



# The catalytic function of SiO<sub>2</sub>-immobilized Mn(II)-complexes for alkene epoxidation with H<sub>2</sub>O<sub>2</sub>

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## ABSTRACT

Two symmetrical acetylacetonate-based Schiff bases were immobilized on a silica surface by grafting and sol–gel procedure. The corresponding supported manganese complexes were prepared and evaluated as heterogeneous catalysts for alkene epoxidation with H<sub>2</sub>O<sub>2</sub>. These heterogeneous catalysts show remarkable effectiveness and selectivity towards epoxide formation in the presence of ammonium acetate. Moreover, the developed heterogeneous catalysts preserve the coordination and catalytic properties of the active-homogeneous manganese catalysts for alkene epoxidation vs. the competitive H<sub>2</sub>O<sub>2</sub> dismutation. EPR spectroscopy shows that in heterogeneous manganese catalysts the Mn<sup>2+</sup> centers are in a flexible, non-tight, coordination environment, as in the corresponding homogeneous manganese catalysts. However, after a first use of the heterogeneous catalysts, the Mn centers are detached from the ligand and are randomly dispersed on the SiO<sub>2</sub> surface. This is responsible for the loss of catalytic activity.

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## 1. Introduction

Epoxidation reactions that involve hydrogen peroxide, which is still the ‘greenest’ terminal oxidant, is of great interest due to the importance of epoxides in the manufacture of both bulk and fine chemicals [1]. Despite success of homogeneous catalysts in the epoxidations, there is a clear demand for heterogeneous catalysts that provide advantages such as easy handling and product separation, catalyst recovery and less level of waste [2,3]. For these reasons, the development of heterogeneous catalysts for epoxidation reactions remains a very active field of research [4,5]. Preparation of heterogeneous catalysts, by covalent immobilization of transition-metal complexes on silica surface represents one of the most usable approaches [6–9]. Many of heterogeneous catalysts contain metal ions and chemically modified silica gels with active organic components [10]. Among the various transition-metals for heterogeneous catalytic epoxidation, manganese stands out as the most efficient, economical and environmental benign. 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 [11–15]. However, the development of efficient manganese-systems that incorporate H<sub>2</sub>O<sub>2</sub> has limitations due to competitive H<sub>2</sub>O<sub>2</sub> dismutation by both the Mn center (catalase-type-activity) and the inorganic support. These limita-

tions can explain why only a few such systems, based on supported manganese catalysts and H<sub>2</sub>O<sub>2</sub>, have been reported for alkene epoxidation [16–20].

Thus, efficient, cost effective and robust manganese catalysts remain at high demand in the field of hydrocarbon oxidation by H<sub>2</sub>O<sub>2</sub>. Within this context, during the last years, our group has developed imidazole based acetamide/Mn(II) systems [18,20] and acetylacetonate-based Schiff bases/Mn(II) systems [19,21] as homogeneous and heterogeneous catalysts for alkene epoxidation with H<sub>2</sub>O<sub>2</sub>. More recently, we have presented homogeneous Mn(II)-catalysts with new symmetrical acetylacetonate-based Schiff bases [22]. Their catalytic efficiency was shown to be switched-on by ammonium acetate achieving remarkable effectiveness and selectivity towards epoxides [22]. EPR spectroscopy provided evidence that the catalytic centers are mononuclear Mn(II) complexes with a flexible ligand–field environment [22].

Herein, the symmetrical acetylacetonate-based Schiff bases are immobilized on a silica surface by grafting and sol–gel procedure. The obtained supported manganese complexes have been evaluated as catalysts for alkene epoxidation with H<sub>2</sub>O<sub>2</sub> and compared with the corresponding homogeneous systems. EPR spectroscopy has been also used to study the coordination environment of the heterogeneous Mn-catalysts.

## 2. Experimental

All substrates were purchased from Aldrich, in their highest commercial purity, stored at 5 °C and purified by passage through

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a column of basic alumina with methanol as the eluting solvent, prior to use. Hydrogen peroxide was 30% aqueous solution.

