Synthesis, characterization, and catalytic activity for thioanisole oxidation of homogeneous and heterogeneous binuclear manganese(II) complexes with amino acid-based ligands

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Abstract A binuclear Mn(II) complex [Mn₂(HL)₂- $(H_2O)_4$], HL = 2-[(2-Hydroxy-benzylidene)-amino]-3-(4hydroxy-phenyl)-propionic acid, has been prepared and characterized by physico-chemical and spectroscopic methods. The results suggest that the amino acid Shiff base ligand is coordinated as a bivalent anion with a tridentate NO2 donor set involving the phenolic and carboxylic acid oxygens and azomethine nitrogen. A heterogenized binuclear manganese catalyst was synthesized by the covalent anchoring of $[Mn_2(HL)_2(H_2O)_4]$ onto a modified silica gel surface, through the reactive (3-chloropropyl)-trimethoxysilane group. The surface properties of the functionalized catalyst were analyzed by physico-chemical and spectroscopic methods. The silica-supported metal complex, $([Mn_2L(HL)(H_2O)_4]/SiO_2)$, catalyzes the oxidation of thioanisole with H_2O_2 , to give the sulfoxide and sulfone. [Mn₂L(HL) (H₂O)₄]/SiO₂ shows lower catalytic activity and turnover number compared to the homogeneous catalyst $[Mn_2^{II}-(HL)_2(H_2O)_4]$. However, the activity of the

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State Key Lab of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China immobilized catalyst remains nearly unchanged after five cycles, indicating that it is truly heterogeneous.

Introduction

The growing applications of sulfoxides have encouraged researchers to delve into new methods for their synthesis. Organic sulfoxides are valuable synthetic intermediates that are employed for the production of a range of chemically and biologically active molecules such as anti-ulcer drugs (proton pump inhibitors), antifungal and anti-atherosclerotic agents. The oxidation of sulfides by different methods provides a straightforward synthetic approach for preparing numerous sulfoxides, and there are several reagents and procedures available for this transformation. Hydrogen peroxide is considered as an ideal 'green' oxidant, due to its absence of toxic by-products [1]. Hence, new oxidative processes based on the activation of H₂O₂ by robust, efficient, and recyclable heterogeneous catalysts have been developed, in view of the disadvantages of homogeneous transition metal catalysts in terms of catalyst recovery and/or reuse affecting the overall economics of the process [2].

Heterogeneous oxidation catalysts are of much current interest because of advantages such as easy handling, product separation, catalyst recovery, and reduced waste [3]. Moreover, in heterogeneous catalysts, mixed inorganic–organic materials are particularly attractive because of the possibility to combine the functional variation of organic chemistry with the thermal stability of an inorganic substrate [4]. Fixation of such complexes by covalent attachment to a functionalized support provides stable heterogeneous catalysts [5]. A simple way to minimize the leaching of the active catalyst in such materials is to anchor polydentate ligands onto the support surface. Recent reports have described the preparation of different heterogeneous forms of transition metal catalysts, based on mesoporous silica [6] and USY zeolite [7], for the catalytic oxidation of thioanisole; however, in spite of good yield and chemoselectivity, a major problem is leaching of the catalyst into solution [8].

Modified Sharpless systems are among the most effective sulfoxidation systems. However, these systems generally give low turnover numbers, low chemoselectivity and require expensive alkylhydroperoxides as oxidants [9, 10]. Thus, it is tempting to look for systems that would combine the high chemoselectivity of Mn-based systems with high turnover numbers [11].

Against this background, we describe here the anchoring of a polydentate amino acid Schiff base manganese(II) complex onto a silica substrate functionalized with (3-chloropropyl)trimethoxysilane. This type of Schiff base complex shows considerable catalytic activity without leaching. These catalysts are efficient and highly selective for oxidation of thioanisole with 30 % aqueous H_2O_2 . Moreover, the manganese complex containing an amino acid Schiff base ligand was characterized by solid-state NMR and magnetic measurements, both before and after immobilization on silica gel.

Results and discussion

Synthesis and immobilization

The Schiff base ligand H_3L was synthesized by the condensation of salicylaldehyde with L-tyrosine in 1:1 molar ratio in methanol [12]. Its manganese complex was prepared with high yield from the reaction of H_3L with an equimolar amount of $Mn(OAc)_2 \cdot 4H_2O$ in dichloromethane. The complex was obtained as a light green powder. The elemental analysis corresponds to the general formula $[Mn_2(HL)_2(H_2O)_4]$, which was further confirmed by spectroscopic and magnetic measurements.

The synthesis of $[Mn_2(HL)_2(H_2O)_4]$ is summarized in Scheme 1. Both H₃L and its complex were immobilized on silica gel using (3-chloropropyl)-trimethoxysilane as a linker, according to the reported method in [13]. Immobilization of the Schiff base and its complex involves reaction of their phenolic groups with (3-chloropropyl)trimethoxysilane (CPTMS) (Schemes 2, 3). Soxhlet extractions of these compounds ensured that only the covalently attached molecules remained on the support.

Characterization

The FTIR spectrum of H₃L does not include bands at 3,245 and 1,745 cm⁻¹, which would be expected for the $v(NH_2)$ and v(C=O) of the starting materials [14]. Instead, a strong



Fig. 1 FTIR spectra of a H_3L , b [$Mn_2(HL)_2(H_2O)_4$], c CPTMS/SiO₂, d H_2L/SiO_2 , e [$Mn_2L(HL)(H_2O)_4$]/SiO₂

band was observed at $1,612 \text{ cm}^{-1}$, assigned to the azomethine v(C=N) linkage [15].

