

Alkene epoxidation by homogeneous and heterogenised manganese(II) catalysts with hydrogen peroxide

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Abstract

Three Schiff base ligands derived from three different 1,3-diones and diethylenetriamine have been synthesized and subsequently grafted on a silica surface via covalent bonds. The organic ligands as well as the heterogenised ligands reacted with manganese(II) ions leading to the formation of the corresponding metal complexes. Supported and non-supported manganese complexes have been evaluated as catalysts for alkene epoxidation with hydrogen peroxide in the presence of ammonium acetate as an additive. Both homogeneous and heterogeneous systems are able to activate hydrogen peroxide towards epoxide formation presenting remarkable catalytic properties. This catalytic ability of the immobilised manganese complexes is further highlighted, since they present efficient systems overcoming competitive H_2O_2 dismutation, in conjunction with advantages of the heterogeneous catalysts. In this context, they gave high yields for limonene epoxidation, significantly higher than the corresponding homogeneous catalysts.

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Keywords: Catalytic epoxidation; Supported manganese complexes; Hydrogen peroxide activation; Modified silica surface

1. Introduction

During the recent years, the catalysis-based chemical production runs into a satisfactory level, however, many of the intermediates in the oxidation processes are not prepared within the 'green concept' [1,2]. Thus, the development research of new 'clean' methods for the preparation of chemical compounds is increased [3].

Replacement of a homogeneous catalyst with an active heterogeneous one changes the synthetic process to a more desirable and clean one providing advantages such as easy handling and product separation, catalyst recovery and less level of waste [4]. A wide variety of heterogenised catalysts rely on metal complexes attached to the silica support by a covalent bond [5–8]. Many of them have been developed by metal ions and chemically modified silica gels with active organic components [9]. In this context, manganese complexes with Schiff bases immo-

bilized on an inorganic matrix can be potentially efficient and applicable as catalysts [10–13].

With respect to environmental and economic considerations, hydrogen peroxide is probably the best oxidant after dioxygen [14]. 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_2O_2 without radical formation. The key point for such clean activation seems to be the heterolytic cleavage of hydrogen peroxide O–O bond and, in the case of a manganese based-catalyst, the subsequent formation of a $\text{Mn}=\text{O}$ adduct which is responsible for an efficient oxygen transfer to the alkene substrate [14]. However, for the oxygen transfer process, the involvement of $\text{Mn}-\text{OOH}$ species was also suggested very recently [15]. When heterogenised catalysts used, the development of efficient systems has to overcome additional problems related to the possible inactivation of H_2O_2 by the inorganic support. These limitations can explain why only a few systems based on supported manganese catalysts and H_2O_2 have been reported for alkene epoxidation [16,17].

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Herein, we report on the synthesis and immobilization process on a silica surface of new Schiff base ligands derived from various 1,3-diones and diethylenetriamine. Supported and non-supported manganese complexes have been evaluated as catalysts for alkene epoxidation with hydrogen peroxide. Both homogeneous and heterogeneous systems are able to activate hydrogen peroxide towards epoxide formation presenting remarkable catalytic properties. Furthermore, the synthesis protocol for the ligands developed here is based on relatively easy steps. This allows relatively cheap catalysts to be produced, which may be a considerable advantage in using such catalysts.

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. Hydrogen peroxide was 30% aqueous solution. Infrared spectra were recorded on a Spectrum GX Perkin-Elmer FT-IR System and UV–vis spectra were recorded using a UV/VIS/NIR JASCO Spectrophotometer. X-band EPR measurements were performed with a Bruker ER-200D-SRC spectrometer interfaced to a personal computer and equipped with an Oxford ESR 900 cryostat, an Anritsu MF76A microwave frequency counter, and a Bruker 035 M NMR Gauss meter. A Bruker bimodal cavity was used to generate microwave fields parallel and perpendicular to the static field. ESI-MS spectra were obtained from a Finnigan MAT system equipped with an ion trap detector and solution NMR spectra were recorded with a Bruker AMX-400 MHz spectrometer with external TMS as reference. Diffuse reflectance UV–vis spectra were recorded at room temperature on a Shimadzu UV-2401PC with a BaSO₄ 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 4-{2-[2-(1,1,1,5,5,5-hexafluoro-4-oxo-pentylideneamino)-ethylamino]-ethylimino}-1,1,1,5,5,5-hexafluoro-pentan-2-one (*L_a*) and its Mn(II) complex [*Mn₂(L_a)*]

In a solution of acetonitrile (6 ml) containing 1,1,1,5,5,5-hexafluoro-pentan-2,4-dione (4 mmol), 2 mmol of diethylenetriamine were added slowly. The resulting mixture was stirred at room temperature for 48 h. After evaporating the solvent, the oil product was solidified by treatment with petroleum ether. The final product was recrystallized from chloroform. m.p. 131–133 °C. Anal. calcd. for C₁₄H₁₃F₁₂N₃O₂·H₂O (%): C, 33.53; N, 8.38; H, 3.00. Found: C, 33.88; N, 8.55; H, 3.31. IR (KBr, cm⁻¹, selected peaks) 3150: ν(NH); 3054, 2935: ν(CH₂); 1665: ν(C=O); 1611: ν(C=N); 1524: δ(NH); 1261, 1208: ν(CF₃). ¹H NMR (CD₃OD, δ) 5.16 (s): C=O–CH₂–CN; 3.03 (m): CN–CH₂–CH₂; 2.88 (m): CN–CH₂–CH₂. ¹³C NMR ((CD₃)₂SO, δ) 176.1 (q, ²J_{C-F} = 33.7 Hz): CO; 176.1 (q, ²J_{C-F} = 33.7 Hz): CN; 119.7 (q, ¹J_{C-F} = 317.5 Hz): CF₃; 86.6: C=O–CH₂–CN; 46.8: CN–CH₂–CH₂; 40.4: CN–CH₂–CH₂.

UV (MeOH, λ_{max} (nm), ε (M⁻¹ cm⁻¹)) 304 (70 000). ESI-MS (*m/z*) 484 ([MH]⁺); 506 ([M + Na]⁺).

To a stirred solution of acetonitrile (10 ml) containing the ligand *L_a* (0.53 g, 1.10 mmol), a solution of MnCl₂·4H₂O (0.30 g, 2.20 mmol) in 10 ml of MeOH was added. The resulting mixture was stirred for 24 h at room temperature. Then the reaction solvents were concentrated under vacuum to about half volume, and the yellow solid product was collected by filtration. The metal complex, Mn₂*L_a* dried under reduced pressure at 50 °C. m.p. 215–218 °C (decomposition). Anal. calcd. for Mn₂Cl₄C₁₄H₁₃F₁₂N₃O₂·4H₂O (%): C, 20.79; N, 5.32; H, 2.60; Mn, 13.61. Found: C, 20.45; N, 5.35; H, 2.82; Mn, 13.25. The water loss determined by thermogravimetric analysis was found to be 8.8% (calcd. 8.9%). IR (KBr, cm⁻¹, selected peaks) 3424: ν(OH) (water molecule); 2993: ν(NH); 2953, 2893: ν(CH₂); 1646: ν(C=O); 1605: ν(C=N); 1534: δ(NH); 1260, 1216: ν(CF₃); 443: ν(Mn–O). UV (MeOH, λ_{max} (nm), ε (M⁻¹ cm⁻¹)) 309 (30 000).

