

Oxovanadium(IV) complex of β -alanine derived ligand immobilised on polystyrene for the oxidation of various organic substrates

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Abstract

Tridentate Schiff base ($H_2fsal-\beta$ -ala) obtained from 3-formylsalicylic acid and β -alanine has been covalently bonded to divinylbenzene cross-linked chloromethylated polystyrene. This chelating resin, abbreviated as PS- $H_2fsal-\beta$ -ala (PS = polymeric support), reacts with vanadyl sulfate in DMF to give polymer bound complex, PS-[VO($fsal-\beta$ -ala) · DMF], formation of which has been confirmed by various physicochemical methods such as elemental analysis, FT-IR and diffused reflectance spectra, thermo gravimetric analysis, and scanning electron micrograph. Catalytic potential of PS-[VO($fsal-\beta$ -ala) · DMF] has been tested for the oxidation of various organic substrates such as benzene, cumene, naphthalene, cyclohexane, styrene, cyclohexene and *trans*-stilbene in the presence of 30% H_2O_2 as an oxidant. Oxidation products obtained from each substrate have been characterised by gas chromatography and their identities confirmed by gas chromatography–mass spectrometry.

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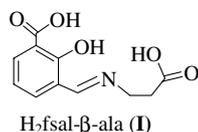
1. Introduction

The current catalytic interest in high-valent vanadium complexes arises from the presence of vanadium in several metalloenzymes [1–3]. These complexes have been considered as new versatile catalytic reagents for a wide range of oxidation reactions like, oxidation of olefins and allylic alcohols [4–7], benzene/alkylaromatic compounds [8,9], sulfides [10–12] and alcohols [13–15]. In presence of inexpensive oxidant such as O_2 , H_2O_2 or hydroperoxides, they work satisfactorily in homogeneous conditions. Immobilisation of homogeneous catalysts to facilitate easy product separation, catalysts recovery and recyclability has been the major concern of industries as well as researchers. The frequently used methods to immobilise homogeneous catalysts are: (i) encapsulation in the nano-cavity of zeolites [16] and (ii) their covalent bonding with organic polymeric materials [17] or inorganic materials like functionalized

MCM-41, SBA-15 etc. [18]. Leaching of the catalysts encapsulated in zeolite-Y has, however, been observed during catalytic action if the molecular size of the catalysts are too small [19]. Such complication can be avoided by using organic polymeric support for homogeneous catalysts. Oxovanadium(IV) Schiff base complexes immobilised on polymeric support have recently been used successfully for the oxidation of (prochiral) sulfides to chiral sulfoxides [10,12].

In continuation of our work on the development of high-valent vanadium complex based heterogeneous catalysts through covalent bonding with cross-linked chloromethylated polystyrene and their possible catalytic potential for the oxidation of organic substrates [20,21], herein we report the synthesis and characterisation of chloromethylated polystyrene-anchored oxovanadium(IV) complex of tridentate Schiff base, $H_2fsal-\beta$ -ala (Scheme 1), derived from 3-formylsalicylic acid and β -alanine. The catalytic potential of PS-[VO($fsal-\beta$ -ala) · DMF] has been explored by considering the oxidation of a series of organic substrates.

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Scheme 1.

2. Experimental

2.1. Materials and methods

Analytic reagent grade styrene, cumene (Acros Organics, USA), vanadyl sulfate (Loba Chemie, India), β-alanine (Sisco Research Laboratories, India), *trans*-stilbene (Lancaster, England), benzene, cyclohexene, cyclohexane and salicylaldehyde (Ranbaxy Limited, India) and 30% H₂O₂ (Thomas Baker, India) were used as such.

Chloromethylated polystyrene (18.9% Cl i.e. 5.3 mmol Cl/g of resin and cross-linked with 5% divinylbenzene) was generously gifted by Thermax Limited, Pune, India. 3-Formylsalicylic acid was prepared according to the procedure reported in literature [22]. Instrumental details and analyses methods are reported elsewhere [20,21].

2.2. Preparations

2.2.1. Preparation of PS-H₂fsal-β-ala (II)

The polymer-anchored ligand, PS-H₂fsal-β-ala was prepared in two successive steps. In the first step, chloromethylated polystyrene beads (10 g, 0.054 mol Cl) were allowed to swell for 2 h in 40 ml of DMF at room temperature. A filtered solution of 3-formylsalicylic acid (17.6 g, 0.106 mol) in 60 ml of DMF was added to the above suspension followed by triethylamine (15 g) in ethylacetate (70 ml); the Cl:3-formylsalicylic acid ratio was approximately 1:2 in order to replace maximum percentage of Cl. The above reaction mixture was heated at ca. 60 °C in an oil bath while continuous mechanical stirring for 36 h. After cooling to room temperature the resin beads were filtered off, washed with DMF followed by hot methanol and dried in air oven at 120 °C.

