



Catecholase activity of a manganese Schiff base complex functionalized over SBA-15 in aqueous heterogeneous medium



Luna Paul ^a, Biplab Banerjee ^b, Asim Bhaumik ^{b, **}, Mahammad Ali ^{a, *}

^a Department of Chemistry, Jadavpur University, Kolkata 700 032, India

^b Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

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ABSTRACT

A novel manganese(III)-Schiff base complex anchored SBA-15 based heterogeneous catalyst SBA-15-SB-Mn was synthesized and characterized by various physicochemical techniques. The catalyst was found to exhibit excellent green catalysis for the aerial oxidation of 3,5-di-*tert*-butyl catechol (3,5-DTBC) to the corresponding 3,5-di-*tert*-butylcatechol-1,2-benzoquinone (3,5-DTBQ) with 83.17% conversion (TON = 515) within 1 h at room temperature and relevant to catechol oxidase behavior.

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1. Introduction

The oxidation of alcohols is traditionally performed in organic solvents. However, after the observation of hydrophobic effect of water on the acceleration of the Diels-Alder reaction [1–3] and benzoin condensation [4] the use of aqueous organic or purely aqueous solutions has become a field of intense study [5–7]. This leads to extensive kinetic measurements on the higher reaction rates for the Diels–Alder reaction and other types of organic reactions in water which have enriched our knowledge about the hydrophobic effect in organic reactions [5,8]. However, transition metal catalyzed reactions in water remain widely unexplored due to the facts that the nucleophilic attack by water [9] leads to the decomposition of the catalyst and also water-sensitivity of reagents and intermediates.

Catechol oxidase (CO), a member of the type-III copper proteins [10] catalyzes exclusively the oxidation of catechols to the corresponding quinones. Although CO is a copper containing protein and many dicopper complexes are found to act as successful models for

such metalloenzymes; there are only few reports on manganese [11–22] complexes with CO activities as well. Mn containing biomolecules like superoxide dismutase [23] and manganese dioxygenase [24] are found to contain manganese as mononuclear centers. Dinuclear species are present in catalases [25–31], ribonucleotide reductase [32], arginase [33] etc. while tetranuclear species are present in oxygen evolving complexes, PS-II [34]. Synthetic chemists and biochemists worked extensively on the structural and functional models of these manganese containing enzymes which have added a wealth of knowledge to our understanding of various aspects of manganese cluster chemistry with respect to structural, electrochemical and magnetic properties. Though a fair number of dinuclear copper complexes with a Schiff base and compartmental ligand backbone have been prepared as functional mimics for catechol oxidase [35–43] or as new biomimetic catalysts for oxidation reactions in homogeneous conditions, there is no single report on Mn(III) analogue as a heterogeneous catalyst, effective in catalytic oxidation of 3,5-di-*tert*-butyl catechol in environmentally benign purely aqueous medium. Some chiral salen based Mn(III) complex heterogenized on silica matrix exhibited a relatively high enantioselectivity for epoxidation reaction [44] and asymmetric borohydride reduction of ketones [45]. Salvadori and coworkers have reported their pioneer work by synthesizing silica gel supported first example of Mn(III)-salen complex which showed asymmetric epoxidation of

* Corresponding author.

** Corresponding author.

E-mail addresses: msab@iacs.res.in (A. Bhaumik), m_ali2062@yahoo.com (M. Ali).

olefins [46]. Resins, organic gels, and fibres are the polymeric organic materials which act as the conventional support for the immobilization of enzymes. But they create problem in disposal and show low reusability. On the other hand, inorganic supports such as porous silica gels are environmentally more acceptable, structurally more stable, and also chemically more resistant to organic solvents and microbial attacks over the organic supports [47–49]. Mesoporous materials due to their controllable pore dimensions (20–500 Å), large specific surface area (~1000 m²/g), and highly ordered pore structure are a very suitable support for immobilization of the enzymes. Among them, SBA-15, supersedes other mesoporous materials such as M41S family because of its much larger pore size (up to 30 nm) and better stability. The larger pores enable immobilization of larger biomolecules, which is not possible in small pores [50–52]. By the incorporation of organic ligand in the pores of the silica wall an Organic–inorganic hybrid is formed which make the materials hydrothermally stable and hydrophobic and higher catalytic efficient during applications for organic process. These kinds of applications of these materials in reaction condition provides a synergistic means of an efficient approach of the reactants to metal sites, and suitable mesochannels to drive out the products for next recycles [53]. Recently Rostamnia et al. have reported a number of Pd based mesoporous SBA-15 materials which showed fantastic catalytic activity in water medium and mild condition such as Mizoroki–Heck cross-coupling reaction [54,55], Suzuki–Miyaura cross-coupling reaction under aqueous conditions [56]. Moreover they added a Cu based heterogeneous material for mild aqueous conversion of aldehydes into primary amides [57]. Herein we report the synthesis of a new Schiff base H₃L (N,N'-bis(3-methoxysalicylaldehyde)-1,3-propylene-2-ol) functionalized mesoporous SBA-15 catalyst grafted with Mn(III) and its catalytic activities towards the oxidation of 3,5-di-*tert*-butyl catechol (3,5-DTBC) in purely aqueous medium. Though there are few manganese (II/III) complexes exhibiting CO activities, all of them are operative in organic solvents under homogeneous conditions.