2.2. Immobilization of (*L_a*) on a silica support and the preparation of the Mn(II) material, [*Mn₂(L_a)·SiO₂*]

To a stirred solution of 50 ml toluene containing 1.0 mmol of *L_a*, 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 1.5 g of SiO₂ and 5 ml of EtOH were added, and the slurred solution maintained at 80 °C for 24 h. The functionalized silica, *L_a*·SiO₂, was isolated by filtration and washed with MeOH and EtOH. It was further purified with EtOH using the soxhlet extraction method and dried under reduced pressure at 80 °C for 12 h. The loading achieved is ca. 0.2 mmol g⁻¹ determined by thermogravimetric and elemental analysis. DRIFTS-IR (cm⁻¹, selected peaks): 2986, 2940: ν(CH₂); 1683: ν(C=O); 1634: ν(C=N); 1455: δ(C–H); 1395: ν(C–O); 1285: ν(CF₃). DRS (λ_{max} (nm)): 323.

To a suspension of *L_a*·SiO₂ (0.25 g) in MeOH, MnCl₂·4H₂O (6.53 mg, 0.033 mmol) was added. The mixture was stirred for 24 h at room temperature and the resulting material, Mn₂(*L_a*)·SiO₂, was filtered, washed with H₂O, MeOH, EtOH and Et₂O and dried at 80 °C for 12 h. The amount of manganese was determined by back-titration of the remaining amount of metal ion into the solution. DRIFTS-IR (cm⁻¹, selected peaks): 2986, 2884: ν(CH₂); 1702: ν(C=O); 1635: ν(C=N); 1394: ν(C–O); 1273: ν(CF₃). DRS (λ_{max} (nm)): 233; 345.

2.3. Synthesis of the ligand 4-{2-[2-(5,5,5-trifluoro-4-oxo-pentylideneamino)-ethylamino]-ethylimino}-1,1,1-trifluoro-pentan-2-one (*L_b*) and its Mn(II) complex [*Mn₂(L_b)*]

In a solution of CH₃CN (6 ml) containing 1,1,1-trifluoro-pentan-2,4-dione (4 mmol), 2 mmol of diethylenetriamine were added slowly. The resulting mixture was stirred at room temperature for 24 h. After evaporating the solvent, the oil product was solidified by treatment with petroleum ether. The final pale yellow product was recrystallized from a chloroform-ether mixture. m.p. 55–57 °C. Anal. calcd. for C₁₄H₁₉F₆N₃O₂

(%): C, 44.76; N, 11.20; H, 5.10. Found: C, 44.55; N, 11.30; H, 4.83. IR (KBr, cm^{-1} , selected peaks) 3059, 2951, 2824: $\nu(\text{CH}_2)$; 1651: $\nu(\text{C}=\text{O})$; 1615: $\nu(\text{C}=\text{N})$; 1534: $\delta(\text{NH})$; 1259, 1200: $\nu(\text{CF}_3)$. ^1H NMR (CD_3OD , δ) 5.24 (s): $\text{C}=\text{O}-\text{CH}_2-\text{CN}$; 3.44 (t): $\text{CN}-\text{CH}_2-\text{CH}_2$; 2.78 (t): $\text{CN}-\text{CH}_2-\text{CH}_2$. ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$, δ) 175.1 (q, $^2J_{\text{C-F}}=34.7\text{ Hz}$): CO ; 172.7: CN ; 119.3 (q, $^1J_{\text{C-F}}=315.4\text{ Hz}$): CF_3 ; 90.1: $\text{C}=\text{O}-\text{CH}_2-\text{CN}$; 48.4: $\text{CN}-\text{CH}_2-\text{CH}_2$; 44.2: $\text{CN}-\text{CH}_2-\text{CH}_2$; 19.0: $-\text{CH}_3$. UV (MeOH, λ_{max} (nm), ϵ ($\text{M}^{-1}\text{ cm}^{-1}$)) 308 (40 000). ESI-MS (m/z) 376 ($[\text{MH}]^+$); 398 ($[\text{M} + \text{Na}]^+$).

The complex $[\text{Mn}_2(\text{L}_b)]$ was prepared by the same method as the $[\text{Mn}_2(\text{L}_a)]$ but using the ligand L_b giving a yellow product. m.p. 175–178 °C (decomposition). Anal. calcd. for $\text{Mn}_2\text{Cl}_4\text{C}_{14}\text{H}_{19}\text{F}_6\text{N}_3\text{O}_2 \cdot 4\text{H}_2\text{O}$ (%): C, 24.03; N, 6.00; H, 3.86; Mn, 15.74. Found: C, 23.79; N, 6.04; H, 3.76; Mn, 16.00. The water loss determined by thermogravimetric analysis was found to be 10.2% (calcd. 10.3%). IR (KBr, cm^{-1} , selected peaks) 3416: (OH) (water molecule); 1624: $\nu(\text{C}=\text{O})$; 1595: $\nu(\text{C}=\text{N})$; 1247, 1188: $\nu(\text{CF}_3)$; 443: $\nu(\text{Mn}-\text{O})$. UV (MeOH, λ_{max} (nm), ϵ ($\text{M}^{-1}\text{ cm}^{-1}$)) 310 (30,000).

2.4. Immobilization of (L_b) on a silica support and the preparation of the Mn(II) material, $[\text{Mn}_2(\text{L}_b) \cdot \text{SiO}_2]$

For the functionalization of silica with L_b , the same procedure has been followed as in the case of L_a , by reacting 1.0 mmol of L_b with 1.0 mmol of (3-glycidyloxypropyl)-trimethoxysilane in 50 ml toluene. The resulting solution was allowed to react at 80 °C for 24 h. After the addition of 1.5 g of SiO_2 and 5 ml of EtOH into the reaction mixture, the resulting slurred solution maintained at 80 °C for 24 h. The functionalized silica, $\text{L}_b \cdot \text{SiO}_2$, was isolated by filtration and washed with MeOH and EtOH. It was further purified with EtOH using the soxhlet extraction method and dried under reduced pressure at 80 °C for 12 h. The loading achieved is ca. 0.22 mmol g^{-1} determined by thermogravimetric and elemental analysis. DRIFTS-IR (cm^{-1} , selected peaks): 2982, 2901, 2829: $\nu(\text{CH}_2)$; 1700: $\nu(\text{C}=\text{O})$; 1630: $\nu(\text{C}=\text{N})$; 1450: $\delta(\text{C}-\text{H})$; 1397: $\nu(\text{C}-\text{O})$; 1280: $\nu(\text{CF}_3)$. DRS (λ_{max} (nm)): 223; 310.