In the second step, the polymer-anchored 3-formylsalicylic acid (3.0 g) was allowed to swell in 40 ml of water for 2 h prior to the reaction. An aqueous KOH solution (1.0 g, 0.016 mol in 10 ml) of β-alanine (1.4 g, 0.016 mol) was added to the above suspension and the reaction mixture was allowed to stir in an oil bath at ca. 60 °C for 48 h. After cooling to room temperature the resin beads were filtered off, washed with hot methanol and dried in vacuum desiccator. Obs. for PS-H₂fsal-ala: C, 79.1%; H, 7.69%; N, 2.86%.

2.2.2. PS-[VO(fsalsal-β-ala) · DMF](1)

The polymer-anchored ligand [PS-(H₂fsal-β-ala)] (3.0 g) was allowed to swell in 20 ml of DMF for 2 h prior to the reaction. Vanadyl sulfate (3.7 g, 0.015 mol) dissolved in 30 ml of DMF was added to the above suspension. The resulting reaction mixture was heated at ca. 70 °C with continuous mechanical stirring for 70 h. The greenish resin

beads were filtered off, washed thoroughly with hot DMF followed by hot methanol and dried in air oven at ca. 120 °C. Obs. for PS-[VO(fsalsal-β-ala) · DMF]: C, 66.65%; H, 4.32%; N, 4.02%; V, 5.52%.

2.2.3. [VO(fsalsal-β-ala) · H₂O] (2)

A solution of 3-formylsalicylic acid (1.66 g, 10 mmol) dissolved in 10 ml of water was added to an aqueous KOH (0.56 g, 10 mmol in 20 ml) solution of β-alanine (0.89 g, 0.010 mol). The resulting reaction mixture was stirred for 2 h where yellow solution was obtained. An aqueous solution of vanadyl sulfate (2.53 g, 0.010 mmol in 30 ml) was added slowly to the above solution while stirring magnetically. This was further stirred for 3 h and there after solvent volume was reduced to ca. 10 ml under vacuum. After keeping the flask in refrigerator at ca. 10 °C overnight, the green solid that had separated slowly was filtered off, washed with diethyl ether and dried in vacuum desiccator. Yield 55%. Obs.: C, 41.36%; H, 3.26%; N, 4.43%, V, 15.66%. Calcd. for C₁₁H₁₁NO₇V (320): C, 41.25%; H, 3.44%; N, 4.38%, V, 15.94%.

2.3. Catalytic activity

2.3.1. Oxidation of aromatic compounds and cyclohexane

Different aromatic compounds such as benzene, cumene, naphthalene and cyclohexane were considered for the oxidation reactions. In a typical representative reaction, benzene (0.78 g, 0.010 mol) in 10 ml of acetonitrile was charged with previously swallowed PS-[VO(fsalsal-β-ala) · DMF] (0.035 g) in 10 ml of acetonitrile for 2 h followed by the addition of 30% H₂O₂ (2.26 g, 0.020 mol). The temperature of the reaction mixture was fixed at 70 °C. The samples were taken periodically out and quantitatively analysed using thermoelectron gas chromatograph equipped with HP-1 capillary column (30 m × 0.25 μm × 0.25 mm) and FID detector. Oxidations of other substrates were performed similarly and identities of the products were confirmed by GC-MS (Perkin-Elmer, Clarus 500) analysis.

2.3.2. Epoxidation of olefins

In a typical reaction, the catalyst PS-[VO(fsalsal-β-ala) · DMF] (0.030 g) was allowed to swell in 20 ml of acetonitrile for 2 h. To this suspension, styrene, cyclohexene or *trans*-stilbene (0.010 mol) was added and the reaction mixture was allowed to stir at 70 °C. After adding 30% H₂O₂ (1.14 g, 0.010 mol), the progress of the reaction was monitored by withdrawing the samples periodically and analysing quantitatively as mentioned above. The Products were confirmed through GC-MS analysis.

3. Results and discussion

3.1. Synthesis and characterisation of catalyst

Synthesis of polymer-anchored ligand, PS-H₂fsal-β-ala (II) was achieved in two steps. In the first step, 3-formylsal-

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