Available online at www.sciencedirect.com
ScienceDirect
Catalysis Communications 9 (2008) 35–39
CATALYSIS COMMUNICATIONS
www.elsevier.com/locate/catcom

Manganese(II) complexes of imidazole based-acetamide as homogeneous and heterogenised catalysts for alkene epoxidation with H_2O_2

Alexia Serafimidou, Aggelos Stamatis, Maria Louloudi *

Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece

Received 5 December 2006; received in revised form 30 April 2007; accepted 8 May 2007
Available online 17 May 2007

Abstract

An acetamide derivative which bears two terminal imidazole rings has been synthesized. This biomimetic ligand, *N*-[2-(1*H*-imidazol-4-yl)-ethyl]-2-({[2-(1*H*-imidazol-4-yl)-ethylcarbamoyl]-methyl}-amino)-acetamide, has been also grafted on silica surface via covalent bond. The supported and non-supported biomimetics reacted with manganese(II) ions leading to the formation of the corresponding metal complexes. These have been evaluated as catalysts for alkene epoxidation with H_2O_2 in the presence of ammonium acetate as an additive. Our data showed that the homogeneous and the supported systems are able to overcome the competitive H_2O_2 dismutation, by the use of only two times H_2O_2 with respect to substrate, favouring productive alkene epoxidations to a significant extent.

Keywords: Biomimetic catalytic epoxidation; Supported manganese complexes; H_2O_2 activation; Modified silica surface

1. Introduction

Inorganic materials with biomimetic organic components are particularly attractive because of the possibility to combine the functional variation of organic chemistry with the advantages of a thermal stable and robust inorganic substrate [1]. This is particularly applicable to heterogeneous catalysis since the organic moiety can serve as a supported ligand for transition metal complexes [2]. Fixation of the bio-inspired ligand with covalent attachment to a functionalized support generates stable heterogeneous catalysts without leaching defects [3,4].

In biology, non-heme manganese-enzymes intervene in a diverse series of oxidation–reduction reactions [5,6]. Among them, activation of H_2O_2 is well known [5,6]. The objective to construct convenient systems for efficient epoxidation using biomimetic manganese complexes with various synthetic ligands i.e., Schiff bases, 2,2′-bipyridine or cyclic triamines as catalysts by activating H_2O_2 is particularly interesting [7–14]. This presents an inexpensive, readily available and environmentally friendly oxidant which gives water as the only byproduct [15]. However, the use of manganese complexes as catalysts ought to avoid the unproductive decomposition of H_2O_2 to H_2O and O_2, which impedes the preferred alkene epoxidation. The heterogenised manganese catalysts have to overcome additional problems related to the possible decomposition of H_2O_2 by the inorganic support. Within this limits, few systems-based on supported manganese catalysts and H_2O_2 for alkene epoxidation have been reported so far [16–20]. Among them, very recently we have reported a system which bears two imidazole residues as biomimetic component and shows significant catalytic activity for epoxidations [20].

Based on these promising data, we present here a new tailored biomimetic ligand with two imidazole residues hanging on two flexible chains. This ligand has been synthesized both in solution and in solid state, while its reaction with manganese acetate provided non-supported and

* Corresponding author. Tel.: +30 26510 98418; fax: +30 26510 44831.
E-mail address: mlouloud@uoi.gr (M. Louloudi).

1566-7367/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2007.05.015

supported manganese complexes, respectively. These complexes have been evaluated as catalysts for alkene epoxidation in the presence of H_2O_2. The catalytic data are discussed and compared with previous results.

2. Experimental

All substrates were purchased from Aldrich in their highest commercial purity, stored at 5 °C and purified by passage through a column of basic alumina prior to use. H_2O_2 was 30% solution in water. Infrared spectra were recorded on a Spectrum GX Perkin–Elmer FT-IR System, UV–Vis spectra were recorded using a UV/VIS/NIR JASCO Spectrophotometer. NMR spectra were recorded with a Bruker AMX-400 MHz spectrometr with external TMS as reference. Continuous-wave (c.w.) EPR spectra were recorded at liquid helium temperatures with a Bruker ER 200D X-band spectrometer equipped with an Oxford Instruments cryostat. The microwave frequency and the magnetic field were measured with a microwave frequency counter HP 5350B and a Bruker ER035M NMR-gaussmeter, respectively. Diffuse reflectance UV–Vis spectra were recorded at room temperature on a Shimadzu UV-2401PC with a $BaSO_4$ coated integration sphere. Thermogravimetric analyses were carried out using Shimadzu DTG-60 analyser. GC analysis was performed using a 8000 Fisons chromatograph with a flame ionization detector and a Shimadzu GC-17A gas chromatograph coupled with a GCMS-QP5000 mass spectrometer.