To a suspension of $\text{L}_b \cdot \text{SiO}_2$ (0.25 g) in MeOH, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (6.53 mg, 0.033 mmol) was added. The mixture was stirred for 24 h at room temperature and the resulting material, $\text{Mn}_2(\text{L}_b) \cdot \text{SiO}_2$, was filtered, washed with H_2O , MeOH, EtOH and Et_2O and dried at 80 °C for 12 h. The amount of manganese was determined by back-titration of the remaining amount of metal ion into the solution. DRIFTS-IR (cm^{-1} , selected peaks): 2985, 2881: $\nu(\text{CH}_2)$; 1708: $\nu(\text{C}=\text{O})$; 1635: $\nu(\text{C}=\text{N})$; 1397: $\nu(\text{C}-\text{O})$; 1285: $\nu(\text{CF}_3)$. DRS (λ_{max} (nm)): 241; 343.

2.5. Synthesis of the ligand 3-{2-[2-(3-hydroxy-1,3-diphenyl-allylideneamino)-ethylamino]-ethylimino}-1,3-diphenyl-propen-1-ol (L_c) and its Mn(II) complex $[\text{Mn}_2(\text{L}_c)]$

We have published earlier the synthesis of L_c [13]. However, for comparison reasons, we mention here its spectroscopic characterisation. $\text{C}_{34}\text{H}_{33}\text{N}_3\text{O}_2 \cdot \text{H}_2\text{O}$. IR (KBr, cm^{-1} , selected peaks) 3400: $\nu(\text{OH})$; 3350: $\nu(\text{NH})$; 3050, 3029, 2843: $\nu(\text{CH}_2)$; 1600:

$\nu(\text{C}=\text{N})$; 1535, 1467: $\nu(\text{C}=\text{C}) + \delta(\text{NH})$, $\nu(\text{C}=\text{C}) + \delta(\text{CH}_2)$; 1398: $\nu(\text{C}-\text{O})$; 1263: $\nu(\text{OH})$. ^1H NMR (CDCl_3 , δ) 7.9 (m), 7.5 (m): phe-H; 6.7 (s): $\text{C}=\text{CH}-\text{CN}$; 4.6 (s): NH ; 2.8 (t): $\text{CN}-\text{CH}_2-\text{CH}_2$; 2.68 (t): $\text{CN}-\text{CH}_2-\text{CH}_2$. ^{13}C NMR (CDCl_3 , δ) 188: CN ; 162: $=\text{C}-\text{OH}$; 138, 136, 128, 126: phe-C; 93: $\text{HO}-\text{C}=\text{CH}-\text{CN}$; 55: $\text{CN}-\text{CH}_2-\text{CH}_2$; 42: $\text{CN}-\text{CH}_2-\text{CH}_2$. UV (MeOH, λ_{max} (nm), ϵ ($\text{M}^{-1}\text{ cm}^{-1}$)) 252 (14,000); 341 (34,000).

The reaction of L_c with $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in MeOH by the same procedure as the previous manganese complexes leads to the formation of Mn_2L_c complex. Anal. calcd. for $\text{Mn}_2\text{Cl}_2\text{C}_{34}\text{H}_{31}\text{N}_3\text{O}_2 \cdot 2\text{MeOH}$ (%): C, 56.99; N, 5.54; H, 5.15; Mn, 14.51. Found: C, 56.70; N, 5.42; H, 5.49; Mn, 14.80. IR (KBr, cm^{-1} , selected peaks) 3402: (OH); 1590: $\nu(\text{C}=\text{N})$; 1520: $\delta(\text{NH})$; 1388: $\nu(\text{C}-\text{O})$; 448: $\nu(\text{Mn}-\text{O})$. UV (MeOH, λ_{max} (nm), ϵ ($\text{M}^{-1}\text{ cm}^{-1}$)) 256 (14,000); 356 (22,000).

2.6. Immobilization of (L_c) on a silica support and the preparation of the Mn(II) material, $[\text{Mn}_2(\text{L}_c) \cdot \text{SiO}_2]$

The immobilization of L_c on a silica surface has been accomplished by the same procedure followed for the anchoring of the other ligands. Loading achieved: 0.25 mmol g^{-1} . DRIFTS-IR (cm^{-1} , selected peaks): 2980, 2935: $\nu(\text{CH}_2)$; 1717: $\nu(\text{C}=\text{O})$; 1629: $\nu(\text{C}=\text{N})$; 1457: $\delta(\text{C}-\text{H})$; 1394: $\nu(\text{C}-\text{O})$. DRS (λ_{max} (nm)): 228; 354.

The $[\text{Mn}_2(\text{L}_c) \cdot \text{SiO}_2]$ complex was prepared, washed and dried by analogous methods as the above mentioned supported manganese complexes. DRIFTS-IR (cm^{-1} , selected peaks): 2975, 2878: $\nu(\text{CH}_2)$; 1705: $\nu(\text{C}=\text{O})$; 1634: $\nu(\text{C}=\text{N})$; 1394: $\nu(\text{C}-\text{O})$. DRS (λ_{max} (nm)): 237; 358.

2.7. Catalytic reactions

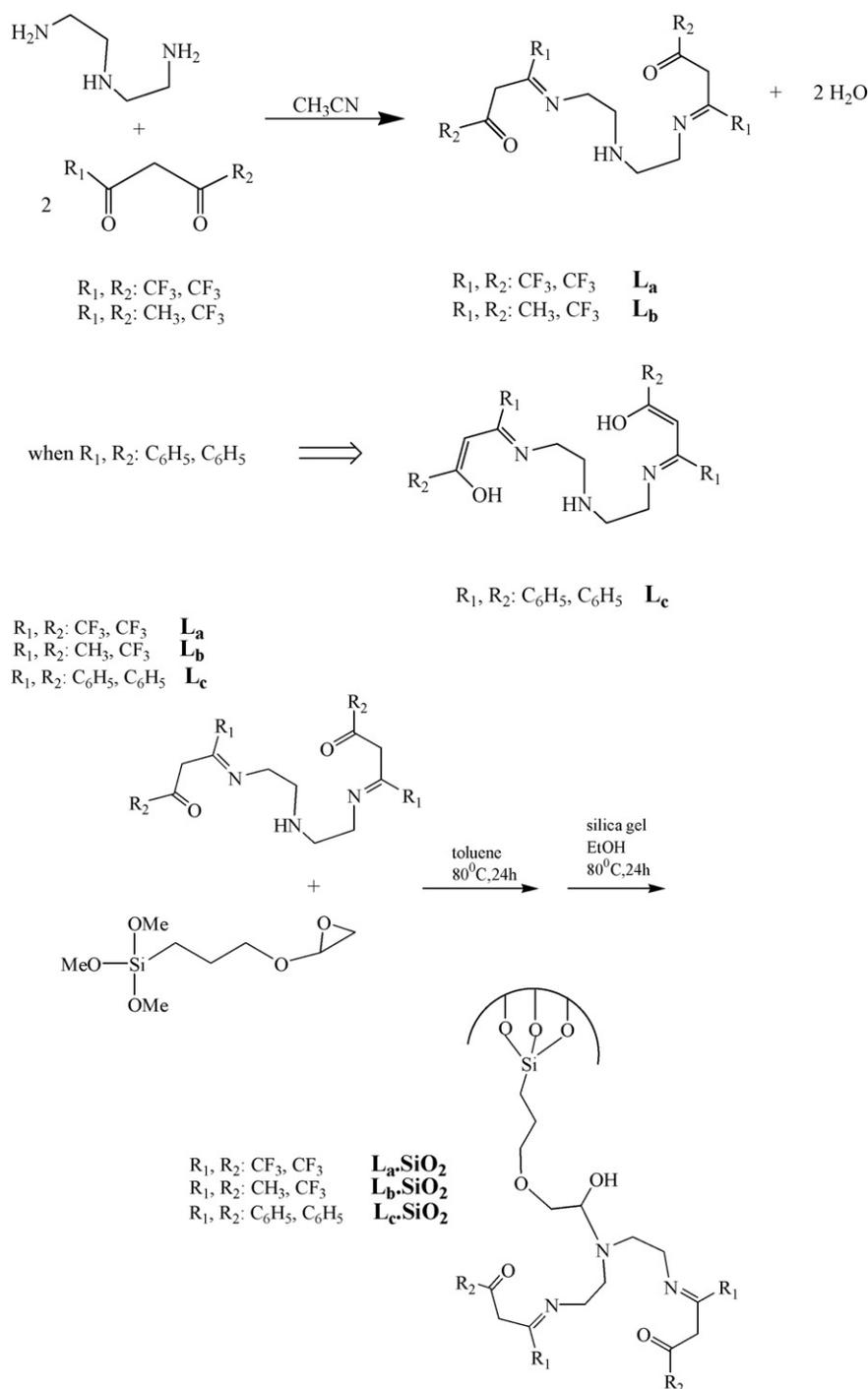
Hydrogen peroxide was slowly added (within a period of 30 min) to solution of alkene and ammonium acetate in an acetone/MeOH (550 μl /300 μl) solvent mixture in the air, at room temperature. As an internal standard, acetophenone or bromobenzene were used. Catalytic reactions were started by adding 1 μmol of corresponding manganese-catalyst. The ratio of catalyst:oxidant:cocatalyst:substrate was equal to 1:2000:1000:1000.