Comparison of the IR spectra of free H₃L and its Mn(II) complex, shown in Fig. 1, provides evidence for the coordination mode of the ligand. The complex shows a band at 1,648 cm⁻¹ which can be assigned to ν (C=N) of the coordinated Schiff base ligand.

In the spectrum of the complex, an extremely broad band at about 3,460 cm⁻¹ is assigned to –OH, possibly involved in intermolecular hydrogen bonding. The $v_{as}(COO)$ is observed at 1,590 cm⁻¹, while $v_s(COO)$ is identified as a medium to strong bond at 1,389 cm⁻¹. Hence, $\Delta v (v_{as}(COO) - v_s(COO))$ is 191–225 cm⁻¹, characteristic of monodentate coordination of the carboxylate group [16]. A medium band at 1,550 cm⁻¹ is assigned to the (Ph–)C–C(=N) bond [17] and is typical of a complex derived from salicylaldehyde [18]. The phenolic (C–O) stretching frequency was observed at 1,247 cm⁻¹ for free H₃L, which was shifted to 1,280 cm⁻¹ in the complex, indicating coordination through phenolic oxygen [19]. Finally, strong to medium bands at ~400 and ~530 cm⁻¹ are attributed to v(M–N)and v(M–O), respectively, for the complex [16].

The infrared spectra of the heterogeneous compounds CPTMS/SiO₂, H₂L/SiO₂, and [Mn₂L(HL)(H₂O)₄]/SiO₂ are very similar and their profile is typical of the silica matrix. Strong bonds at 460 cm⁻¹ correspond to δ (Si–O–Si). A band at 960 cm⁻¹ is due to ν (Si–OH), while the band at 1,090 cm⁻¹ is assigned to ν_{as} (Si–O–Si) [20].

The introduction of the CPTMS onto the SiO₂ (Fig. 1c) led to a number of new bands, such as C–H stretching vibrations at 2,935 and 2,860 cm⁻¹ [21]. The IR spectrum of H₂L/SiO₂, Fig. 1d, shows bands at 2,965, 2,937, and 2,865 cm⁻¹, associated with propyl groups, and other new bands at 1,612, 1,515, and 3,215 cm⁻¹. These suggest that the Schiff base is successfully grafted onto the support. In addition, the IR spectrum of ([Mn₂L(HL)(H₂O)₄]/SiO₂),





Scheme 2 Immobilization of the ligand on a modified silica support



Scheme 3 Preparation of the supported complex [Mn₂L(HL)(H₂O)₄]/SiO₂

Fig. 1e, shows bands at 2,980, 2,933, and 2,904 cm⁻¹, associated with propyl groups, and other new bands at 1,472, 1,517, 1,597, and 1,648 cm⁻¹ are shifted relative to the ligand bands, indicating that the complex is grafted onto the support. Hence, the FTIR characterization confirmed the successful immobilization of the Mn(II) complex.

The liquid- and solid-state NMR spectra of H_3L , CPTMS/SiO₂, H_2L/SiO_2 , and $[Mn_2L(HL)_2(H_2O)_4]/SiO_2$ confirm that the compounds are immobilized on the silica gel surface. Figure 2 shows the ¹H MAS SS NMR spectra for samples of H_3L , $[Mn_2L(HL)_2(H_2O)_4]$, and CPTMS/SiO₂ recorded with a spinning rate of 55 kHz. The use of a "Very Fast" (VF) spinning rate makes it possible to exceed the strength of the homonuclear proton dipolar

coupling. In this way, ¹H MAS NMR spectra of satisfactory resolution were been obtained. The three distinct proton resonances of the $-Si-CH_2CH_2CH_2-$ moiety for CPTMS/SiO₂ are observed at $\delta = 0.69$, 1.35, and 2.98 ppm. The same signals are observed for H₂L/SiO₂ and [Mn₂L(HL)₂(H₂O)₄]/SiO₂ (Fig. 2b, c). For the ¹H MAS NMR spectra of the ligand and its metal complex immobilized on silica, the resonances of the aromatic and imine protons are also visible in the range of 4–12 ppm. Additionally, a ¹H–¹H NOESY experiment for the dipole–dipole interactions between protons in H₂L/SiO₂ was performed and the results are shown in Fig. 3.

¹H–¹H NOESY NMR is suitable for the analysis of long-range contacts between protons. The interactions



Fig. 2 ¹H MAS NMR spectra performed at 55 kHz spinning rate: a CPTMS/SiO₂, b H_2L/SiO_2 , c $[Mn_2L(HL)(H_2O)_4]/SiO_2$

between the Schiff base and CPTMS/SiO₂ protons (labeled in Fig. 3) indicated that the ligand is chemically attached to the silica matrix.

The ¹³C CP-MAS NMR spectra of CPTMS/SiO₂, H_2L/SiO_2 , $[Mn_2L(HL)(H_2O)_4]/SiO_2$, and H_3L recorded with a spinning rate of 8 kHz at ambient temperature are shown in Fig. 4.

