The catalytic function of a silica gel-immobilized Mn(II)-hydrazide complex for alkene epoxidation with H$_2$O$_2$

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ABSTRACT

An efficient and highly selective heterogeneous catalyst was developed by immobilization of a manganese complex on an inorganic support to yield (silica gel)–O$_2$(EtO)Si–L^1–Mn(HL^2) [(L^1)$^-$= modified salicylaldiminato and H$_2$L^2=(E)-N′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide]. Mn(II) has been anchored on the surface of functionalized silica by means of N,O-coordination to the covalently Si–O bound modified salicylaldiminato Schiff base ligand. The prepared material (silica gel)–O$_2$(EtO)Si–L^1–Mn(HL^2), was characterized by elemental and thermogravimetric analyses (TGA and DTA), UV–vis and FT-IR spectroscopy. This new material is demonstrated to be a very active catalyst in clean epoxidation reactions using a combined oxidant of aqueous hydrogen peroxide and actonitrile in the presence of aqueous sodium hydrogencarbonate. The effects of reaction parameters such as solvent, NaHCO$_3$ and oxidant in the epoxidation of cis-cyclooctene were investigated. Cycloalkenes were oxidized efficiently to their corresponding epoxide with 87–100% selectivity in the presence of this catalyst. This catalytic system showed also good activities in the epoxidation of linear alkenes. The obtained results show that this catalyst is a robust and stable heterogeneous catalyst which can be recovered quantitatively by simple filtration and reused multiple times without loss of its activity.

1. Introduction

Epoxidation reactions with hydrogen peroxide, one of the 'greenest' terminal oxidants, are of great interest due to the importance of epoxides in the manufacture of both bulk and fine chemicals [1]. Epoxidation reactions that use hydrogen peroxide in conjunction with cheap, manageable and relatively non-toxic metal-based catalysts are potentially viable for large-scale production. However, good epoxidation catalysts must activate H$_2$O$_2$ without radical formation. Metal-catalyzed epoxidation of alkenes with hydrogen peroxide has been reviewed [2]. In agreement with the ever increasing environmental awareness, new oxidative processes based on the activation of H$_2$O$_2$ by robust, efficient and recyclable heterogeneous catalysts were developed [3,4]. Heterogeneous catalysts for epoxidations are attracting a lot of attention and are actively investigated because of advantages such as easy handling and product separation, catalyst recovery and less waste [5]. Among the various transition metals for heterogeneous catalytic epoxidation, manganese stands out as the most efficient, economical and environmental benign one. Various manganese complexes immobilized on an inorganic matrix are known to be efficient and applicable as catalysts for the epoxidation of a wide range of alkenes [6]. Manganese porphyrin complexes have been extensively investigated as models for enzymes and used in catalysis with various single oxygen atom donors including H$_2$O$_2$ [7]. Alkene epoxidation reactions catalyzed by manganese complexes in homogeneous and heterogeneous media and the mechanism involved in these reactions are well established [8,9]. The mechanism of alkene epoxidation by manganese-based catalysts in the presence of bicarbonate was studied theoretically [10]. However, the development of efficient manganese systems that incorporate H$_2$O$_2$ has limitations due to competitive H$_2$O$_2$ dismutation by both the Mn center (catalase-type activity) and the inorganic support. These limitations can explain why only a few systems, based on supported manganese catalysts and H$_2$O$_2$, have been reported for alkene epoxidation [11,12]. Castaman et al. employed a binuclear carboxylated bridged manganese complex immobilized on silica for epoxidation of alkenes [13]. This catalyst was able to epoxidize cyclohexene and cyclooctene with iodosylbenzene. With H$_2$O$_2$ and tert-butylhydroperoxide as oxidant in homogeneous and heterogeneous media, products were obtained in lower yields. Imidazole-based acetamide/Mn(II) systems [14,15] and acetylacetone-based Schiff base/Mn(II) systems [16] have also been reported as homogeneous and heterogeneous catalysts for alkene epoxidation with H$_2$O$_2$.