The progress of the reaction was monitored by GC-MS, by removing small samples of the reaction mixture. Reactions were usually complete within 24 h. To establish the identity of the products unequivocally, the retention times and spectral data were compared to those of commercially available compounds. Blank experiments showed that without catalyst or cocatalyst the epoxidation reactions do not take place (in any case, the observed yields were lower than 1%).

3. Results and discussion

3.1. Synthesis and immobilization of the ligands and their manganese complexes

Recently we have reported the synthesis of the ligand L_c by reaction of diethylenetriamine and 1,3-diphenylpropan-1,3-dione [13]. To examine the effect of substituents



Scheme 1. Synthesis and immobilization of the ligands.

on keto-groups, we have designed the ligands **L_a** and **L_b** prepared by condensation of diethylenetriamine and 1,1,1,5,5,5-hexafluoro-pentan-2,4-dione and 1,1,1-trifluoro-pentan-2,4-dione, respectively (Scheme 1). The synthesis was accomplished as a non-template procedure using a molar ratio of diethylenetriamine:β-diketone equal to 1:2. The presented ligands **L_a** and **L_b** were the only isolated products exhibiting, at ESI-mass spectra, molecular peaks $[\text{MH}]^+$ at m/z 484 and 376, respectively. The IR bands at 1665, 1611 and 1651, 1615 cm^{-1} were attributed to the keto- and imine-stretching bands, $\nu(\text{C}=\text{O})$

and $\nu(\text{C}=\text{N})$. ^1H and ^{13}C NMR data clearly suggested the formation of the ligands. For example, in the ^{13}C NMR spectrum of **L_a**, a quarter for the carbon atoms connected with the trifluoromethyl substituents is located at 176.1 ppm ($^2J_{\text{C-F}} = 33.7$ Hz, $\text{O}=\text{C}-\text{CF}_3$ and $\text{N}=\text{C}-\text{CF}_3$) and a quarter also for the trifluoromethyl groups was seen at 119.7 ppm ($^1J_{\text{C-F}} = 317.5$ Hz, CF_3) [17,18]. Characteristic signals were detected for **L_b** at 175.1 (q, $^2J_{\text{C-F}} = 34.7$ Hz, $\text{O}=\text{C}-\text{CF}_3$), 172.7 (s, $\text{N}=\text{C}-\text{CH}_3$) and 119.3 ppm (q, $^1J_{\text{C-F}} = 315.4$ Hz, CF_3) attributing to the keto-, imine- and trifluoro-methyl-carbon atoms, respectively [18,19].

The ligands were subsequently reacted with (3-glycidyloxypropyl)-trimethoxysilane in dry toluene, producing a 3-propoxy-2-hydroxypropyl-silane substituent on the secondary amine group. The formed precursors were immobilized on SiO_2 by reacting at 80°C for 24 h leading to the $\text{L}_a\cdot\text{SiO}_2$ and $\text{L}_b\cdot\text{SiO}_2$ hybrid materials (Scheme 1). This anchoring process is a one step path [13], instead of surface glycidylation and subsequent ligand immobilization [16,20], presenting a considerable advantage from the point of view of economy of synthetic steps. Soxhlet extractions of the organically modified silicas ensure that only the covalently attached ligand molecules remain on the support. The loading achieved is about 0.2 mmol g^{-1} of silica. The infrared spectra of the immobilised ligands $\text{L}_a\cdot\text{SiO}_2$ and $\text{L}_b\cdot\text{SiO}_2$ show bands at 1683, 1634 and 1700, 1630 cm^{-1} , respectively, attributed to the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ stretching vibrations [11]. Anchoring of the organic ligands on the silica surface can be conveniently followed also by DR UV spectroscopy; in the corresponding spectra, the presence of the $\pi \rightarrow \pi^*$ transitions attributed to the immobilised ligands can be seen.

The distribution of heteroatoms in the frame of the ligands L_a , L_b and L_c yielded two metal coordination sites. Thus, their reaction with manganese(II) chloride results in the formation of binuclear Mn_2L_a , Mn_2L_b and Mn_2L_c complexes. In particular, especially relevant are the shifts (a) in IR of the $\text{C}=\text{N}$ imine- and $\text{C}=\text{O}$ keto-vibrations and (b) in their optical spectra of $\pi \rightarrow \pi^*$ transitions. In general our data indicate metal coordination to both imine- and amine-nitrogen as well as to the keto-(in the case of $[\text{Mn}_2\text{L}_a]$ and $[\text{Mn}_2\text{L}_b]$) or enolic-(in the case of $[\text{Mn}_2\text{L}_c]$) oxygen atoms.

The manganese(II) containing $\text{L}_a\cdot\text{SiO}_2$, $\text{L}_b\cdot\text{SiO}_2$, and $\text{L}_c\cdot\text{SiO}_2$ materials present the $\text{C}=\text{O}$ and $\text{C}=\text{N}$ stretching vibrations at about 1705 and 1635 cm^{-1} clearly indicating the interaction of metal ion with the imine-nitrogen and the keto-oxygen of the immobilised ligands. This is also supported by DR UV spectra.

3.2. EPR studies

Dual mode X-band EPR spectroscopy at liquid helium temperatures was applied in order to study the properties of the Mn ions in the hybrid material $[\text{Mn}_2\text{L}_a\cdot\text{SiO}_2]$. The details of the analysis are discussed in Supplementary data.