The ¹³C CP-MAS NMR spectrum of CPTMS functionalized silica gel is shown in Fig. 4a. For CPTMS/SiO₂, three resonances at 9.47, 26.01, and 46.06 ppm are assigned to the $-Si-CH_2-$, $-CH_2-$, and $-CH_2-Cl$ groups, respectively. Three similar signals are also observed for [Mn₂L(HL)(H₂O)₄]/SiO₂ and H₂L/SiO₂ (Fig. 4b, c). In the ¹³C CP-MAS NMR spectra of the ligand and its complex immobilized on silica (Fig. 4b, c), the resonances of the aromatic and imine carbons are observed, in addition to the expected aliphatic signals. In order to compare the results obtained for the Schiff base grafted to silica, the ¹³C

"Dipolar Dephasing" CP-MAS NMR and standard liquid ¹³C NMR spectra for the pure Schiff base were recorded (Fig. 4d, e, f). Comparison between the ¹³C CP-MAS NMR spectra and ¹³C CP DD MAS NMR spectrum revealed the presence of three quaternary carbon signals. The DD pulse sequence is often used as a spectral editing technique. In the simplest approach, the ¹H decoupler is turned off for ca. 50 us after CP. This is sufficient time for the ${}^{13}C{}^{-1}H$ dipolar coupling to diphase the transverse magnetization of any ¹³C isotope with a directly bonded ¹H isotope. Consequently, CH and CH₂ are effectively suppressed, and only quaternary carbon signals are observed. The comparison of the results of solid-state NMR and standard liquid NMR (Fig. 4d, f) confirmed the structure of H₃L and its manganese complex and chemical bonding of these species to the silica.

Additional and complementary data about the silicagrafted catalyst were obtained from the ${}^{1}\text{H}{-}^{29}\text{Si}$ invHET-COR NMR spectra performed under Very Fast MAS. Pruski and coworkers have recently published a few applications of inverse detected HETCOR NMR experiments under Very Fast MAS in the structural studies of inorganic–organic hybrid materials [22–25]. In our studies, the ${}^{1}\text{H}{-}^{29}\text{Si}$ invHETCOR MAS NMR experiment was especially useful for ${}^{29}\text{Si}$ resonance detection and allowed us to fully assign the spectra of the ligand and complex grafted on silica. The results for [Mn₂L(HL)(H₂O)₄]/SiO₂ are presented in Fig. 5. Additionally, the ${}^{1}\text{H}{-}^{29}\text{Si}$ inv-HETCOR MAS NMR spectra for CPTMS/SiO₂ and H₂L/ SiO₂ are presented in the Supplementary Materials.

It is well known that the spectrum of SiO₂ generally exhibits three resonances at -110, -101, and -92 ppm, corresponding to the Q⁴ [siloxane, (SiO)₄Si], Q³ [single $(SiO)_3Si(OH)$, and Q^2 [geminal silanol. silanol,(SiO)₂Si(OH)₂] sites of the silica framework, respectively [26]. In the case of $[Mn_2L(HL)(H_2O)_4]/SiO_2$, two signals from the Si environment of Q^4 ($\delta = -102.10$ ppm) and Q^3 ($\delta = -100.70$ ppm) are observed. In addition to these two peaks, the sample displays two more peaks at -68.50 ppm, assigned to T^3 [C-Si(OSi)₃], and at -58.50 ppm, attributed to T² [C-Si(OSi)₂(OH)]. The presence of T³ species confirms that the silica gel has been modified by organic moieties [27]. The solid-state NMR results thus provide direct evidence that the hybrid CPTMS/SiO₂ sample consists of a highly condensed siloxane network with the organic group covalently bonded to the silica. Moreover, the dipolar interactions between ¹H nuclei in the ligand and ²⁹Si nuclei on the silica surface are visible. ¹H-²⁹Si correlations associated with Si-CH₂, Si-CH₂-CH₂-, and -CH₂-Cl were present in the ¹H-²⁹Si invHETCOR MAS NMR spectrum (Fig. 5).

This is further substantiated by the atomic absorption (A.A). According to the A.A analysis, the loading of the

Fig. 3 ¹H–¹H NOESY NMR spectrum recorded at 55 kHz spinning rate for H₂L/SiO₂



complex was 1.58 mmol CPTMS/g of silica gel, 0.18 mmol complex/g of silica gel, and 0.36 mmol Mn/g of silica gel.

Plots of $\chi_M T$ and χ_M^{-1} versus $T (\chi_M$ is the molar magnetic susceptibility) of $[Mn_2L(HL)(H_2O)_4]$ are shown in Fig. 6. The magnetic susceptibility measurement was performed in the 1.8–300 K range under 0.1 T applied field on a powdered sample. At room temperature, the $\chi_M T$ value is 9.24 cm³ K mol⁻¹, which is slightly larger than the spinonly value (8.75 cm³ K mol⁻¹) expected for two uncoupled high-spin Mn(II) centers (S = 5/2 and g = 2.0). The $\chi_M T$ value remains almost constant above 200 K, from which it decreases, finally attaining a value of 0.67 cm³ K mol⁻¹ at 1.8 K. This behavior, which is very similar to that of reported dimanganese(II) complexes [28], is characteristic of two high-spin (S = 5/2) Mn(II) centers experiencing weak antiferromagnetic coupling.

