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Polystyrene-bound 1,4-phenylenediamine as a heterogeneous axial ligand for Mn(salophen)Cl and its use as biomimetic alkene epoxidation and alkane hydroxylation catalyst with sodium periodate

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Abstract

In the present work, Mn(III) salophen has been successfully bonded to 1,4-phenylenediamine modified polystyrene, PSP. Polystyrene-bound 1,4-phenylenediamine is a heterogeneous axial ligand and a support for immobilization of Mn(III) salophen. Mn(salophen)Cl-PSP catalyzes alkene epoxidation with sodium periodate under agitation with magnetic stirring. This catalytic system shows a good activity in the epoxidation of linear alkenes. Alkyl aromatic and cycloalkanes were oxidized efficiently to their corresponding alcohols and ketones in the presence of this catalyst. This new heterogeneous catalyst is of high stability and reusability in the oxidation reactions and can be reused several times without loss of its activity. The effect of reaction parameters such as solvent and oxidant in the epoxidation of *cis*-cyclooctene were investigated. The heterogeneous catalyst Mn(salophen)Cl-PSP has been characterized by FT-IR, UV–Vis spectroscopic techniques, thermal and elemental analysis.

Keywords: Biomimetic; Epoxidation; Hydroxylation; Manganese salophen; Periodate

1. Introduction

A number of biomimetic systems have been developed to mimic the function of P-450 enzymes [1]. P-450 enzymes are known to oxidize a very extensive range of endogenous and exogenous organic compounds, ranging from medium chain alkanes such as *n*-heptane and *n*-octane, to steroidal and polyaromatic compounds, and very large molecules such as triterpenes and cyclosporine. These reactions are important in biological systems because they are crucial steps in biosynthesis, cellular biochemistry, metabolism, pharmacology and medicine [2,3]. In the last decade, salen and salophen ligands have received more attention, mainly because of their extensive applications in the fields of synthesis and catalysis [4–6].

This attention is still active and considerable research efforts are devoted to the synthesis of modified and supported reagents for catalysis and materials chemistry [7–11]. Transition metal salen complexes were recognized as powerful homogeneous catalysts in the oxidation reactions with various single oxygen atom donors such as NaClO, PhIO, $KHSO_5$, H_2O_2, $NaIO_4$ [11–19]. The catalytic activity of the model complexes in homogeneous medium decreases because of formation of inactive dimeric μ-oxo manganese (IV) species [20,21]. In comparison with the homogeneous catalysts, heterogeneous systems present many advantages such as easy separation and recovery of the catalyst from the reaction media, higher stability of the catalytic species and catalyst protection against destruction. Schiff base complexes (salen or salophen) can be immobilized on the support

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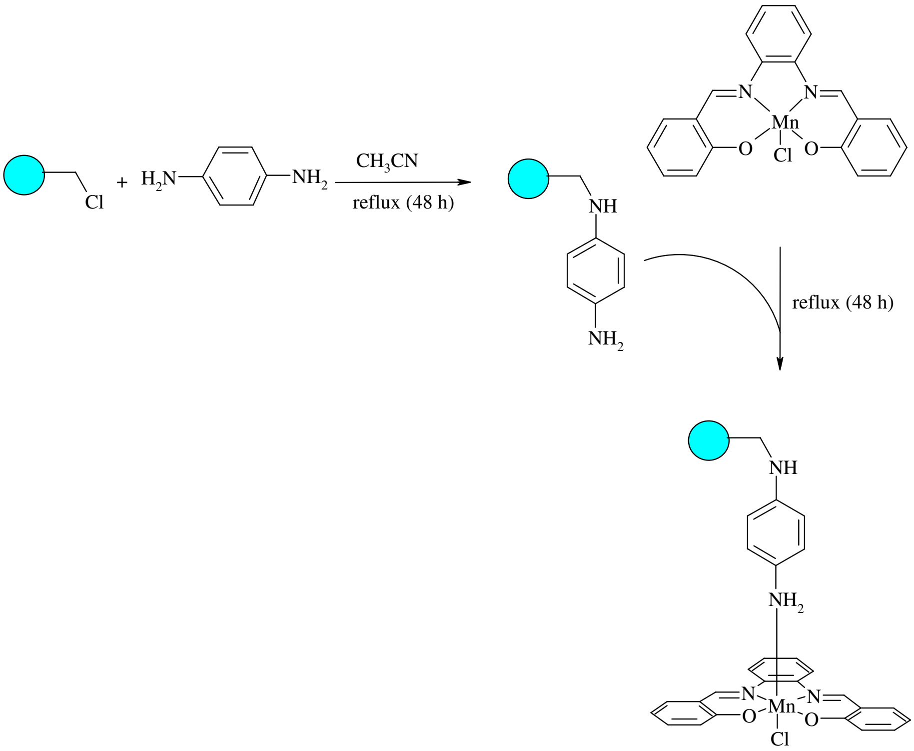