2.1. Synthesis of the ligand N-[2-(1H-imidazol-4-yl)-ethyl]-2-({[2-(1H-imidazol-4-yl) -ethylcarbamoyl]-methyl}-amino)-acetamide (L) and its Mn(II) complex ($Mn_2(acet)_4(L)$)

Iminodiacetic acid (IMDA) (1 mmol) was added in a solution of $SOCl_2$ (20 ml) and the resulting mixture was refluxed under N_2 for 7 h. Evaporation of the reaction mixture until dryness led to a yellow solid. This solid was added to a stirred solution of dry MeOH (100 ml) containing 2 mmol of histamine dihydrochloride and the mixture was refluxed under N_2 for 48 h. After reducing the volume of the reaction solvent by evaporation, the ligand was precipitated and isolated as solid. The final product was obtained by recrystallization from methanol and ethanol, respectively. Anal. Calcd. for $C_{14}H_{21}N_7O_2 \cdot 2HCl$: C, 42.86.45; N, 25.00; H, 5.87. Found: C, 42.19; N, 24.80; H, 5.73. IR (KBr, cm^{-1}, selected peaks) 3400: ν(NH); 3102, 3018, 2888: ν(CH); 1625: ν(C=O) (amide I); 1523: ν(C–N) (amide II); 1473, 1437: CH and ring stretching modes (imidazole); 1234: δ(NH) (amide III); 618: (N–C=O) deformation (amide IV). ^{1}H NMR (D_2O, δ) 8.7 (s): (Im-*H*); 7.4 (s): (Im-*H*); 3.8 (s): C=O–C*H*$_2$–NH; 3.4 (t): C=O–NH–C*H*$_2$–CH$_2$-Im; 3.2 (t): C=O–NH–CH$_2$–C*H*$_2$-Im. ^{13}C NMR (D_2O, δ) 167.7: *C*O; 133.8: *C*=N (Im); 128.8: N–C=C (Im); 116.7: C=*C*–NH (Im); 46.5: C=O–*C*H$_2$–NH; 37.2: NH–*C*H$_2$–CH$_2$-Im; 22.2: NH–CH$_2$–*C*H$_2$-Im. UV (MeOH, λ_{max} (nm), ε (M^{-1} cm^{-1})) 213 (39 500).

$[Mn_2^{II}(CH_3COO)_4(L) \cdot 2H_2O]$(**1**). To a stirred solution of methanol (20 ml) containing the ligand (1.0 mmol) and triethylamine (2.0 mmol), a solution of $Mn(CH_3COO)_2 \cdot 4H_2O$ (2.0 mmol) in methanol (5 ml) was added. The resulting mixture was stirred for 24 h at room temperature and a solid light brown product was separated by slow evaporation of methanol. The complex thus obtained, $[Mn_2^{II}(CH_3COO)_4(L_A)]$, was washed with small amounts of cold EtOH and dried under reduced pressure at 40 °C. Anal. Calcd. for $Mn_2C_{22}H_{33}N_7O_{10} \cdot 2H_2O$ (%): C, 37.67; N, 13.98; H, 5.28; Mn, 15.67. Found: C, 37.58; N, 12.86; H, 5.20; Mn, 15.43. IR (KBr, cm^{-1}, selected peaks): 3293: ν(NH); 1579: ν_{sym}(COO^-); 1407: ν_{as}(COO^-); 603: (N–C=O) deformation (amide IV). UV (MeOH, λ_{max} (nm), ε (M^{-1} cm^{-1})) 219 (14 700).

2.2. Immobilization of the ligand on a silica support and the preparation of the supported $Mn_2(L) \cdot SiO_2$ complex

To a stirred solution of 60 ml toluene containing 1.0 mmol of iminodiacetic acid (IMDA), 1.0 mmol of (3-glycidyloxypropyl)-trimethoxysilane was added. The resulting mixture was allowed to react at 80 °C for 24 h. To this solution 3.0 g of SiO_2 and 5 ml of EtOH were added, and the slurred solution was maintained at 80 °C for 24 h. The functionalized silica, $[C_4H_6NO_4–CH_2CH(OH)CH_2O-(CH_2)_3–SiO_{3/2}]_n \cdot xSiO_2$, was isolated by filtration, washed with MeOH and EtOH and dried under reduced pressure at 100 °C for 8 h. DRIFTS-IR (cm^{-1}, selected peaks): 1735: ν(COOH); 1400: δ(CH).

$[C_4H_6NO_4–CH_2CH(OH)CH_2O(CH_2)_3–SiO_{3/2}]_n \cdot xSiO_2$ (3.0 g) was added in a solution of $SOCl_2$ (20 ml) and the slurred solution was refluxed under N_2 for 7 h. Then the reaction mixture was evaporated until dryness and the resulted solid was added to a stirred solution of dry MeOH (100 ml) containing 2 mmol of histamine dihydrochloride. The mixture was refluxed under N_2 for 20 h. The grafted silica $L \cdot SiO_2$ was isolated by filtration, washed with MeOH and dried at 80 °C for 24 h. It was further purified with MeOH using the soxhlet extraction method and dried under reduced pressure at 50 °C for 12 h. Anal. Found for $L \cdot SiO_2$: C, 3.12; N, 1.30. The loading achieved is ca. 0.13 mmol g^{-1}, as determined by elemental and thermogravimetric analysis which gave a 4.9% weight loss. DRIFTS-IR (cm^{-1}, selected peaks): 2956, 2854: ν(CH); 1630 (br): ν(C=O) (amide I); 1462, 1448, 1400: CH and ring stretching modes (imidazole). DRS (λ_{max} (nm)): 224.

$Mn_2^{II}(L) \cdot SiO_2$(**2**).The pH of a solution of $L_A \cdot SiO_2$ (0.15 g) in H_2O was adjusted to seven by addition of 0.1 N NaOH and then $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.05 g) was added. The mixture was stirred for 24 h at room temperature and the resulting light pink material, $Mn_2^{II}(L_A) \cdot SiO_2$, was filtered, washed thoroughly with MeOH, EtOH and Et_2O and dried at 80 °C for 2 h. The amount of Mn^{II} was determined by back-titration of the