

Comparative catalytic activity of Mn(Salen) complexes grafted on SBA-15 functionalized with amine, thiol and sulfonic acid groups for selective aerial oxidation of limonene

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Abstract

SBA-15 molecular sieves were functionalized with propylamine, propylthiol and propylsulfonic acid groups. Mn(Salen)Cl complexes were grafted on these organo-functionalized SBA-15. The support and the type of organo-functional group influenced the electronic structure (oxidation state and redox behavior) and chemoselectivity of the Mn-complexes in the oxidation of limonene. The Mn ions were reduced from +3 to +2, the extent of this reduction on different supports decreasing in the order: SBA-15-*pr*-SH > SBA-15-*pr*-SO₃H > SBA-15-*pr*-NH₂. Mn(Salen)Cl supported on propylthiol-functionalized SBA-15 yielded the 1,2-limonene epoxide with 100% chemo- and regioselectivity. Higher electron density at the site of Mn ions and the consequent lower redox potential of the Mn-complexes on immobilization are the probable causes for their efficient and selective catalytic activity. Solvents, additives (*N*-MeIm) and co-reagents (*iso*-butyraldehyde), which facilitated formation of Mn²⁺ ions, enhance the catalytic activity. A part of the Mn complexes was leached out of the solid phase during the reaction and the extent of this with different catalysts decreased in the order: SBA-15-*pr*-NH₂-Mn(Salen)Cl > SBA-15-*pr*-SO₃H-Mn(Salen)Cl > SBA-15-*pr*-SH-Mn(Salen)Cl.

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1. Introduction

Design of solid oxidation catalysts that are highly active and chemoselective at mild reaction conditions utilizing molecular oxygen instead of peroxides is a challenging area in heterogeneous catalysis research [1]. Limonene epoxide is a key raw material in the synthesis of pharmaceuticals, fragrances, perfumes and food additives [2]. Conventional manufacturing processes utilizing stoichiometric amounts of peroxides are not eco-friendly. There have been several reports on the use of solid catalysts for this reaction [3–14]. Most of these utilize expensive oxidants such as

alkyl hydroperoxides or H₂O₂. Moreover, allylic oxidation (yielding carveol and carvone) predominated olefinic oxidation (yielding epoxides) with these solid catalysts. Manganese complexes are known to be efficient in the Mukaiyama-type of epoxidation of terpenes at mild conditions in the presence of molecular oxygen (oxidant), *iso*-butyraldehyde (co-reagent) and N-containing bases (additive) [15]. Schuster and Hölderich [9] used Mn and Co complexes of (*R,R*)-(*N,N'*)-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diphenylethylene-1,2-diamine encapsulated in faujasites for this reaction (epoxide selectivity \cong 50% and diastereomeric excess (de) = 36%). Bhattacharjee et al. [13] reported the use of chiral sulfonato-salen-Mn(III) complexes entrapped in layered double hydroxide hosts. Recently, we had reported [16] that Mn(Salen)Cl complexes, immobilized on sulfonic acid-functionalized, mesoporous SBA-15 molecular sieves exhibit catalytic activity

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superior to those encapsulated in zeolite-Y. We had found a change in the oxidation state of Mn from +3 in the “neat” complex to +2 when immobilized on the sulfonated surface. This change was proposed [16] as the possible cause for the enhanced catalytic activity. In continuation of our earlier work [16], we, now, report the chemoselective oxidation of *R*(+)-limonene over immobilized Mn(Salen)Cl complexes. The surface of SBA-15 was systematically modified with organo-functional groups (propylamine, propylthiol and propylsulfonic acid) having varying acid-base properties. A relationship between catalytic activity and the redox characteristics of the immobilized Mn-complexes is proposed.

2. Experimental

2.1. Materials preparation

SBA-15 was prepared [17] using tetraethyl orthosilicate (TEOS, Aldrich Co.) as the silica source, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, EO₂₀PO₇₀EO₂₀, average molecular weight = 5800, Aldrich Co.) as the template and HCl as the pH controlling agent. “Neat” Mn(Salen)Cl, where salen = N,N'-ethylenebis(salicylidenaminato) was also prepared as per the known procedures [18]. 3-Amino-propyltrimethoxysilane (APTMS) and 3-mercaptopropyl-trimethoxysilane (MPTMS; Aldrich Co.) were procured from Aldrich Co. All the solvents and chemicals were of A.R. grade and purchased from Merck India Ltd.