Scheme 1. Preparation of polymer supported catalyst, [Mn(salophen)Cl-PSP].

in many ways, namely: (a) non-covalent immobilization in zeolites, clay or siloxane membranes [22–25]; (b) covalent grafting onto inorganic supports such as silica or MCM-41 [26–30]; (c) co-polymerization of a functionalized salen monomer into an organic polymer [31]; and (d) attachment or build-up of a salen structure to a performed polymer [32–37]. Polymers, which are used as supports, have gained much attention being inert, non-toxic, non-volatile, insoluble and often recyclable. Imidazoles and pyridines were chosen since they ligate strongly to the axial positions of metallosalens in free solution [38,39], and furthermore, such a nitrogen base can increase the catalytic efficiency in the epoxidation with single oxygen atom donors.

This paper describes a catalytic system based on a chloromethylated polystyrene support modified with 1,4-phenylenediamine, which can act as an axial ligand for Mn(salophen) by covalent attachment (Scheme 1). The heterogeneous Mn(salophen) catalyst, [Mn(salophen)Cl-PSP], was characterized by FT-IR, UV–Vis and TG–DTG. Catalytic activity and reusability of this catalyst in the heterogeneous epoxidation of alkenes and hydroxylation of alkanes has also been demonstrated.

2. Results and discussion

2.1. Preparation of polymer-supported manganese salophen catalyst, [Mn(salophen)Cl-PSP]

Chloromethylated polystyrene (cross-linked with 2% divinylbenzene, 4–5% Cl content, 1.14–1.40 mmol/g Cl) was treated with an appropriate quantity of 1,4-phenylenediamine, using CH_3CN as solvent, and was refluxed for 48 h [40]. The supported [Mn(salophen)] was prepared by stirring a suspension of the support, (PSP), in a solution of Mn(salophen) in CH_3CN as solvent, because of better solvation and swelling of the polymer in it. The degree of incorporation of manganese salophen into the polymer was determined by neutron activation analysis (NAA). The covalent bonding of the polymer and the manganese salophen is so strong that Mn(III)-salophen is not eluted from the polymer with water and common organic solvents.

2.2. Characterization of catalyst

The prepared catalyst was characterized by IR, UV and TGA. [Mn(salophen)Cl-PSP] was characterized by elemental analysis. The amount of grafted Mn(salophen), which was calculated by neutron activation analysis (NAA), was 0.136 mmol/g base on Mn. The nitrogen content of this resin was 2.06%. According to this value, the degree of 1,4-phenylenediamine which was introduced into the polymer composition was 0.735 mmol/g of support. This shows that only 53–64% of the total chlorine was substituted by 1,4-phenylenediamine.

The diffuse reflectance spectra provide further evidence for the presence of the Mn(salophen) complex on the support. The absorption spectrum of [Mn(salophen)Cl-PSP] exhibits a broad peak near 450 nm which could be due to the d–d transition of Mn(III). Its homogeneous counterpart also shows a peak near 450 nm, which indicates the presence of the manganese catalyst on the polymer (Fig. 1).