Elemental analyses (C, H, N) were obtained using a Perkin-Elmer Series II 2400 elemental analyser. The manganese amount was determined by flame atomic absorption spectroscopy on a Perkin-Elmer AAS-700 spectrometer. Infrared spectra were recorded on a Spectrum GX Perkin-Elmer FT-IR System. Continuous-wave (c.w.) Electron Paramagnetic Resonance (EPR) spectra were recorded with a Bruker ER200D spectrometer at liquid N<sub>2</sub> temperature, equipped with an Agilent 5310A frequency counter. The spectrometer was running under a home-made software based on LabView. Diffuse reflectance UV-Vis spectra were recorded at room temperature on a Shimadzu UV-2401PC with a BaSO<sub>4</sub> coated integration sphere. Thermogravimetric analyses were carried out under atmosphere using Shimadzu DTG-60 analyser. GC analysis was performed using an 8000 Fisons chromatograph with a flame ionization detector and a Shimadzu GC-17A gas chromatograph coupled with a GCMS-QP5000 mass spectrometer. The N<sub>2</sub> adsorption-desorption isotherms were measured at 77 K on a Sorptomatic 1990, thermo Finnigan porosimeter. Specific surface areas were determined with the Brunauer-Emmett-Teller (BET) method using adsorption data points in the relative pressure ( $P/P_0$ ) range of 0.05–0.30 and assuming a closely packed BET monolayer. H<sub>2</sub>O<sub>2</sub> was added by a digitally controlled syringe pump type SP101IZ WPI over 1 h under stirring. Solution potential  $E_h$  was measured by a Metrohm platinum redox electrode (type 6.0401.100).

### 2.1. Ligand synthesis

Ligands **1** and **2** have been synthesized and characterized recently [22].

### 2.2. Grafting procedure

In a typical synthesis, 2.0 mmol of **1** or **2** and 1.7 mmol of (3-chloropropyl)-trimethoxysilane were stirred for 48 h in 50 ml of MeOH under N<sub>2</sub> at 60 °C. To this solution 3.0 g of SiO<sub>2</sub> and 5 ml of EtOH were added, and the slurred solution maintained at 60 °C under N<sub>2</sub> for 24 h. Filtering gave **G-1** or **G-2**, respectively. The resulting materials were washed with MeOH and EtOH; they were 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. 0.28 mmol g<sup>-1</sup> for **G-1** and 0.26 mmol g<sup>-1</sup> for **G-2** determined, in both cases, by thermogravimetric and elemental analysis.

**G-1**: DRIFTS-IR (cm<sup>-1</sup>, selected peaks): 1652:  $\nu(\text{C}=\text{O})$ ; 1618:  $\nu(\text{C}=\text{N})$ ; 1516:  $\nu(\text{C}=\text{C})$ ; 1463:  $\delta(\text{C}-\text{H})$ ; 1410:  $\nu(\text{C}-\text{O})$ . DRS ( $\lambda_{\text{max}}$  (nm)): 232, 313, 491.

**G-2**: DRIFTS-IR (cm<sup>-1</sup>, selected peaks): 1656:  $\nu(\text{C}=\text{O})$ ; 1619:  $\nu(\text{C}=\text{N})$ ; 1511:  $\nu(\text{C}=\text{C})$ ; 1465:  $\delta(\text{C}-\text{H})$ ; 1410:  $\nu(\text{C}-\text{O})$ ; 1212:  $\nu(\text{CF}_3)$ . DRS ( $\lambda_{\text{max}}$  (nm)): 228, 320, 489.

### 2.3. Metalation procedure

Approximately 0.3 mmol of MnCl<sub>2</sub>·4H<sub>2</sub>O or Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and 0.5 g of **G-1** or **G-2** were stirred in MeOH overnight before filtering. To remove any weakly coordinated metal, the metalated materials, **G-1Mn<sup>II</sup>Cl**, **G-1Mn<sup>II</sup>acet**, **G-2Mn<sup>II</sup>Cl** and **G-2Mn<sup>II</sup>acet**, were exhaustively washed with MeOH, EtOH and Et<sub>2</sub>O and dried at 60 °C for 3 h. The amount of manganese was determined by back-titration of the remaining amount of metal ion into the solution and by atomic absorption spectroscopy.

**G-1Mn<sup>II</sup>Cl**: Metal loading: 0.26 mmol g<sup>-1</sup>. DRIFTS-IR (cm<sup>-1</sup>, selected peaks): 1706:  $\nu(\text{C}=\text{O})$ ; 1658:  $\nu(\text{C}=\text{N})$ ; 1406:  $\nu(\text{C}-\text{O})$ . DRS ( $\lambda_{\text{max}}$  (nm)): 230, 315, 483. This material had an average surface area of ca. 203 m<sup>2</sup> g<sup>-1</sup>.

**G-1Mn<sup>II</sup>acet**: Metal loading: 0.28 mmol g<sup>-1</sup>. DRIFTS-IR (cm<sup>-1</sup>, selected peaks): 1704:  $\nu(\text{C}=\text{O})$ ; 1645:  $\nu(\text{C}=\text{N})$ ; 1548:  $\nu_{\text{sym}}(\text{COO}^-)$ ; 1441:  $\nu_{\text{as}}(\text{COO}^-)$ ; 1408:  $\nu(\text{C}-\text{O})$ . DRS ( $\lambda_{\text{max}}$  (nm)): 229, 310, 489. This material had an average surface area of ca. 286 m<sup>2</sup> g<sup>-1</sup>.