2. Experiment

2.1. Materials

Tetraethylorthosilicate (TEOS), poly(ethylene oxide), poly(propylene oxide), poly(ethylene oxide), pluronic P123 [EO₂₀-PO₇₀-EO₂₀], 3-chloropropyl triethoxysilane, *o*-vaniline, 2-hydroxy-1,3-diamino propane and all other reagents were obtained from commercial sources (Merck or Sigma-Aldrich) and were used as received without further purification.

2.2. Sample preparation

2.2.1. Synthesis of SBA-15

SBA-15 material was synthesized according to the procedure described below by using pluronic123 triblock copolymer (EO₂₀-PO₇₀-EO₂₀; Aldrich) as template. In this typical preparation, 4.0 g of pluronic P123 was dissolved in 30 g of water and 120 g (3.28 mol) of 2 M HCl solution with stirring at 35 °C. Then 8.50 g (40.8 mmol) of tetraethylorthosilicate (TEOS; Aldrich) was added to the solution and stirred at 35 °C for 20 h. The mixture was aged at 80 °C for 24 h under static condition. The solid product was recovered, washed by distilled water repeatedly to free from acid by centrifugation and air dried at room temperature overnight, followed by calcination at 550 °C for 6 h with air to remove the residual organic template materials, yielding the mesoporous SBA-15 material.

2.2.2. Organofunctionalization of SBA-15 (SBA-15-Cl)

Chloro grafted SBA-15 silica support was prepared following the literature method [58]. A suspension of 3-Chloropropyltriethoxysilane (11.05 g, 50 mmol) and 1 g of calcined SBA-15 in 50 mL of dry toluene was heated to reflux at 80 °C with stirring under inert atmosphere for 24 h. The suspension was cooled to 25–30 °C and filtered. The solid was filtered and washed successively with ethyl alcohol and then diethyl ether, finally dried under vacuum at 70 °C for 8 h. A white powder was recovered SBA-15-Cl. IR (KBr, cm⁻¹): 3437 (m, O–H), 1062 (w, Si–O), 810 (s), 460 (s).

2.2.3. Synthesis of ligand (N,N'-bis(3-methoxysalicylaldehyde)-1,3-propylene-2-ol) (H₃L)

H₃L Schiff base ligand was prepared as per reported method [59]. The Schiff base ligand was obtained by condensation of 2-hydroxy-1,3-diaminopropane (0.9 g, 10 mmol) and *o*-vanillin (3.04 g, 20 mmol) in ethanol with stirring at 60 °C for 4 h, during which time a yellow solid separated out from the reaction mixture. The analytically pure solid was dried, and stored in a desiccator under vacuum over anhydrous CaCl₂ for subsequent uses. Anal. Calc. for C₁₉H₂₂O₅N₂: C, 63.67; H, 6.1; N, 7.81. Found: C, 63.94; H, 6.73; N, 7.90%. ¹H NMR (300 MHz, CDCl₃): 3.75 (d, *J* = 3.5 Hz, 4H, methylene), 3.85 (s, 6H, methyl), 4.24 (s, 1H, aliphatic –OH), 6.88 (d, *J* = 7.5 Hz, 2H, H₄), 6.78–6.92 (m, 6H, aromatic), 8.38 (s, 2H, azo-methine), 13.5 (s, 2H, phenoxo –OH).

2.2.4. Synthesis of Schiff base functionalized mesoporous SBA-15 (SBA-15-SB)

An ethanolic solution of ligand H₃L (0.06 g, 5 mL) was added drop wise into the 0.2 g chloro functionalized SBA-15 material dispersed in dry toluene (15 mL) under continuous stirring condition. After the complete addition the reaction mixture was refluxed for about 3 h at 60 °C. The color of the reaction mixture was changed into deep yellow and no further color change occurred on further reflux. The reaction mixture was cooled at room temperature and the final yellow product was collected by filtration, washed repeatedly with hot methanol to remove the unreacted ligand. The yellow material, SBA-15-SB, was obtained and dried in air.

2.2.5. Synthesis of Mn(III) anchored mesoporous SBA-15 catalyst (SBA-15-SB-Mn)

0.15 g of dried Schiff base anchored mesoporous SBA-15 was suspended in absolute ethanol (20 mL) solution of manganese(II) chloride (0.5 g) and was stirred for 30 min. Then 0.97 g sodium azide was added to the solution and the total mixture was kept under refluxing condition for about 4 h at 90 °C. The color of the mesoporous material was slowly changed from greenish to dark brown and no further color change occurred on further reflux. The reaction mixture was cooled at room temperature and the resulting deep brown mesoporous material was filtered through suction with thoroughly washing with ethanol. After washing it was dried under vacuum. The dark brown mesoporous material was designated as **SBA-15-SB-Mn**. The outline for the preparation of this Mn(III) anchored SBA-15 catalyst is shown in [Scheme 1](#).

2.3. Characterization techniques

Powder X-ray diffraction (XRD) patterns of different samples were taken in a Bruker D8 advance X-ray diffractometer using Ni filtered CuK α (λ = 0.15406 nm) radiation. UV–visible diffuse reflectance spectra (DRS) for the immobilized catalysts were recorded on a Shimadzu 2401 PC UV–visible spectrophotometer with an integrating sphere attachment using BaSO₄ as the background standard. Nitrogen adsorption-desorption isotherms were

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