The low temperature EPR spectra for the homogeneous catalyst in methanol show the same main features, though broader, to those shown in Fig. 1 for the heterogeneous. The broader linewidth observed in the frozen solution for the homogeneous catalyst is due to random dipolar interactions between neighboring paramagnetic complexes, commonly observed in analogous cases. Noteworthy in the heterogeneous catalysts, Fig. 1, such unwanted linebroadening is reduced most likely due to the stereoarrangement of the grafted complexes onto the SiO_2 particles.

For the heterogenised system $[\text{Mn}_2\text{L}_a\cdot\text{SiO}_2]$, representative spectra recorded in perpendicular mode at 4.2 and 10 K under non-saturating conditions are shown in Fig. 1. The spectra consist of several signals spanning a broad region. The strongest signal is in the form of a broad derivative at $g \sim 2.0$ with an

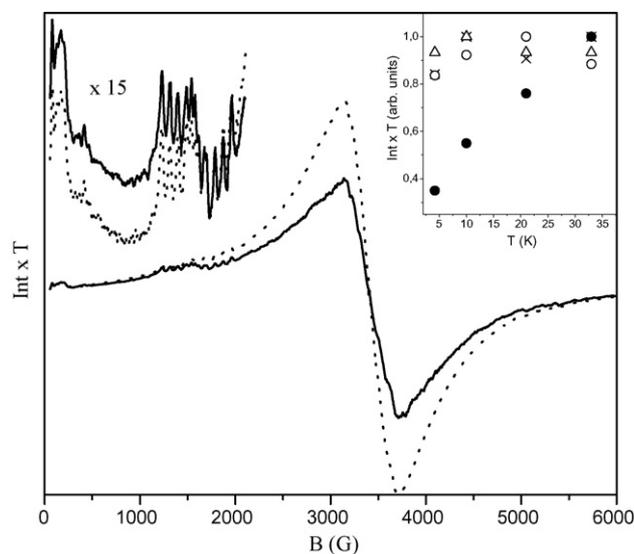


Fig. 1. A. Perpendicular mode EPR spectra from $\text{Mn}_2\text{L}_a\cdot\text{SiO}_2$ at 4.2 K (solid) and 10 K (dotted) temperatures scaled with respect to temperature. EPR conditions: EPR conditions, microwave power 40 mW, mod. ampl., 10 G_{pp} , microwave frequency, 9.60 GHz. Inset: Temperature dependence of the intensity of the signals plotted in the form $\text{Int.} \times T$ vs. T . Full circles: broad $g \sim 2.0$ signal (perpendicular mode); open circles: low field signal ($< 500\text{G}$), perpendicular mode; triangles: “multiline signal” (1250–2500G), perpendicular mode; crosses: parallel mode signal (figepr2, supporting information).

apparent peak-to-peak width of $\sim 550\text{ G}_{\text{pp}}$. Weaker signals are observed in the low magnetic field region. These signals consist of a characteristic feature for $B < 500\text{G}$ and a “multiline” pattern in the 1000–2000G region.

The temperature dependence of the intensity Int. of the various signals in the form $\text{Int.} \times T$ versus T is shown in the inset of Fig. 1. It can be readily seen that the product $\text{Int.} \times T$ of the broad signal at $g \sim 2.0$ increases with temperature. On the contrary, the signals at low field region follow approximately the Curie law (i.e. constant $\text{Int.} \times T$). From this behavior it is inferred that the broad $g \sim 2.0$ and the low field signals belong to different species. The “multiline” pattern in the 1000–2000G magnetic field region indicates hyperfine interactions and consists of approximately 11 lines. Such a hyperfine spacing is consistent with a monomeric Mn^{2+} ($S = 5/2$) where D and E are the axial and rhombic parts of the zero field splitting term (zfs) and A is the hyperfine tensor of the ^{55}Mn nucleus ($I = 5/2$) [21–28].

We conclude that both low field ($< 500\text{G}$) and the “multiline” features (1000–2000G), recorded in perpendicular mode and the parallel mode spectrum, both can be attributed to a unique Mn^{2+} ($S = 5/2$) mononuclear site with a zero field splitting term of the order of $|D| \sim 0.1\text{ cm}^{-1}$ and isotropic hyperfine interaction, $A_{\text{iso}} \sim 250\text{ MHz}$.

3.3. Catalytic performance of homogeneous and heterogenised Mn(II) complexes

To evaluate the catalytic behaviour of the manganese systems prepared, oxidations of several alkenes have been carried out at room temperature in a mixture of ace-

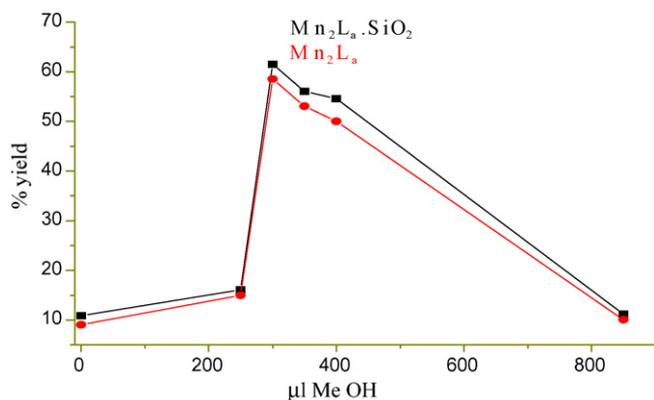


Fig. 2. Yields for cyclooctene epoxidation catalysed by homogeneous Mn_2L_a and heterogenised $\text{Mn}_2\text{L}_a\cdot\text{SiO}_2$ complexes at different methanol–acetone solvent mixture. In any case, the total volume of the solvents was fixed and equal to 0.850 ml.

tone:methanol (equal to 0.55/0.30, v/v). The used molar ratio of catalyst: H_2O_2 : $\text{CH}_3\text{COONH}_4$:substrate was equal to 1:2000:1000:1000.

We have observed that the amount of protic methanol affected the catalytic oxidations. To explore the optimum reaction mixture, the cyclooctene epoxidation has been chosen as a model reaction. The highest epoxidation yield was obtained for a mixture of methanol–acetone equal to 0.30/0.55 (v/v) (see Figs. 2 and 3). This solvent mixture functions perfectly in both homogeneous and heterogenised systems indicating that the methanol is required for reasons other than to dissolve the catalyst.