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Mn(III) Schiff base complexes have been heterogenized by their covalent binding to organic polymers, encapsulation, entrapment, adsorption and covalent attachment to porous inorganic supports, such as zeolites, MCM-41 and clays [17,18]. Preparation of heterogeneous catalysts, by covalent immobilization of transition-metal complexes on silica surface represents one of the most usable approaches [19]. Many heterogeneous catalysts contain metal ions and chemically modified silica gels with active organic components [20]. Modified silica exhibits some advantages over modified resins such as high surface area, high thermal and chemical stability. Since the early 1990s and the advent of mesoporous silicas, the development of new solid catalysts and the heterogenation of homogeneous systems for oxidation processes have become very attractive topics. A major drawback of transition-metal catalysts coordinated to monodentate ligands is that they usually undergo leaching of the active species into solution, especially in the presence of protic agents such as alcohols or organic peroxides [21]. A simple way to minimize the leaching of the active ingredient is to anchor polydentate ligands onto the support surface, as this type of chelating system offers high coordinative stability for the catalytic ingredient.

Against this background, we investigate here the anchoring of a manganese(II) hydrazide Schiff base moiety onto a silica substrate functionalized with a polydentate salicylaldiminato ligand. The product of salicylaldehyde and benzhydrazide condensation has some similarities to non-symmetrical salen-type ligands. These types of hydrazone Schiff base complexes show considerable catalytic activities. The efficiency of homogeneous hydrazone based catalysts in alkene epoxidations [22,23] led us to the design of their heterogeneous analogues using silica as a support. This article describes the efficient and highly selective epoxidation of alkenes with 30% aqueous H_2O_2 in the presence of silica–Mn(II)–hydrazide Schiff base as a reusable solid catalyst.

2. Experimental

2.1. Materials and equipments

Silica gel (0.063–0.200 mm) and all other reagents were obtained from commercial sources (Merck or Fluka) and were used as received without further purification. Aqueous 30% hydrogen peroxide (8.12 mol/L) was used and its exact concentration was determined before use by titration with standard $KMnO_4$. (E)-N′-(2-Hydroxy-3-methoxybenzylidene)benzohydrazide, H_2L^2, was synthesized according to a reported procedure [22]. ^{1}H NMR spectra were recorded by use of a Bruker 250 MHz, spectrometer. Elemental analyses were determined on a CHN Perkin-Elmer 2400 analyzer. IR spectra were recorded on a Perkin-Elmer 597 spectrometer. The solution and diffuse reflectance DR UV–Vis spectra in the range of 300–800 nm were measured on a CARY 5E spectrophotometer, with the spectra referenced to $BaSO_4$ (disk diameter 13 mm, thickness 2 mm). The manganese content of the final material was determined by ICP model ARL 3410, or alternatively, by a Varian spectrometer AAS-110. The reaction products of the oxidation were determined and analyzed by an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m × 320 μm × 0.25 μm) with flame-ionization detector and gas chromatograph–mass spectrometry (Hewlett-Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector).

2.2. Synthesis of N-(triethoxysilylpropyl)salicylaldimine [(EtO)₃Si–L¹H]

The linker was synthesized according to a reported procedure [24]. A solution of aminopropyltriethoxysilane (2.21 g, 10.0 mmol)