The magnetic susceptibilities were fitted between 300 and 20 K (solid line in Fig. 6) by using Eq. 1:

$$\begin{aligned} \vec{H} &= -2J\vec{S}_{1}\vec{S}_{2} \\ \chi_{\rm M} &= \frac{2Ng^{2}\mu_{\rm B}^{2}}{k_{\rm B}T} \frac{e^{2x} + 5e^{6x} + 14e^{12x} + 30e^{20x} + 55e^{30x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x}} \\ &\times (1-\rho) + \frac{Ng^{2}\mu_{\rm B}^{2}S(S+1)}{3k_{\rm B}T}\rho + \text{TIP} \end{aligned}$$
(1)

obtained from the Hamiltonian, where $S_1 = S_2 = 5/2$ and $x = J/k_{\rm B}T$. The best fitting gave $J = -1.70 \text{ cm}^{-1}$ and g = 2.07 with $\rho = 2 \%$ and TIP = $1.5 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$, indicating that the two Mn(II) atoms in the complex are antiferromagnetically coupled.

Therefore, according to the magnetic properties, we conclude that $[Mn_2(LH)_2(H_2O)_4]$ is a binuclear Mn complex.

Catalytic activity studies

The catalytic performance of the complexes was checked for thioanisole oxidation with 30 % aqueous H_2O_2 and the results are listed in Table 1. In this reaction, hydrogen peroxide should be used carefully, due to the possibility of over-oxidation [29]. The effect of different amounts of H_2O_2 was investigated, keeping a fixed amount of thioanisole (1.0 mmol) and catalyst [$Mn_2(LH)_2(H_2O)_4$] (1 mg) in 3 mL of acetonitrile at 60 ± 1 °C. As shown in Table 1 (entries 1–5), the conversion and selectivity drastically increase with the molecular ratio of H_2O_2 to thioanisole, until the ratio is equal to 3. The catalytic oxidation gave 95 % sulfoxide with 3 mmol of H_2O_2 in 120 min (Table 1, entry 4). Higher ratios of H_2O_2 resulted in decreased yield, due to the over-oxidation of the corresponding sulfone. The excess H_2O_2 required in this catalytic system can be Fig. 4 13C CP-MAS NMR spectra of a CPTMS/SiO2, b [Mn2L(HL)(H2O)4]/SiO2, c H2L/SiO2, d H3L. 13C DD CP-MAS NMR spectra of e H3L and 13C NMR spectrum in liquid DMSO-d6 of f H3L



attributed to its decomposition in the presence of the catalyst. A variety of salen complexes [30] are able to catalyze the oxidation of sulfides to sulfoxides with hydrogen

peroxide, but a drawback of these systems is often the use of chlorohydrocarbon solvents or anhydrous H_2O_2 in ethanol as well as over-oxidation to sulfones. Fast NMR regime) of sample

[Mn2L(HL)(H2O)4]/SiO2





Fig. 6 $\chi_M T$ (box) and $\chi_M - 1$ versus T (circle) plots of [Mn2(HL)2(H2O)4]. The solid line represents calculated data, as described in the text

In control experiments without the catalyst, the yield of sulfoxide is low (Table 1, entry 7). Furthermore, when the catalyst was replaced with Mn(OAc)₂·4H₂O, extensive peroxide decomposition was observed and no sulfoxide was obtained (Table 1, entry 8).

Next, the catalytic oxidation was studied in various solvents (Table 2). The catalytic activity decreases in the order acetonitrile (dielectric constant $\varepsilon/\varepsilon_0 = 37.5$) > methanol (32.7) > chloroform (5.5) at 60 °C. Chloroform is not miscible with aqueous H₂O₂ which could also be the reason for low catalytic efficiency in this case. In agreement with studies previously reported in the literature, solvents of high hydrogen bonding capacity, such as methanol, favor the formation of sulfoxide [31]. However, the best performance of the catalyst was observed in acetonitrile, which is therefore the solvent of choice.

The oxidation is significantly influenced by the reaction temperature (Table 3, entries 1-3). The optimum results were obtained at 60 °C; higher temperatures gave lower yields (Table 3, entry 3). It seems likely that higher temperatures facilitate the decomposition of H₂O₂.

These results show that $[Mn_2(LH)_2(H_2O)_4]$ is a good catalyst for the oxidation of thioanisole to the sulfoxide with hydrogen peroxide.

Comparing the homogeneous and heterogeneous systems reveals that the heterogeneous catalyst exhibits lower activity than the homogeneous catalyst (Table 1, entry 9). It seems likely that the use of a supported manganese catalyst in the present case gives rise to additional problems related to the probable dismutation of H_2O_2 by the inorganic support. This would explain why only a few systems based on supported manganese catalysts and H₂O₂ have been reported for oxidation reactions [32]. Similar difficulties were previously encountered for Mn(III) and Mo(IV)-salen complexes immobilized on mesoporous silica gel [3].