Ammonium acetate is added as an additive and it is absolutely required in order to produce an efficient catalytic system [29,30]. The reactions were usually complete within 24 h. Interestingly, the time-dependent epoxidations catalysed by homogeneous or heterogeneous catalysts show analogous profiles (Fig. 4). When the catalyst is filtered from the reaction mixture, the substrate conversion does not progress any more. Generally the heterogenised catalysts recovered by filtration from the catalytic reactions exhibited (a) identical IR spectra with the ‘unused’ catalysts and (b) almost the same loading determined

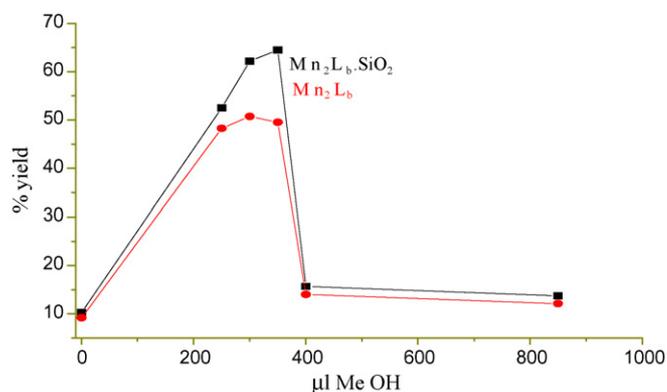


Fig. 3. Yields for cyclooctene epoxidation catalysed by homogeneous Mn_2L_b and heterogenised $\text{Mn}_2\text{L}_b\cdot\text{SiO}_2$ complexes at different methanol–acetone solvent mixture. In any case, the total volume of the solvents was fixed and equal to 0.850 ml.

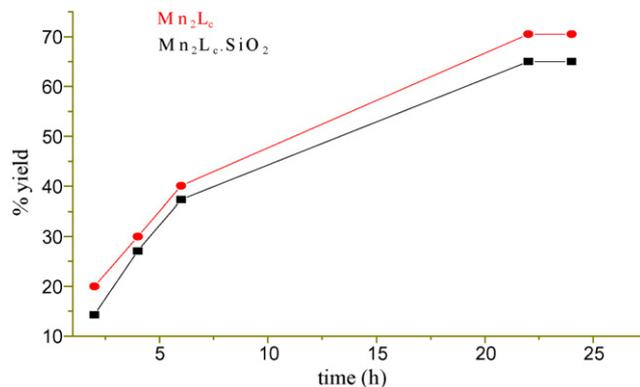


Fig. 4. Time-dependent reaction profiles for cyclooctene epoxidation catalysed by homogeneous Mn_2L_c and heterogenised $\text{Mn}_2\text{L}_c\cdot\text{SiO}_2$ complexes.

by thermogravimetric analysis. These results indicate that there is no leaching of the supported catalysts during the catalytic reactions.

Table 1 lists the results of catalytic experiments. Based on these data, we observe that the new manganese systems led to the epoxidation of various alkenes with significant to excellent yields (56–97%) and turnover numbers 560 till 970, respectively. Almost complete conversion of limonene to its epoxides obtained with $\text{Mn}_2\text{L}_c\cdot\text{SiO}_2$ catalyst. This was not the case for all alkenes, especially when less reactive alkenes like hex-1-ene, were used. For example depending upon the nature of catalyst, the yields for cyclooctene, cyclohexene, hex-1-ene, styrene, *cis*-stilbene, isoprene and limonene epoxidation were 65.0–72.6, 35.8–68.2, 6.0–19.0, 19.6–47.3, 16.2–60.0, 8.0–59.8 and 40.0–97.3%, respectively (Table 1). In all cases, the epoxides formed are the favoured products. Products from possible cleavage of the double bond in styrene, or from allylic oxidation in alkenes have been not detected. The limit of detection was less than two turnovers.

The products detected from oxidation of limonene by hydrogen peroxide were two *cis*- and *trans*-epoxides derived from epoxidation of the electron-rich double bond in 1,2- position and two diastereoisomers derived from the more accessible but less electron-rich double bond in 8,9- position. The total epoxide yield was found to be dependent on the nature of the catalyst. It varied from 40.0% for the homogeneous Mn_2L_a catalyst to 71.4% for the homogeneous Mn_2L_c catalyst. The heterogenisation of these catalysts results in remarkably enhanced catalytic performance, providing limonene epoxidation yield 69.2% for $\text{Mn}_2\text{L}_a\cdot\text{SiO}_2$, 77.8% for $\text{Mn}_2\text{L}_b\cdot\text{SiO}_2$ and 97.3% for $\text{Mn}_2\text{L}_c\cdot\text{SiO}_2$. Moreover, the ratio between the 1,2- and 8,9-epoxides seems to be dependent on the nature of the catalyst and on the presence of the inorganic support. It varied from 7.5 for the less hindered Mn_2L_a catalyst to 5.6 for Mn_2L_c , which bears four phenyl rings (Table 2). The control of the regioselectivity of limonene epoxidation by using hindered metal-catalysts with lower access of the metal-active species to the more electron-rich but more hindered 1,2-double bond has been already reported for metalloporphyrin-catalysts [31]. However, the results of Table 2 show that the use of supported metal catalysts favours epoxidation of the most reactive but less accessible 1,2-double bond of

Table 1
Alkene epoxidations catalysed by manganese-complexes in the presence of H₂O₂

Substrate	Yield (%) ^a TOF ^b (h ⁻¹) TON ^c					
	Mn ₂ L _a	Mn ₂ L _a ·SiO ₂	Mn ₂ L _b	Mn ₂ L _b ·SiO ₂	Mn ₂ L _c	Mn ₂ L _c ·SiO ₂
Cyclooctene	70.7	72.6	71.2	72.1	70.5	65.0
	29.5	30.2	29.7	30.0	29.4	27.1
	707	726	712	721	705	650
Cyclohexene	56.8	68.2	49.7	64.5	42.5	35.8
	23.7	28.4	20.7	26.9	17.7	14.9
	568	682	497	645	425	358
Hex-1-ene	14.0	14.7	6.0	12.8	19.0	11.0
	5.8	6.1	2.5	5.3	7.9	4.6
	140	147	60	128	190	110
Styrene	47.3	42.5	38.0	19.6	30.0	23.6
	19.7	17.7	15.8	8.2	12.5	9.8
	473	425	380	196	300	236
<i>cis</i> -Stilbene	32.0	17.0	16.2	16.4	52.0	60.0
	13.3	7.1	6.8	6.8	21.7	25.0
	320	170	162	164	520	600
Isoprene	57.8	59.8	8.0	21.4	50.3	55.7
	24.0	24.9	3.3	8.9	21.0	23.2
	578	598	80	214	503	557
Limonene ^d	40.0	69.2	48.5	77.8	71.4	97.3
	16.7	28.8	20.2	32.4	29.8	40.5
	400	692	485	778	714	973

Conditions-ratio of catalyst:H₂O₂:CH₃COONH₄:substrate = 1:2000:1000:1000; equivalent of catalyst = 1 μmol in 0.85 ml CH₃COCH₃:CH₃OH (0.55:0.3); reactions were usually complete within 24 h.

^a Yields based on epoxides formed.

^b TOF: turnover frequency which is calculated by the expression [epoxide]/[catalyst] × time (h⁻¹).

^c TON: total turnover number, moles of epoxide formed per mole of catalyst.

^d Limonene 1,2-oxide was found as a mixture of *cis*- and *trans*-isomers and limonene 8,9-oxide as a mixture of two diastereoisomers.

limonene. In the case of Mn₂L_c·SiO₂ catalyst, the ratio between the 1,2- and 8,9-epoxides was found to be close to the value observed when the homogeneous Mn₂L_c catalyst was used. These findings agree with the idea that the inorganic support does not introduce any steric hindrance, which would prevent the substrate access.

