



Aerobic oxidation and oxidative bromination in aqueous medium using polymer anchored oxovanadium complex



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ABSTRACT

Polymer anchored oxovanadium catalyst was synthesized and characterized. Its catalytic activity was evaluated for the oxidation of various primary and secondary alcohols with molecular oxygen under mild reaction conditions. This catalyst was also effective for the oxidative bromination reaction of organic substrates with 90–100% selectivity of mono substituted products with H₂O₂/KBr at room temperature. The above reactions require low temperature, short time period and most importantly all the above reactions occur in aqueous medium. The developed catalyst can be facilely recovered and reused six times without significant decrease in activity and selectivity.

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Introduction

The selective aerobic oxidation and oxidative bromination of organic compounds are useful and fundamental transformations in organic synthesis [1,2]. In recent years, there has been an increasing interest in developing environmental friendly greener processes which are also economically viable in industrial chemistry [3]. With environmental and economic concerns, heterogeneous catalysis reaction using molecular oxygen as an oxidant is developed as desired green process for selective oxidation of alcohol and oxidative bromination of various organic substrates [4–10].

Up to now, numerous expensive metal (e.g. palladium and ruthenium) catalyst and toxic organic solvents have been traditionally used to accomplish most of the aerobic oxidation of alcohols [11–13]. On other hand, conventional bromination reaction requires hazardous and toxic elemental bromine [14–16]. In order to overcome these problems, several safe systems for the aerobic oxidation and oxidative bromination have been developed. One is the use of inexpensive metal catalyst for the aerobic oxidation and

use of bromide ion as a bromine source instead of bromine for oxidative bromination [17–21].

We have chosen polymer anchored vanadium complex as the heterogeneous catalyst and water as the green solvent for the aerobic oxidation and oxidative bromination. Vanadium exists on the surface of the earth more abundantly than copper, palladium or ruthenium [22]. It plays an important role in aerobic oxidation and oxidative bromination processes. In addition, heterogeneous catalysts have some advantages compared to homogeneous catalyst. Metals supported on materials such as alumina [23], amorphous silicates [24], polymers [25], zeolites [26], and MCM-41 [27] are commonly in use in heterogeneous catalysis. Nowadays functionalized polystyrene anchored catalysts are used to carry out various catalytic organic transformations [28–31]. Among them chloromethylated polystyrene are widely used as polymer support. These polystyrene anchored metal complexes are inert and reusable catalysts for various organic reactions.

In the chemical processes, traditional organic solvents are used in large quantities, which have led to various environmental and health concerns. As part of green chemistry efforts, a variety of cleaner solvents have been used as replacements [32–35]. As an alternative solvent, water has been paid extraordinary attention. Apart from being a chemically interesting solvent, water provides a cheap alternative for organic solvents, making it environmentally

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and economically interesting as well. So, based on the above two concepts, we tried to synthesize a polymer anchored oxovanadium complex which catalyse the aerobic oxidation of primary and secondary alcohols and oxidative bromination of various aromatic amines, aldehydes in aqueous medium.

Herein we report the synthesis and characterization of a polymer anchored oxovanadium complex and illustrate its application for the aerobic oxidation and oxidative bromination reactions in aqueous medium using hydrogen peroxide as an oxidant.

Experimental

Materials and instruments

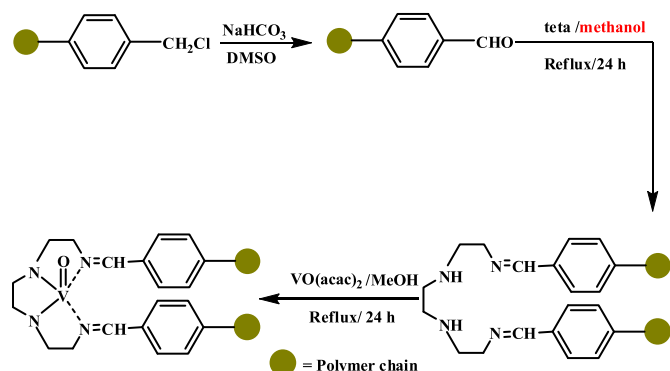
All the reagents used were chemically pure and were of analytical reagent grade. The solvents were dried and distilled before use following the standard procedures [36]. Chloromethylated polystyrene was supplied by Sigma–Aldrich chemicals Company, USA. Other reagents were obtained from Merck or Fluka. A Perkin–Elmer 2400C elemental analyzer was used to collect micro analytical data (C, H and N). Vanadium content of the sample was measured by Varian AA240 atomic absorption spectrophotometer (AAS). The FT-IR spectra of the samples were recorded on a Perkin–Elmer FT-IR 783 spectrophotometer using KBr pellets. Diffuse reflectance spectra (DRS) were registered on a Shimadzu UV/3101 PC spectrophotometer. Mettler Toledo TGA/SDTA 851 instrument was used for the thermogravimetric analysis (TGA). Morphology of functionalized polystyrene and complex was analysed using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility.