In order to investigate the possibility of recycling the ([Mn₂L(HL)(H₂O)₄]/SiO₂) catalyst, it was separated from the reaction mixture by centrifugation after the reaction. The supernatant was decanted, and the solid catalyst was

Table 1 Oxidation of thioanisole by the catalyst $[Mn_2(LH)_2(H_2O)_4]$ and $([Mn_2L(HL)(H_2O)_4]/SiO_2)/H_2O_2$

No.	Sulfoxide/sulfone yield (%) ^a	H ₂ O ₂ :Substrate molar ratio	Sulfoxide selectivity(%) ^b	TON ^c
1	26.4/3.6	1:1	88	187
2	40.5/4.5	1.5:1	90	281
3	55.8/4.2	2:1	93	375
4	95/0	3:1	100	593
5	95/4	4:1	96	619
6	0	0:1	0	-
7	14/25	3:1 ^d	36	-
8	0	3:1 ^e	0	-
9	60/0	3:1	100^{f}	375

Reaction conditions: catalyst ($[Mn_2(LH)_2(H_2O)_4]$) 1 mg (0.0016 mmol catalyst), thioanisole 1 mmol, CH₃CN 3 ml, temperature 60 ± 1 °C, and time 120 min

^a Conversions are based on the starting substrate

^b Sulfoxide selectivity: %sulfoxide/(sulfoxide + sulfone)

^c TON = moles of converted sulfide/moles of catalyst

- ^d Without catalyst
- e Mn(OAC)2·4H2O is used as catalyst

^g Reaction conditions: catalyst (([Mn₂L(HL)(H₂O)₄]/SiO₂)) 9 mg (0.0016 mmol catalyst), substrate 1 mmol, CH₃CN 3 ml, temperature 60 ± 1 °C, and time 120 min

Table 2 Solvent effect on the oxidation of thioanisole with $[Mn2(HL)2(H2O)4]/H_2O_2$

Entry	Solvent	Conv. (%) ^a	Sulfoxide selectivity (%) ^b
1	CHCl ₃	20	90
2	CH ₃ OH	90	99
3	CH ₃ CN	95	100

Reaction conditions: catalyst ($[Mn_2(LH_2O)_4]$) 1.0 mg (0.0016 mmol), MeSPh 1.0 mmol, solvent 3 ml, H₂O₂ 3 mmol, time 2 h, temperature 60 ± 1 °C

^a Conversions are based on the starting substrate

^b Sulfoxide selectivity: %sulfoxide/(sulfoxide + sulfone)

Table 3 Temperature effect on the oxidation of thioanisole with $[Mn2(HL)2(H2O)4]/H_2O_2$

Entry	Temp(°C)	Conv. (%) ^a	Sulfoxide selectivity(%) ^b
1	25	11	60
2	60	95	100
3	80	80	95

Reaction conditions: catalyst $([Mn_2(LH)_2(H_2O)_4])$ 1.0 mg (0.0016 mmol), MeSPh 1.0 mmol, solvent 3 ml, H_2O_2 3 mmol, time 2 h

^a Conversions are based on the starting substrate

^b Sulfoxide selectivity: %sulfoxide/(sulfoxide + sulfone)

washed twice by adding acetonitrile and centrifugation. The used catalyst was then recycled for further reactions, up to five times. No significant loss in the activity of the immobilized catalyst was observed; therefore, recycling is possible in the case of this catalyst.

The stability of the supported catalyst for oxidation of thioanisole was also investigated. In these experiments, the catalyst was separated from the reaction mixture after each experiment by simple filtration, washed with methanol, and dried before use in the subsequent run. After using catalyst for five consecutive times, the oxidation yields were 60 %. The filtrates were collected for determination of Mn leaching. Analysis by atomic absorption method showed no detectable (<0.02 ppm) manganese. Hence, the obtained catalytic results are derived exclusively from the heterogeneous catalyst.

These recycling results are promising when compared to the literature. Heterogeneous Mn(II) catalysts, with acetylacetone-based Schiff base ligands, have been reported for alkene epoxidation with H_2O_2/CH_3COONH_4 [33]. However, they are not stable and could not be recycled. Mn(III)—salen complex immobilized into pillared clays was applied in the heterogeneous epoxidation of styrene with PhIO [34]. Again this system was not very stable, leaching and deactivation took place.

Conclusion

In summary, the present study has described the synthesis of a Schiff base ligand, H_3L , and its Mn_2^{II} complex and immobilization of these two compounds onto a modified silica gel surface. A range of characterization techniques confirm that the metal complex is attached to the silica gel support.

 $[Mn_2(HL)_2(H_2O)_4]$ and $[Mn_2(HL)L(H_2O)_4]/SiO_2$ provide homogeneous and heterogeneous catalysts for oxidation of thioanisole by hydrogen peroxide in acetonitrile. The supported catalyst $[Mn_2L(HL)(H_2O)_4]/SiO_2$ gave low activity and turnover number compared to its homogeneous counterpart. However, the supported catalyst was easily separated from the reaction mixture via filtration and could be recycled for several catalytic runs, without significant loss of activity. This system could be useful for many other base-catalyzed oxidations.