Finally, for limonene epoxidation, silica support clearly enhances the catalysts performance and in the cases of Mn₂L_a·SiO₂ and Mn₂L_b·SiO₂ catalysts modulates the regio-

selectivity by favouring epoxidation of 1,2-double bond. In fact, it is tempting to rationalize these results, as a synergism between the active complex and the solid support. The latter should play a principal role other than providing a large surface to anchor the active centre.

Comparing the present macrocyclic manganese systems with analogous macrocyclic systems [29], we observe that the Mn-ligand systems presented here lead to higher cyclooctene and limonene epoxidation at room temperature with hydrogen

Table 2
Regioselectivity of limonene epoxidation by H₂O₂ catalysed by manganese-complexes

Limonene epoxides ^a	Yield (%) ^b					
	Mn ₂ L _a	Mn ₂ L _a ·SiO ₂	Mn ₂ L _b	Mn ₂ L _b ·SiO ₂	Mn ₂ L _c	Mn ₂ L _c ·SiO ₂
<i>cis</i> -1,2	18.4	33.2	20.4	39.2	34.7	46.1
<i>trans</i> -1,2	16.9	32.1	19.0	36.1	26.0	35.3
<i>cis/trans</i>	1.1	1.0	1.1	1.1	1.3	1.3
8,9-Epoxides	4.7	3.1	9.1	2.6	10.8	15.9
1,2/8,9	7.5	21.3	4.3	29.5	5.6	5.1
Total yield	40.0	69.2	48.5	77.8	71.4	97.3

Conditions-ratio of catalyst:H₂O₂:CH₃COONH₄:substrate = 1:2000:1000:1000; equivalent of catalyst = 1 μmol in 0.85 ml CH₃COCH₃:CH₃OH (0.55:0.3); reactions were usually complete within 24 h.

^a Limonene 1,2-oxide was found as a mixture of *cis*- and *trans*-isomers and limonene 8,9-oxide as a mixture of two diastereoisomers.

^b Yields based on epoxides formed.

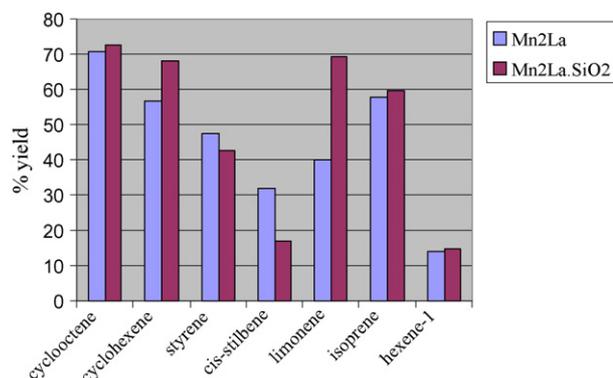


Fig. 5. Bar chart representation of alkene epoxidations catalysed by homogeneous Mn₂L_a and heterogenised Mn₂L_a·SiO₂ catalysts in the presence of H₂O₂.

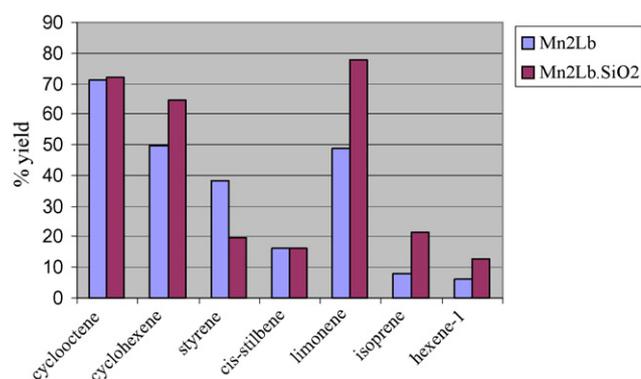


Fig. 6. Bar chart representation of alkene epoxidations catalysed by homogeneous Mn₂L_b and heterogenised Mn₂L_b·SiO₂ catalysts in the presence of H₂O₂.

peroxide, while at the same time, they show much less lower epoxidation yields for isoprene and cyclohexene. When we evaluate the performance of the three manganese-ligand systems for alkene epoxidation based on the data of Table 1, we observe that the Mn₂L_a and Mn₂L_c catalysts exhibit higher reactivity.

In general, heterogenisation process does not affect the catalytic properties of the supported manganese complexes since these complexes present analogous epoxidation yields maintaining their catalytic activity. However, in some cases, i.e. limonene epoxidation, the heterogenised catalysts clearly show enhanced

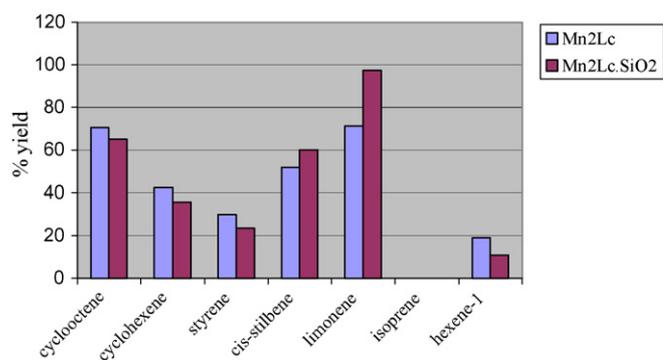


Fig. 7. Bar chart representation of alkene epoxidations catalysed by homogeneous Mn₂L_c and heterogenised Mn₂L_c·SiO₂ catalysts in the presence of H₂O₂.

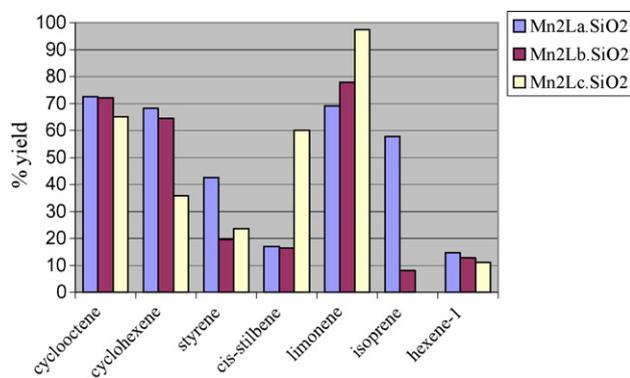


Fig. 8. Bar chart representation of alkene epoxidations by H₂O₂ catalysed by supported manganese complexes.

catalytic activity compared with the corresponding homogeneous catalysts (Table 1; Figs. 5–7).

Overall, the present supported manganese complexes are able to overcome the competitive H₂O₂ dismutation e.g. by the use of a double only excess of H₂O₂, favouring useful alkene epoxidations in a significant extent (Fig. 8).

4. Conclusions

It is well-accepted that efficient epoxidation manganese-salen catalysts which activate hydrogen peroxide heterolytically cleave the hydrogen peroxide O–O bond probably forming Mn=O systems. This mechanistic pathway is desirable leading to a direct oxygen transfer from the Mn=O species to alkene substrates; that is, a Fenton-type chemistry with radical formation based on a homolytic cleavage of hydrogen peroxide O–O bond is bypassed [14]. Oxomanganese intermediates are also the active species in the Mn-porphyrin-mediated epoxidations with H₂O₂ [32,33].

