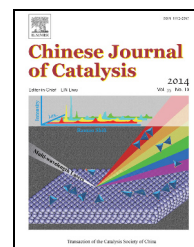


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Article

Novel polystyrene-anchored zinc complex: Efficient catalyst for phenol oxidation



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ABSTRACT

The novel recyclable free -ONNO- tetradentate Schiff base ligand *N,N'*-bis(2-hydroxy-3-methoxybenzaldehyde)4-methylbenzene-1,2-diamine (3-MOBdMBn) was synthesized. Complexation of this ligand with zinc (3-MOBdMBn-Zn) was performed, and the catalytic activity of the complex was evaluated. The polymer-supported analog of this complex (P-3-MOBdMBn-Zn) was synthesized, and its catalytic activity was studied. These free and polymer-anchored zinc complexes were prepared by the reactions of metal solutions with one molar equivalent of unsupported 3-MOBdMBn or P-3-MOBdMBn in methanol under nitrogen. The catalytic activity of 3-MOBdMBn-Zn and P-3-MOBdMBn-Zn was evaluated in phenol oxidation. The activity of P-3-MOBdMBn-Zn was significantly affected by the polymer support, and the rate of phenol conversion was around 50% for polystyrene-supported 3-MOBdMBn. The experimental results indicated that the reaction rate was affected by the polymer support, and the rate of phenol conversion was 1.64 $\mu\text{mol}/(\text{L}\cdot\text{s})$ in the presence of polystyrene-supported 3-MOBdMBn.

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1. Introduction

Schiff base complexes have various applications in organic reactions such as oxidation [1,2], olefin epoxidation [3,4], and polymerization of ethylenes to give narrow molecular-mass distributions [5,6]. However, homogeneous Schiff base catalytic systems have two major disadvantages: (1) lack of product control, which causes reactor fouling and (2) limited use in solution processes. The binding of Schiff base metal catalysts to polymer supports is a promising solution to these problems. In general, the catalytic activity of heterogeneous Schiff base systems (or supported systems) is lower than that of the homogeneous analogs, but polymer-supported transition-metal complexes have shown high catalytic activity [7,8] compared with

homogeneous and unsupported catalysts. Polymer-supported palladium complexes have been used in Heck reactions [9–11], generating the corresponding products in good to excellent yields. Heterogeneous catalysts are particularly attractive for phenol oxidation because of their practical advantages and catalyst reusability. The Schiff base complexes of metal ions have also been used in phenol oxidation [12,13].

Phenol oxidation is an industrially important reaction because its products, i.e., catechol and hydroquinone, have a range of applications as antioxidants, polymerization inhibitors, photographic chemicals, flavoring agents, and drug intermediates. Since 1970, phenol oxidation has been widely investigated using various homogeneous and heterogeneous catalysts [13]. Phenol is an intermediate in the oxidation of many

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aromatic compounds, and it is toxic and resistant to biotreatment. The treatment of wastewater containing highly concentrated, toxic, or poorly biodegradable compounds by oxidation of the organic pollutants to non-toxic products in the presence of a catalyst is a promising approach [14,15].

The oxidation of phenols using various chemical reagents such as H₂O₂, permanganate, molecular oxygen, and ozone is widely used [16]. The use of H₂O₂ has the advantage of producing oxygen, which can be used to augment biological degradation [17]. The use of H₂O₂ as an alternative to current industrial oxidation processes has environmental advantages such as (1) replacement of stoichiometric metal oxidants, (2) replacement of halogens, (3) replacement or reduction of solvent use, and (4) avoidance of salt by-products. H₂O₂ works either alone or with a catalyst, but the catalytic process gives better results. Fe is the most common homogeneous catalyst used with H₂O₂ [18]. In the present investigation, phenol oxidation was chosen as the model reaction to study the catalytic activity of the synthesized unsupported and polymer-supported zinc metal complexes; zinc was used because it is a bioactive metal.

Although the oxidation of phenol in the presence of polymer-supported Schiff base transition-metal complexes has been reported [8], the catalytic activity of the zinc complex of the Schiff base *N,N'*-bis(2-hydroxy-3-methoxybenzaldehyde)-4-methylbenzene-1,2-diamine (3-MOBdMBn) has not been reported in the literature. We therefore attempted to synthesize and characterize polystyrene-supported transition-metal complexes of 3-MOBdMBn, evaluate their catalytic activity in phenol oxidation with H₂O₂ as the oxidant, and compare their activity with that of the unsupported zinc complex.