Experimental

All solvents, L-tyrosine, salicylaldehyde (Sal), $Mn(OAc)_2$ · 4H₂O, and MeSPh were purchased from Merck and used as received. Silica gel (0.063–0.200 mm) was purchased from Merck and activated at 550 °C for 6 h before use. Aqueous 30 % hydrogen peroxide (12.5 mol/L) was used and its exact concentration was determined before use by titration with standard KMnO₄. Elemental analyses were determined on a CHN Perkin-Elmer 2400 analyzer. FTIR spectra were recorded on a Perkin-Elmer 597 spectrometer. Manganese contents were determined by a Varian spectrometer AAS-110 spectrophotometer, using a flame approach, after alkali melting of a known amount of the complex in a platinum crucible. The magnetic susceptibility of the complex was measured with a Quantum Design MPMS XL7 magnetometer in the 1.8–300 K range. under 0.1 T applied field. ¹H NMR spectra were recorded on a 250 MHz Bruker spectrometer and a 500 MHz Bruker Avance III spectrometer. The solid-state cross-polarization magic angle spinning (CP-MAS) NMR were obtained on a 400 MHz Bruker Avance III spectrometer, equipped with a MAS probe head using 4 mm ZrO₂ rotors, at a frequency of 100.61 MHz for ¹³C. A sample of ¹³C-labeled tyrosine was used to set the Hartmann-Hahn condition for ¹³C. A sample of Q8M8 was used to set the Hartmann-Hahn condition for ²⁹Si. The acquisition was made with a SPINAL decoupling sequence [35]. The ¹H-²⁹Si HETCOR (with indirect detection of ²⁹Si) experiments were performed using the pulse sequence described by Mao et al. [24]. The following parameters were used: 55 kHz spin rate, proton 90° pulse length of 2.5 µs, first contact time of 9.5 ms, second contact time of 9.5 ms or 200 µs, and proton π pulse (5 µs) in the middle of the evolution period (instead of CW¹H decoupling as mentioned by Ishii and Tycko) [36]. The reaction products of the oxidation were analyzed by an HP Agilent 6890 gas chromatograph, equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m \times 320 μ m \times 0.25 μ m) with flame-ionization detector.

Synthesis of the ligand

A mixture of L-tyrosine (0.36 g, 2.0 mmol) and NaOH (0.08 g, 2.0 mmol) in toluene (10 mL) was added to a solution of salicylaldehyde (0.244 g, 2.0 mmol) in toluene (10 mL) and refluxed for 2 h. The resulting yellow solid was filtered off, washed repeatedly with methanol, and dried in air. Yield 0.50 g (88 %). IR (KBr, cm⁻¹): 3,208 (w) (O-H), 3,026 (w), 2,963 (w), 2,930 (w), 1,612 (vs) (C=N), 1,609 (s), 1,514 (m), 1,455 (m), 1,364 (m), 1,332 (s), 1,245 (s), 1,100 (m), 842 (s), 740 (m), 650 (s), 576 (s), 530 (s), 493 (w), 434 (w). ¹H NMR, 500 MHz, DMSO-d₆, $\delta = 2.77$ (1H, dd, J = 9.0 Hz, J = 13.5 Hz, CH₂, H-2), 3.13 (1H, dd, J = 4.0 Hz, J = 15.0 Hz, CH, H-1), 3.74 $(1H, dd, J = 4.0 Hz, J = 9.5 Hz, CH_2, H-2), 6.56 (2H, d, J)$ J = 8.5 Hz, CH_{Ar}), 6.63 (1H, d, J = 6.5 Hz, CH_{Ar}), 6.69 $(1H, d, J = 8.0 \text{ Hz}, CH_{Ar}), 6.90 (2H, d, J = 8.5 \text{ Hz})$ CH_{Ar}), 7.16–7.20 (2H, m, CH_{Ar}), 8.04 (1H, s, CH = N, H-7), 9.14 (1H, br s, -COOH), 14.29 (1H, br s, OH) ppm. ¹³C NMR, 125.77 MHz, DMSO-d₆, $\delta = 36.96$ (CH₂, C2, overlapped by DMSO), 74.44 (CH, C1), 114.84 (2CH_{Ar},

C5, C5'), 116.30 (CH_{Ar},C12), 117.76 (CH_{Ar}, C10), 117.99 (C_{Ar}, C8), 129.93 (2CH_{Ar}, C4, C4'), 130.23 (C_{Ar}, C3), 131.60 (CH_{Ar}, C9), 132.18 (CH_{Ar}, C11), 155.27 (C_{Ar}, C6), 163.31 (CH=N, C7), 164.50 (C_{Ar}, C13), 171.24 (COOH, C14) ppm. ¹³C CP-MAS NMR, 100.63 MHz, δ = 37.20 (CH₂, C2), 56.53 (CH, C1), 116.90 (2CH_{Ar}, C5, C5'), 118.40 (2CH_{Ar}, C10, C12), 124.10 (2C_{Ar}, C8, C3), 131.2 (4CH_{Ar}, C4, C4', C9, C11), 156.00 (2C_{Ar}, C6, C13, also CH=N, C7), 176.10 (COOH, C14) ppm.

Synthesis of the complex

A mixture of L-tyrosine (0.36 g, 2.0 mmol) and NaOH (0.08 g, 2.0 mmol) in CH₂Cl₂ (10 mL) was added to a solution of salicylaldehyde (0.244 g, 2.0 mmol) in CH₂Cl₂ (10 mL) and refluxed, where upon the colorless solution rapidly turned yellow. The mixture was refluxed for 2 h, then Mn(OAc)₂·4H₂O (2 mmol, 0.498 g) was added and the mixture was stirred under reflux for 5 h. The light green precipitate was collected and washed with methanol and dried in air. Yield: 0.5 g (67 %). Anal. calc. for C₃₂H₃₄Mn₂N₂O₁₀: C, 51.3; H, 4.5; N, 3.7; Mn 14.6. Found: C, 52.9; H, 4.0; N, 3.6; Mn, 15.3 %. IR (KBr, cm⁻¹): 3,424 (br), 3,077 (w), 3,035(w), 2,921 (m), 2,854 (w), 1,648 (vs), 1,589 (vs), 1,549 (w), 1,515 (m), 1,471 (s), 1,444 (s), 1,385 (s), 1,280 (m), 1,187 (m), 823 (m), 757 (s), 526(m), 449 (m).