In addition to monomeric species, several dinuclear species of Mn-TACN- and Mn-pyridyl-amine-derived catalysts with oxo, peroxy or carboxylate bridges have been reported to be active in alkene epoxidation by hydrogen peroxide [34–36].

The EPR data demonstrate that the improved catalytic activity does not necessarily require the formation of the Mn-dimers. Monomeric Mn-complexes show good catalytic activity just because of the immobilisation on to SiO₂ surface. This might indicate that proper stereospecificity is more important than dimer formation for an improved catalytic activity of Mn-catalysts.

The successful transfer of the activity of homogeneous systems to heterogeneous ones still remains a challenge. Within this, we set off the efficiency of the present immobilised complexes to activate hydrogen peroxide towards epoxide formation in conjunction with the advantages of the heterogeneous catalysts. Moreover, it is stressed that the new catalysts are easy to synthesise. As concerned limonene epoxidation, our supported manganese complexes present very good to excellent yields. However, further improvement of the rate of reactions is warranted.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.08.025.

References

- [1] J.H. Clark, *Green Chem.* (1999) 1–8.
- [2] P.T. Anastas, L.B. Bartlett, M.M. Kirchoff, T.C. Williamson, *Catal. Today* 55 (2000) 11–22.
- [3] W.F. Holderich, F. Kollmer, *Pure Appl. Chem.* 72 (2000) 1273–1287.
- [4] M.H. Valkenberg, W.F. Holderich, *Catal. Rev.* 44 (2002) 321–374.
- [5] D. Brunel, N. Bellocq, P. Sutra, A. Cauvel, M. Lasperas, P. Moreau, F.D. Renzo, A. Galarneau, F. Fajula, *Coord. Chem. Rev.* 178–180 (1998) 1085–1108.
- [6] J.S. Rafelt, J.H. Clark, *Catal. Today* 57 (2000) 33–44.
- [7] J.H. Clark, D.J. Macquarrie, *Chem. Commun.* (1998) 853–860.
- [8] D.E. De Vos, P.A. Jacobs, *Catal. Today* 57 (2000) 105–114.
- [9] P.M. Price, J.H. Clark, D.J. Macquarrie, *J. Chem. Soc., Dalton Trans.* (2000) 101–110.
- [10] P. Sutra, D. Brunel, *Chem. Commun.* (1996) 2485–2486.
- [11] I.C. Chisem, J. Rafelt, M.T. Shieh, J. Chisem, J.H. Clark, R. Jachuck, D. Macquarrie, C. Ramshav, K. Scott, *Chem. Commun.* (1998) 1949–1950.
- [12] X.-G. Zhou, X.-Q. Yu, J.-S. Huang, S.-G. Li, L.-S. Li, C.-M. Che, *Chem. Commun.* (1999) 1789–1790.
- [13] M. Louloudi, K. Mitopoulou, E. Evaggelou, Y. Deligiannakis, N. Hadjiliadis, *J. Mol. Catal. A* 198 (2003) 231–240.
- [14] B.S. Lane, K. Burgess, *Chem. Rev.* 103 (2003) 2457–2473.
- [15] G.C. Yin, M. Buchalova, A.M. Danby, C.M. Perkins, D. Kitko, J.D. Carter, W.M. Scheper, D.H. Busch, *Inorg. Chem.* 45 (2006) 3467–3474.
- [16] Y.V.S. Rao, D.E. De Vos, T. Bein, P.A. Jacobs, *Chem. Commun.* (1997) 355–356.
- [17] M.A. Martinez-Lorente, P. Battioni, W. Kleemiss, J.F. Bartoli, D. Mansuy, *J. Mol. Catal. A* 113 (1996) 343–353.
- [18] S.P. Singh, J.K. Kapoor, D. Kumar, M.D. Threadgill, *J. Fluorine Chem.* 83 (1997) 73–79.
- [19] V.I. Saloutin, Y.V. Burgart, O.G. Kuzueva, C.O. Kappe, O.N. Chupakhin, *J. Fluorine Chem.* 103 (2000) 17–23.
- [20] P.M. VanBerkel, W.L. Driessen, G.J.A.A. Kodhaas, J. Reedijk, D.C. Sherrington, *J. Chem. Soc., Chem. Commun.* (1995) 147–148.
- [21] R.B. Birdy, M. Goodgame, *Inorg. Chem.* 18 (1979) 472–475.
- [22] C.J.H. Jacobsen, E. Pedersen, J. Villadsen, H. Weihe, *Inorg. Chem.* 32 (1993) 1216–1221.
- [23] A.K. Whiting, Y.R. Boldt, M.P. Hendrich, L.P. Wacket, L. Que Jr., *Biochemistry* 35 (1996) 160–170.
- [24] M.M. Whittaker, J.W. Whittaker, *Biochemistry* 36 (1997) 8923–8931.
- [25] S.T. Warzeska, F. Micciche, M.C. Mimmi, E. Bouwman, H. Kooijman, A.L. Spek, J. Reedijk, *J. Chem. Soc., Dalton Trans.* (2001) 3507–3512.
- [26] D.M.L. Goodgame, H.E. Mkami, G.M. Smith, J.P. Zhao, E.J.L. McInnes, *Dalton Trans.* (2003) 34–35.
- [27] B.S. Pierce, T.E. Elgren, M.P. Hendrich, *J. Am. Chem. Soc.* 125 (2003) 8748–8759.
- [28] D. Kovala-Demertzi, U. Gangadharmath, M.A. Demertzis, Y. Sanakis, *Inorg. Chem. Commun.* 8 (2005) 619–622.
- [29] Ch. Kolokytha, M. Louloudi, N. Hadjiliadis, *J. Mol. Catal. A* 180 (2002) 19–24.
- [30] D. Zois, Ch. Vartzouma, Y. Deligiannakis, N. Hadjiliadis, L. Casella, E. Monzani, M. Louloudi, *J. Mol. Catal. A*, submitted for publication.
- [31] P. Battioni, J.P. Renaud, J.F. Bartoli, M. Reina-Artiles, M. Fort, D. Mansuy, *J. Am. Chem. Soc.* 110 (1988) 8462–8470.
- [32] J.T. Groves, M.K. Stern, *J. Am. Chem. Soc.* 110 (1988) 8628–8638.
- [33] J.T. Groves, J. Lee, S.S. Marla, *J. Am. Chem. Soc.* 119 (1997) 6269–6273.
- [34] R. Hage, J.E. Iburg, J. Kerschner, J.H. Keek, E.L.M. Lempers, R.J. Martens, U.S. Racherla, S.W. Russel, T. Swarthoff, M.R.P. van Vliet, J.B. Warnaar, L. van der Wolf, B. Krijnen, *Nature* 369 (1994) 637–639.
- [35] J.W. de Boer, J. Brinksma, W.R. Browne, A. Meetsma, P.L. Alsters, R. Hage, B.L. Feringa, *J. Am. Chem. Soc.* 127 (2005) 7990–7991.
- [36] J. Brinksma, R. Hage, J. Kerschner, B.L. Feringa, *Chem. Commun.* (2000) 537–538.