**G-2Mn<sup>II</sup>Cl**: Metal loading: 0.24 mmol g<sup>-1</sup>. DRIFTS-IR (cm<sup>-1</sup>, selected peaks): 1704:  $\nu(\text{C}=\text{O})$ ; 1645:  $\nu(\text{C}=\text{N})$ ; 1406:  $\nu(\text{C}-\text{O})$ ; 1209:  $\nu(\text{CF}_3)$ . DRS ( $\lambda_{\text{max}}$  (nm)): 227, 325, 476. This material had an average surface area of ca. 198 m<sup>2</sup> g<sup>-1</sup>.

**G-2Mn<sup>II</sup>acet**: Metal loading: 0.25 mmol g<sup>-1</sup>. DRIFTS-IR (cm<sup>-1</sup>, selected peaks): 1706:  $\nu(\text{C}=\text{O})$ ; 1645:  $\nu(\text{C}=\text{N})$ ; 1528:  $\nu_{\text{sym}}(\text{COO}^-)$ ; 1441:  $\nu_{\text{as}}(\text{COO}^-)$ ; 1402:  $\nu(\text{C}-\text{O})$ ; 1209:  $\nu(\text{CF}_3)$ . DRS ( $\lambda_{\text{max}}$  (nm)): 227, 324, 487. This material had an average surface area of ca. 277 m<sup>2</sup> g<sup>-1</sup>.

### 2.4. Sol-gel procedure

By adaptation of grafting-methodology used, 1.2 mmol of **1** and 1.0 mmol of (3-chloropropyl)-trimethoxysilane were stirred for 48 h in 10 ml of MeOH under N<sub>2</sub> at 60 °C in order to generate **OS-1** silicon precursor. After cooling, to this solution 2.4 mmol of MnCl<sub>2</sub>·4H<sub>2</sub>O were added. The obtained solution was stirred overnight at room temperature under N<sub>2</sub> leading to metalated precursor **OS-1Mn<sup>II</sup>Cl**. The **S-1Mn<sup>II</sup>Cl** catalyst was prepared by sol-gel method, through hydrolysis of TEOS and **OS-1Mn<sup>II</sup>Cl** precursor in MeOH-H<sub>2</sub>O mixture in the presence of NaF as catalyst. For this, to the precursor solution 4.5 ml TEOS, 3.6 ml H<sub>2</sub>O and 4.2 mg NaF were added and mixed together for 10 min. The final molar ratio silicon precursor:NaF:TEOS:H<sub>2</sub>O was equal to 1:0.1:20:200. The gelation of the sol was observed in the next 3 h and the obtained gel was kept for aging for 3 days at room temperature. The filtered solid was extensively washed with water and methanol. The **S-1Mn<sup>II</sup>Cl** material was further purified with MeOH using the soxhlet extraction method and dried under reduced pressure at 60 °C for 12 h. The loading achieved is ca. 0.19 mmol g<sup>-1</sup> determined by thermogravimetric and elemental analysis.

**S-1Mn<sup>II</sup>Cl**: Metal loading: 0.20 mmol g<sup>-1</sup>. DRIFTS-IR (cm<sup>-1</sup>, selected peaks): 1686:  $\nu(\text{C}=\text{O})$ ; 1658:  $\nu(\text{C}=\text{N})$ ; 1403:  $\nu(\text{C}-\text{O})$ . DRS ( $\lambda_{\text{max}}$  (nm)): 244, 315, 480. This material had an average surface area of ca. 465 m<sup>2</sup> g<sup>-1</sup>.

### 2.5. Representative catalytic conditions

The alkene (1 mmol), acetophenone or bromobenzene (internal standard, 1 mmol), catalyst (1  $\mu\text{mol}$ ) and CH<sub>3</sub>COONH<sub>4</sub> additive (1 mmol) in a acetone/MeOH (450  $\mu\text{l}$ /400  $\mu\text{l}$ ) solvent mixture were cooled to 0 °C. H<sub>2</sub>O<sub>2</sub> (2 mmol) was added by a digitally controlled syringe pump type SP101IZ WPI over 1 h under stirring. 10 min later, the test tube was removed from the ice bath and allowed to warm to room temperature 26  $\pm$  1 °C. The progress of the reaction was monitored by GC-MS, for small samples taken from the reaction mixture. GC analysis of the solution provided the substrate conversion and product yield relative to the internal standard integration. To establish the identity of the epoxide product unequivocally, the retention time and spectral data were compared to those of an authentic sample. Blank experiments showed that without Mn-catalyst or CH<sub>3</sub>COONH<sub>4</sub>, epoxidation reactions do not take place.

## 3. Results and discussion

### 3.1. Synthesis of the materials

Immobilization of the ligands **1** and **2** requires their derivatization which occurs *via* phenolic groups with (3-chloropropyl)-trimethoxysilane (Scheme 1). The propyl-trimethoxysilane moiety

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