Grafting of the linker

Anchoring of (3-chloropropyl)-trimethoxysilane on the surface of silica gel was carried out according to the reported method [13]. The light cream powder, CPTMS/SiO₂, was dried at room temperature. Linker loading = 1.16 mmol/g silica gel, IR (KBr, cm⁻¹): 3,429 (br, w), 2,968 (w), 2,935 (w), 2,860 (w), 1,086 (vbr, vs), 821 (vs), 471 (s). ¹H MAS NMR, 600 MHz, $\delta = 0.26$ (protons of silica gel), 0.69 (Si–CH₂–), 1.35 (Si–CH₂–CH₂–), 2.98 (–CH₂–Cl), 5.57 (–OH) ppm. ¹³C CP-MAS NMR, 100.63 MHz, $\delta = 9.47$ (Si–CH₂), 26.01 (Si–CH₂–CH₂–), 46.06 (–CH₂–Cl) ppm. ²⁹Si CP-MAS (as determined in ¹H–²⁹Si HETCOR NMR experiment), 116.22 MHz, $\delta = -110.10$ (Q⁴ [siloxane, (SiO)₄Si]), -102.10 (Q³ [single silanol,(SiO)₃Si(OH)]), -57.40 (T³ [C–Si(OSi)₃]), -50.50 (T² [C–Si(OSi)₂(OH)]) ppm.

Immobilization of the ligand

In a typical synthesis, a mixture of CPTMS/SiO₂ (0.5 g) and LH₃ (0.1 g) was refluxed in toluene for 24 h, followed by Soxhlet extraction with CH₂Cl₂ for 4 h in order to remove adsorbed H₃L. The yellow material, H₂L/SiO₂, was dried at room temperature. H₃L loading = 0.30 mmol/g

silica gel. IR (KBr, cm⁻¹): 3,477 (br, w), 2,935 (w), 2,860 (w), 1,612 (s), 1,084 (vbr, vs), 811 (vs), 653 (m), 577(w), 474 (s); ¹H MAS NMR, 600 MHz, $\delta = 0.26$ (protons of silica gel), 1.36 (Si-CH₂), 2.38 (CH₂–O), 3.81 (CH_{Ar}), 5.97 (CH_{Ar}), 8.18 (–CH=N), 9.46 (–OH) ppm. ¹³C CP-MAS NMR, 100.63 MHz, $\delta = 10.55$ (Si–CH₂), 26.49 (Si–CH₂–CH₂–), 37.06 (CH₂, C2), 47.59 (–CH₂–Cl), 56.95 (CH, C1), 115.51 (2CH_{Ar}, C5, C5'), 118.60 (2CH_{Ar}, C10, C12), 123.96 (2C_{Ar}, C8, C3), 130.99 (4CH_{Ar}, C4, C4', C9, C11), 155.93 (2C_{Ar}, C6, C13, also CH=N, C7), 175.78 (COOH, C14) ppm. ²⁹Si CP-MAS (as determined in ¹H–²⁹Si HETCOR NMR experiment), 116.22 MHz, $\delta = -100.70$ (Q⁴ [siloxane, (SiO)₄Si]), -102.10 (Q³ [single silanol,(SiO)₃Si(OH)]), -60.50 (T³ [C–Si(OSi)₃]), -59.90 (T² [C–Si(OSi)₂(OH)]) ppm.

Preparation of the supported complex

For complex grafting, the functionalized silica gel CPTMS/ $SiO_2(0.5 \text{ g})$ and $[Mn_2(LH)_2(H_2O)_4](0.1 \text{ g})$ were refluxed in CH₂Cl₂ for 24 h, followed by Soxhlet extraction with CH₂Cl₂ for 4 h. The light green material, [Mn₂L(LH)-(H2O)4]/SiO2, was dried at room temperature. Mn loading = 0.36 mmol/g silica gel, Complex loading = 0.18 mmol/g silica gel. IR (KBr, cm^{-1}): 3,428 (br, w), 3,071 (w), 2,930 (w), 2,859 (w), 1,647 (s), 1,597 (s), 1,517 (w), 1,471 (m), 1,446 (m), 1,390 (s), 1,068 (vbr, vs), 825 (vs), 758 (m), 684(w), 472 (s).⁾. ¹H MAS NMR, 600 MHz, $\delta = 0.25$ (protons of silica gel), 1.35 (Si-CH₂), 2.93 (CH₂-O), 3.48 (CH_{Ar}), 5.79 (CH_{Ar}) ppm. ¹³C CP-MAS NMR, 100.63 MHz, $\delta = 7.75$ (Si-CH₂), 24.46 (Si-CH₂-CH₂-), 37.20 (CH₂, C2), 44.07 (-CH2-Cl) ppm. ²⁹Si CP-MAS (as determined in $^{1}\text{H}^{-29}\text{Si}$ HETCOR NMR experiment), 116.22 MHz, $\delta =$ $-104.10 (Q^4 [siloxane, (SiO)_4Si]), -101.40 (Q^3 [single])$ silanol,(SiO)₃Si(OH)]), -60.50 (T³ [C-Si(OSi)₃]), -58.50 $(T^2 [C-Si(OSi)_2(OH)])$ ppm.