in methanol (10 mL) was added to a solution of salicylaldehyde (1.22 g, 10.0 mmol) in methanol (10 mL) and refluxed for 2 h. The colorless solution immediately turned yellow. The reaction was maintained in reflux for 2 h and then the solvent was removed under reduced pressure. The resulting viscous yellow oil was dissolved in dichloromethane and washed repeatedly with water. The organic layer was separated and dried over anhydrous magnesium sulfate followed by solvent evaporation and drying at room temperature for several hours. Yield 2.30 g, 71.0%. IR (KBr, cm^{-1}): 3449 (w) (O–H), 3065 (w), 2977 (vs), 2930 (s), 2894 (s), 2744 (w), 1634 (vs) (C=N), 1585 (m), 1498 (m), 1462 (m), 1391 (m), 1344 (w), 1281 (s), 1191 (w), 1167 (s), 1107 (vs), 1084 (vs), 959 (s), 899 (w), 871 (w), 795 (m), 758 (s), 641 (w), 568 (w), 526 (w), 465 (m). ^{1}H NMR (CDCl$_3$) δ = 0.604 (m, 2H, SiCH$_2$), 1.154 (t, ^3J = 7.0 Hz, 9H, SiOCH$_2$CH$_3$), 1.742 (m, 2H, NCH$_2$CH$_2$), 3.473 (t, ^3J = 6.75 Hz, NCH$_2$), 3.748 (q, ^3J = 7.0 Hz, 6H, SiOCH$_2$), 6.722–7.212 (m, 4H, Ar), 8.190 (s, 1H, N=CH), 13.418 (s, 1H, Ar–OH) ppm.

2.3. Functionalization of silica gel to (silica gel)–O₂(EtO)Si–L¹H (1)

The N-(triethoxysilylpropyl)salicylaldimine linker was anchored onto the silica surface via a grafting method. The procedure of synthesis was similar to the reported procedure with some modifications [25]. The amorphous silica gel was preliminary heated in an oven at 500 °C for 24 h to remove adsorbed water. A 5.0 g sample of the pretreated silica gel powder was suspended in 50 mL of dry toluene in a round bottomed flask (100 mL) which was flushed with N$_2$. (EtO)$_3$Si–L^{1}H (1.2 g, 3.7 mmol) was then added and the suspension stirred for 24 h under reflux at N$_2$ atmosphere. The resulting suspension was filtered and washed with Et$_2$O (3 × 15 mL). The recovered powder was extracted in a Soxhlet using refluxing CH$_3$OH (750 mL) for 24 h. The functionalized silica gel, designated as (silica gel)–O$_2$(EtO)Si–L^{1}H, was dried under vacuum at room temperature for 18 h. A yellow powder was recovered. IR (KBr, cm^{-1}): 3444 (m, br), 2935 (w), 2864 (w), 1647 (m), 1101 (vs, br), 813 (m), 473 (s).

2.4. Immobilization of the manganese complex to (silica gel)–O₂(EtO)Si–L¹–Mn(HL²) (2)

Mn(O$_2$CCH$_3$)$_2$·4H$_2$O (20 μmol, 0.005 g) and H$_2$L^2 (19 μmol, 0.005 g) were dissolved in 30 mL of dichloromethane. The functionalized silica gel (silica gel)–O$_2$(EtO)Si–L^{1}H (2.0 g) was then added to the solution and the mixture stirred under reflux for 24 h followed by Soxhlet extraction with CH$_3$OH for 24 h. The green material was dried under vacuum overnight, yielding 1.840 g. Most of the (silica gel)–O$_2$(EtO)Si–L^1–Mn(HL^2) was found lost in the Soxhlet extraction since the cleaning of the Soxhlet timble was difficult. CHN analyses showed the presence of both L^1 and L^2. In order to confirm that the Mn is indeed bound as L^1–Mn–L^2 and not (at least to some extent) as L^1–Mn–L^1 from two neighboring L^1-groups, the UV–vis spectra of the compounds (silica gel)–O$_2$(EtO)Si–L^{1}H (1) and (silica gel)–O$_2$(EtO)Si–L^1–Mn(HL^2) (2) were compared with its homogeneous analogues (not shown). IR (KBr, cm^{-1}): 3443 (br, w), 3217 (w), 3075 (w), 2935 (w), 2858 (w), 1617 (m), 1574 (m), 1442 (m), 1216 (s), 1085 (vbr, vs), 808 (s), 741 (w), 712 9 w), 740 (vs).

2.5. General procedure for the epoxidation of alkenes

The epoxidation of alkenes with hydrogen peroxide was performed in a 25-mL round-bottom flask. In a typical experiment, the flask was charged with 3.0 mL of CH$_3$CN, 1.0 mmol alkene, 1.0 mmol NaHCO$_3$, 0.1 g chlorobenzene as internal standard and