



# Transition metal coordination polymers: Synthesis and catalytic study for hydroxylation of phenol and benzene

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## ABSTRACT

New coordination polymers of Ni(II) and Cu(II) of the polymeric salen-type Schiff base ligand derived from the condensation of 5,5'-methylene bis-(salicylaldehyde) with 1,2-diaminopropane yielded *N,N'*-1,2-propylenebis(5-methylenesalicylideneamine) abbreviated  $[-CH_2(H_2sal-1,2-pn)-]_n$  have been synthesized. Both coordinated polymers with the general formula of  $[-CH_2(MLXDMF)-]_n$ , where X = 0, M = Cu; *N,N'*-1,2-propylenebis(5-methylenesalicylideneaminato)copper(II) and X = 2, M = Ni; *N,N'*-1,2-propylenebis(5-methylenesalicylideneaminato)nickel(II) have been characterized by elemental analysis, magnetic susceptibility measurements, IR, electronic spectra and thermogravimetric studies. The ligand behaves as a bis-bidentate molecule coordinating through the phenolic oxygen and azomethine nitrogen atoms.

These coordinated polymers have been assessed as catalysts for liquid phase hydroxylation of phenol and benzene using  $H_2O_2$  as an oxidant. The results show a high activity and selectivity of both catalysts toward the formation of diphenols from phenol, and a low activity in the oxidation of benzene. The Cu-based catalyst exhibited higher activity than Ni-based catalyst for hydroxylation of phenol and benzene. The activity and efficiency of  $H_2O_2$  depends on the reaction parameters viz., temperature, molar ratio of the reactants and the solvent. Concentration of the oxidant and other reaction parameters has been optimised for the maximum oxidation of these substrates. These catalysts can be recovered and reused without notable loss of activity.

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## 1. Introduction

Production of phenol and diphenols from the hydroxylation of aromatic compounds is an important industrial application. Therefore, much attention has been focused on their production through catalytic routes, in particular direct hydroxylation of benzene and phenol by  $H_2O_2$  [1]. Hydrogen peroxide which has high active oxygen content has been widely explored as a green oxidant in oxidation reactions, because it is readily available and the resulting by-products (water and molecular oxygen) are environmentally friendly. Hydroxylation of phenol usually produces catechol and hydroquinone which are used in industrial syntheses as antioxidants, polymerization inhibitors, photographic chemicals and fine chemical industries [2,3]. Mineral acids, simple metal ions and transition metal-based complexes are well-known traditional catalysts for the hydroxylation of phenol [4]. Metal ion-exchanged or supported on zeolites, hydrotalcites, and resins [5–11] have been increasingly studied in order to overcome the disadvantage of homogeneous catalysts viz., recovery and reuse of the catalyst.

TS-1 was revealed to be novel and the most highly efficient heterogeneous catalyst (Enichem) in this area [12]. To date, many researchers have been interested in the development of heterogeneous catalysts which are more active than TS-1 for hydroxylation of phenol, but most of them suffer from leaching of the active metal in the liquid phase and behave as homogeneous rather than heterogeneous catalysts [13].

On the other hand, phenol is mainly manufactured by a three-step cumene process, and has many disadvantages such as low yield, high energy consumption and production of an equal amount of acetone as the by-product [14]. Hence, finding alternative ways to produce phenol that overcome the disadvantages of the current cumene process has become one of the most challenging tasks in oxidation catalysis from an economical and environmental viewpoint. Direct hydroxylation of benzene to produce phenol is performed both in the liquid and gas phase. Direct hydroxylation of benzene is mainly focused on three preparation routes using the oxidants nitrous oxide [15–18], hydrogen peroxide [6,19,20], and molecular oxygen [21]. Moreover, various heterogeneous catalysts have been studied for this reaction [22]. Currently, transition metal coordination polymers have found increasing interest due to their possible technological and industrial applications such as separation, ion-exchange and catalysis. Coordination polymers,

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