General oxidation procedure

Oxidation reactions were carried out under air at 60 ± 1 °C, with acetonitrile as a solvent and aqueous 30 % H₂O₂ (12.5 M) as oxidant. In a typical experiment, a mixture of 1.0 mg as the homogeneous catalyst, 3.0 mL solvent, and 1.0 mmol of the sulfide was mixed in a 25 mL glass flask. After the mixture was heated to 60 °C, H₂O₂ was added. At appropriate intervals, aliquots were removed and analyzed immediately by GC. The oxidation products were identified by comparing their retention times with those of authentic samples. Yields are based on the added substrate and were determined by a calibration curve.

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References

- 1. Hosseinpoor F, Golchoubian H (2006) Tetrahedron Lett 47:5195–5197
- Singla M, Mathur P, Gupta M, Hundal MS (2008) Transit Met Chem 33:175–182
- Ghorbanloo M, Hosseini Monfared H, Janiak C (2011) J Mol Catal A: Chem 345:12–20
- 4. Grigoropoulou G, Clark JH, Elings JA (2003) Green Chem 5:1-7
- 5. Valkenberg MH, Holderich WF (2002) Catal Rev 44:321–374
- Trukhan NN, Derevyankin AY, Shmakov AN, Paukshits EA, Kholdeeva OA, Romannikov V (2001) Microp Mesop Mater 44–45:603–608
- 7. Fuerte A, Iglesias M, S'anchez F, Corma A (2004) J Mol Catal A: Chem 211:227–235
- 8. Arends IWCE, Sheldon A (2001) Appl Catal A Gen 212:175-187
- 9. Fernandez I, Khiar N (2003) Chem Rev 103:3651-3706
- Kagan HB (2000) In: Ojima I (ed) Catalytic asymmetric synthesis, 2nd edn. Wiley-VCH, Inc, New York
- 11. Bryliakov KP, Talsi EP (2007) J Mol Catal A: Chem 264:280–287
- 12. Heinert D, Martell AE (1962) J Am Chem Soc 84:3257-3263
- Huh S, Wiench JW, Yoo J, Pruski M, Lin WSY (2003) Chem Mater 15:4247–4425
- 14. Carlin RL (1965) Transition metal chemistry, 2nd edn. Marcel Decker, New York
- Bellamy LJ (1971) The infrared spectra of complex molecules. Wiley, New York
- Nakamoto K (1986) Infrared and raman spectra of inorganic and coordination compounds. Wiley, New York
- 17. Leadbetter JW (1977) J Phys Chem 81:54-59
- Cavaco I, Costa Pessoa J, Costa D, Duarte MTL, Henriques RT, Matias PM, Gillard RD (1996) J Chem Soc Dalton Trans 1989–1996
- Van Wyk JL, Mapolie SF, Lennartson A, kansso MH, Jagner S (2008) Inorg Chim Acta 361:2094–2100
- Neves A, Erthal SMD, Vencato I, Ceccato AS, Mascarenhas YP, Nascimento OR, Horner M (1992) Inorg Chem 31:4749–4751
- 21. Finocchio E, Macis E, Raiteri R, Busca G (2007) Langmuir 23:2505–2509
- 22. Wiench JW, Avadhut YS, Maity N, Bhaduri S, Lahiri GK, Pruski M, Ganapathy S (2007) J Phys Chem B 111:3877–3885
- Kao HM, Chang PC, Wu JD, Chiang AST, Lee CH (2006) Microp Mesop Mater 97:9–20
- Mao K, Wiench JW, Lin VSY, Pruski M (2009) J Magn Reson 196:92–95
- Azaïs T, Hartmeyer G, Quignard S, Laurent G, Tourné-Péteilh C, Devoisselle F, Babonneau JM (2009) Pure Appl Chem 81:1345–1355
- 26. Parida KM, Singha S, Sahoo PC (2010) J Mol Catal A: Chem 325:40–47
- Jiang D, Yang Q, Wang H, Chen H, Zhu G, Yang J, Li C (2006) J Catal 239:23–29
- Gultneh Y, Tesema YT, Ahvazi B, Yisgedu TB, Butcher RJ, Tuchagues JP (2006) Inorg Chim Acta 359:4463–4469
- 29. Noyori R, Aoki M, Sato K (2003) Chem Commum 1977-1986
- Jeong YC, Choi S, Hwang YD, Ahn KH (2004) Tetrahedron Lett 45:9249–9252
- Choudary BM, Bharathi B, Venkat Reddy Ch, Kantam ML (2002) J Chem Soc Perkin Trans 1:2069–2074

- 32. Rao YVS, De Vos DE, Bein T, Jacobs PA (1997) Chem Commun 355–356
- Gournis D, Louloudi M, Karakassides MA, Kolokytha C, Mitopoulou K, Hadjiliadis N (2002) Mater Sci Eng, C 22:113–116
- 34. Cardoso B, Pires J, Carvalho AP, Kuzniarska-Biernacka I, Silva AR, de Castro B, Freire C (2005) Micropor Mesopor Mater 86:295–302
- 35. Fung BM, Khitrin AK, Ermolaev K (2000) J Magn Reson 142:97–101
- 36. Ishii Y, Tycko R (2000) J Magn Reson 142:199-204