Synthesis of polymer anchored ligand PS-teta

Ligand was readily prepared in two steps. Firstly, chloromethylated polystyrene (PS–CH₂Cl) was converted into PS–CHO according to literature [37]. Triethylenetetramine (teta) was reacted with PS–CHO (in 1:2 M ratio) in methanol solvent at refluxing condition for 24 h to prepare the yellow Schiff base compound. The mixture was cooled to room temperature and then filtered. The residue was washed with ethanol and dried under vacuum (Yield = 60%).

Loading of metal ions on to the polymer anchored ligand PS-teta

The loading of metal ions on the polymeric support was carried out as follows: the polymer anchored ligand (1.00 g) was stirred for 24 h with 0.100 g of VO(acac)₂ in 20 mL of methanol under refluxing condition. At the end of this reaction the metal loaded polymer was



Scheme 1. Preparation of polymer anchored VO(IV) complex.

Table 1A

Chemical composition of polymer anchored ligand and oxovanadium complex.

Compound	Colour	C%	H%	Cl %	N%	Metal%
PS-teta	Yellowish	77.76	6.52	3.37	7.20	–
PS-teta–VO	Greenish	70.60	5.96	3.30	6.56	4.72

filtered, washed thoroughly with ethanol, dioxane and methanol to ensure the removal of any unreacted metal ions and dried in vacuum for 6 h at 90 °C (Yield = 80%).

General procedure for aerobic oxidation reaction catalysed by PS-teta–VO

The aerobic oxidation reactions were carried out in a 50 mL stainless steel autoclave at different temperatures under vigorous stirring for a certain period of time. We examined the catalytic activity of vanadium complex using alcohol as the substrate and molecular oxygen as the primary oxidant. The oxidation of alcohol (5 mmol) was conducted under oxygen pressure (5.0 bar) at 60 °C for 5 h in the presence of vanadium complex (5 mg) in water (5 mL). After the reaction, the organic products were separated from the reaction mixture by extraction with dichloromethane (5 mL × 2). The combined organic portions were dried and concentrated. Product analysis was performed by Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column.

General procedure for oxidative bromination reaction of organic substrates catalysed by PS-teta–VO

In a typical reaction, aqueous 30% H₂O₂ (20 mmol) was added to the mixture of substrates (10 mmol) and KBr (20 mmol) taken in 10 mL of water. Catalyst (50 mg) and HClO₄ (5 mmol) were added to it and the reaction mixture was stirred at room temperature. An additional 15 mmol HClO₄ was added to the reaction mixture in three equal portions at 30 min intervals under continuous stirring. After specified time of the reaction, the catalyst was filtered and the solid was washed with ether. The combined filtrates were washed with saturated sodium bicarbonate solution and then shaken with ether in a separating funnel. The organic extract was dried over anhydrous sodium sulphate. The products were analysed by Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a Flame Ionization Detector.

Results and discussion

Characterization of polymer anchored oxovanadium complex

The reaction of aldehyde functionalised polystyrene and triethylenetetramine (teta) in methanol leads to the formation of polymer anchored Schiff base ligand. During this process CHO group of the polymer reacts with amine group of the triethylenetetramine (teta) moiety as shown in Scheme 1. The polymer anchored Schiff base ligand, on reaction with VO(acac)₂, gave an oxovanadium(IV) complex which we designate as PS-teta–VO. The physicochemical data of the polymer anchored ligand and polymer

Table 1B

Chemical composition of polymer supported oxovanadium complex.

Compound	Ligand loading (mmol equiv. g ⁻¹ of resin)	Metal ion loading (mmol equiv. g ⁻¹ of resin)	Ligand:metal
PS-teta–VO	1.17	0.93.	1.26:1

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