2.1.1. Preparation of organo-functionalized SBA-15 materials

2.1.1.1. SBA-15-*pr*-NH₂. Amine-functionalization was accomplished by condensation of APTMS with the surface silanol groups of SBA-15 [19]. In a typical synthesis, 4 g of calcined SBA-15 was first activated under vacuum at 423 K for 4 h. It was then dispersed in 100 ml of dry-toluene taken in a double-necked round-bottom flask (250 ml) fitted with a water-cooled condenser. To it, 4.13 g of APTMS was added slowly over 10 min. The contents of the flask were refluxed for 24 h in nitrogen. The solid was filtered off, dried and Soxhlet extracted, initially with toluene (overnight) and, then, with dichloromethane (for 6 h). The amine-functionalized SBA-15 (hereafter referred to as SBA-15-*pr*-NH₂), thus obtained, was dried at 353 K for 6 h and used in further preparations.

2.1.1.2. Preparation of SBA-15-*pr*-SH. Thiol-functionalized SBA-15 (SBA-15-*pr*-SH) was prepared [16,19] by reacting MPTMS with a pre-formed SBA-15. Thiol loading in these materials (estimated by sulfur analysis) was 1.5 mmol/g.

2.1.1.3. Preparation of SBA-15-*pr*-SO₃H. Sulfonic acid-functionalized SBA-15 (hereafter referred to as SBA-15-*pr*-SO₃H) was prepared [16,20] from SBA-15-*pr*-SH and 30% aqueous H₂O₂. Sulfonation was accomplished by oxi-

dizing the thiol-groups with H₂O₂. Ion exchange capacity of this solid was estimated to be 0.725 meq./g silica.

2.1.2. Preparation of immobilized Mn(Salen)Cl complexes

The organo-functionalized SBA-15 materials (SBA-15-*pr*-NH₂, SBA-15-*pr*-SH and SBA-15-*pr*-SO₃H; 3 g) were first activated at 353 K, under vacuum, for 2 h and then dispersed in 50 ml of dry-toluene. “Neat” Mn(Salen)Cl (0.45 g) was added and the contents of the flask were refluxed, under nitrogen atmosphere, for 24 h. The solid was filtered, dried at 333 K and Soxhlet-extracted, initially with toluene for 12 h and then, with dichloromethane for another 12 h. The light brown solid Mn catalyst materials (SBA-15-*pr*-NH₂-Mn(Salen)Cl, SBA-15-*pr*-SH-Mn(Salen)Cl and SBA-15-*pr*-SO₃H-Mn(Salen)Cl, respectively), thus prepared, were dried (353 K, 12 h) and used further in characterization and catalytic activity studies.

2.2. Characterization techniques

The catalysts were characterized as described earlier [16] using atomic absorption spectroscopy (AAS), elemental analyses (C, H, N and S; Carlo-Erba 1106 analyzer), X-ray diffraction (Philips-X'Pert Pro; Cu K α radiation), transmission electron microscopy (TEM; JEOL-model 1200 EX), surface area analysis (BET; NOVA 1200 Quanta Chrome instrument), thermal analysis (Seiko DTA-TG 320), FT-IR spectroscopy (Shimadzu 8201 PC) and diffuse-reflectance UV-visible spectroscopy (DRUV-visible; Shimadzu UV-2500 PC) techniques. Electron paramagnetic resonance (EPR) spectra were recorded with a Bruker EMX spectrometer operating at X-band ($\nu = 9.42$ GHz) frequency and a 100 kHz field-modulation. The spectra were recorded at 80 K using a Bruker BVTB 3500 variable temperature controller. The magnetic field was calibrated with a Bruker ER 035 M NMR gaussmeter and the microwave-frequency was calibrated with a frequency counter fitted in a Bruker ER 041 XG-D microwave bridge unit.

Electrochemical studies were performed at 298 K using a three-electrode system (Solatron SI-1287 electrochemical interface). The immobilized Mn complex (60 wt.%) and graphite powder were mixed with 0.1 ml of Teflon powder. The slurry was then pasted onto a Pt disc (1.5 mm diameter) and dried under an infrared (IR) lamp. This modified Pt disc was used as the working electrode. Pt foil was used as a counter electrode and a Pt wire was used as the reference electrode. All these three-electrodes were placed in a glass compartment containing DMF. LiClO₄ (0.1 M) was used as a supporting electrolyte. Prior to cyclic voltammetric experiments (scan speed = 25 mV/s), the electrolytic solutions were deoxygenated by purging with argon gas.

2.3. Reaction procedure

In a typical reaction, 0.1 g of immobilized Mn(Salen)Cl, 3.75 mmol of *R*(+)-limonene, 9 mmol of iso-butyralde-

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