2. Experimental

2.1. Materials

Divinylbenzene cross-linked chloromethylated polystyrene beads were obtained from Ion Exchange India Ltd., Mumbai, India. Anhydrous zinc chloride was purchased from Thermo Fisher Scientific India Pvt., Ltd., Mumbai, India and used without further purifications. Phenol, H₂O₂ (30.0 wt%), 2-hydroxy-3-methoxybenzaldehyde (3-MOBd), and 4-methylbenzene-1,2-diamine (MBn) were procured from E. Merck, India. Other chemicals and solvents were of analytical grade (> 99.0 wt%) and used after drying.

2.2. Synthesis of 3-MOBdMBn Schiff base and its zinc complex

The 3-MOBdMBn Schiff base was synthesized using a modified version of the procedure reported in the literature [7]. A reaction mixture consisting of 3-MOBd (20.00 mmol, 3.04 g) and MBn (10.00 mmol, 1.22 g) in methanol was refluxed at 60 °C for 2 h. The reaction mixture was cooled to a low temperature, producing light-straw-colored crystals, which were filtered and recrystallized with methanol. The metal complex of 3-MOBdMBn was prepared by refluxing a methanolic solution (100 mL) of Schiff base (20.00 mmol, 7.81 g) and zinc salt

(20.00 mmol, 2.725 g) in a round-bottomed flask at 60 °C for 6 h. All reactions were performed under nitrogen. The metal complex was recrystallized from dichloromethane and dried in a vacuum desiccator.

2.3. Synthesis of P-3-MOBdMBn Schiff base and its zinc complex

Polymer-anchored zinc complexes were prepared by nitrosation of 3-MOBdMBn (7.81 g, 20.00 mmol) with sodium nitrite (20.00 mmol) in 1.0 mol/L hydrochloric acid (100 mL) in an ice bath. The resultant NO-3-MOBdMBn was filtered and washed with hot and cold water to remove reaction impurities. Reduction of NO-3-MOBdMBn was performed using the nitrosated Schiff base (20.00 mol) in 1.0 mol/L hydrochloric acid (50 mL) in the presence of metallic iron, which produced *N,N'*-bis(4-amino-2-hydroxy-3-methoxybenzaldehyde)-4-methylbenzene-1,2-diamine (A-3-MOBdMBn). Then methanol-swollen cross-linked chloromethylated polystyrene beads (5.0 g) were refluxed in methanol (50 mL) containing A-3-MOBdMBn (20 mmol). After 10 h, the polymer beads with anchored 3-MOBdMBn were separated and dried in a vacuum desiccator. Zinc ions were then loaded by keeping P-3-MOBdMBn (5.0 g) for 10 h in 50 mL of an aqueous solution of zinc ions. The metal ion loadings on the free and polymer-supported 3-MOBdMBn were calculated as a complexation of the metal ions based on the initial amount of 3-MOBdMBn and the amount of metal ions loaded on the polymer beads.

2.4. Characterization of the samples

Infrared (IR) spectra (KBr pellets) were recorded using a Perkin-Elmer 1600 Fourier-transform (FT) IR spectrophotometer. Electronic spectra were recorded with a Shimadzu 1601 PC ultraviolet-visible (UV-Vis) spectrophotometer using sample mulls in a cuvette. Thermogravimetric (TG) analysis was performed using a Perkin-Elmer Pyris Diamond thermal analyzer under nitrogen at a heating rate of 10 °C/min. The metal ion loading on the Schiff base was determined by analyzing the loading solution using a Perkin-Elmer 3100 atomic absorption spectrometer at the zinc ion λ_{\max} . The compositions of 3-MOBdMBn and its zinc complex were estimated using a Haraeus Carlo Ebra 1108 elemental analyzer. ¹H nuclear magnetic resonance (NMR) spectra were recorded with a Bruker FT-NMR 300 MHz spectrometer using DMSO-*d*₆ as the solvent and tetramethylsilane as an internal reference. The magnetic moments (μ) of the metal complexes were measured using a Vibrating Sample Magnetometer-155. The molecular mass of 3-MOBdMBn and its zinc complex was determined using a vapor pressure osmometer (Merck VAPRO 5600, Germany).

2.5. Catalytic activity of zinc complexes in phenol oxidation

Phenol oxidation was performed using H₂O₂ as the oxidant, with a fixed ionic strength (0.10 mol/L) and hydrogen ion concentration (pH = 7.0) in the reaction mixture. A calculated amount of polymer-anchored zinc was placed in a two-necked round-bottomed flask containing phenol (4.70 g, 0.05 mol/L);

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