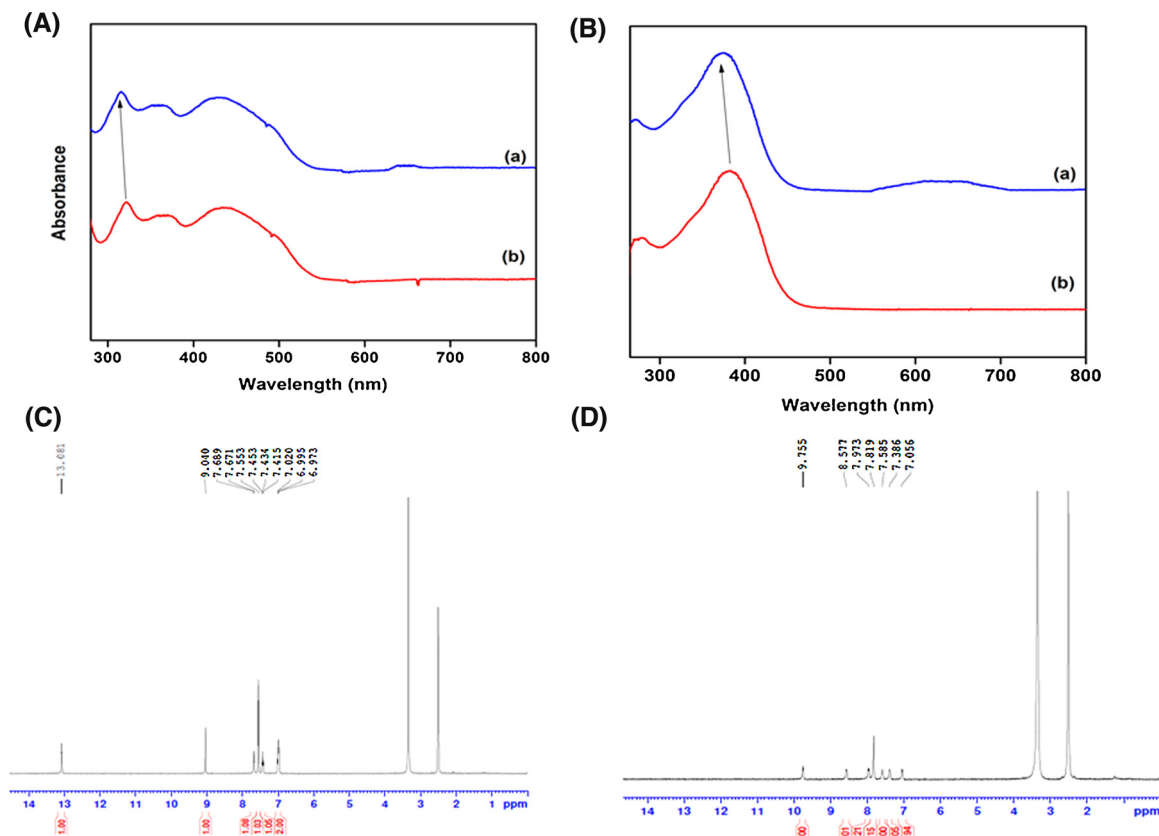


Fig. 1. (A) UV–vis spectrum of (a) complex C1 and (b) ligand L1 (B) UV–vis spectrum of (a) complex C2 and (b) ligand L2 (C) HNMR of L1 and (D) HNMR of L2.

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