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Activated Carbon Functionalized with Mn(II) Schiff base Complexes as Efficient Alkene Oxidation Catalysts: Solid Support Matters

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Abstract

A new synthetic methodology to covalently anchor Mn^{II} -Shiff-base catalysts onto activated carbon (ACox) has been applied, resulting in heterogeneous Mn^{II} -L@ACox materials. These catalysts are effective and selective towards epoxides with H₂O₂, in the presence of CH₃COONH₄, as co-catalyst, providing TONs equivalent-to/or higher than the homologous Mn^{II} -L@SiO₂ catalysts for certain substrates. Moreover Mn^{II} -L@ACox catalysts are re-usable and kinetically faster than the corresponding Mn^{II} -L@SiO₂ catalysts resulting in considerably higher TOFs. Combining catalytic and EPR spectroscopic data we propose a catalytic reaction mechanism which elucidates the co-catalytic function of CH₃COONH₄ which is of key importance for the successful performance of the studied Mn^{II} -catalysts.



Keywords: catalytic epoxidation; supported complexes; manganese complexes; H₂O₂ activation; activated carbon, D-strain.

1. Introduction

Among the desirable characteristics of a catalyst-support are stability, inertness, reusability, high surface area, porosity and appropriate chemical structure. Among a wide range of support-materials, so far, materials that appear to meet optimally these characteristics optimally are Al_2O_3 , SiO_2 and carbon, mainly activated carbon (AC) [1]. The potential of activated carbon as catalyst support is based on its low-cost and surface chemical properties, which can be tailored appropriately. These features have motivated researchers to immobilize, on AC surface, acetylacetonate-[2-5], Schiff base- [6-8] and salen- [9-11] metal complexes for oxidation catalysis.

So far, heterogenisation of these complexes has been realized via their adsorption or covalent binding on AC surface [2-11]. For covalent attachment of metal complexes, to avoid leaching during catalysis, the oxygen functionalities of AC surface allow application of a range of synthetic strategies: [i] direct attachment of the catalyst either via binding of functional groups derived from the periphery of the ligand [7], or via axial coordination of a metal centre onto phenolate groups of the modified activated carbon [8]. The most applicable method involves the use of bifunctional coupling agents which are able to bridge active groups of both the modified/activated carbon surface and the metal complexes. In this context, diamines [2-5,11] and cyanuric chloride [6,11] have been used as bifunctional binding agents. [ii] in the case of silica based supports, heterogenisation of complexes often is done via reaction of -OH surface silanol groups of SiO₂ with bifunctional organosilanes e.g. to form siloxane bonds. Recently, a similar procedure has been successfully applied for the heterogenisation of a Rh-catalyst on AC with aminosilane as coupling agent [12,13]. This heterogeneous catalyst has been tested for hydrogenation of cyclohexene. Thus, so far aminopropyl-triethoxy silane (APTES) offers a tool to functionalize AC in order to covalently attach an oxidation catalyst on carbon matrices [11]. The silvlation reaction of APTES with multi-walled carbon nanotubes has been investigated recently confirming the binding of alkoxy-moieties to surfacial -OH groups [14]. However, NH₂-groups could also react with carbonyl surface groups of the support resulting in a NH₂-silicon side-polymerization which finally reduces free NH₂-groups desirable for a future catalyst attachment [14]. In the present work, to avoid such drawbacks, we report a novel methodology to modify the AC surface, synthesizing functional ligand-organosilanes> ensuring their attachment

only via their alkoxy-groups with surface –OH of AC. The, so obtained, carbon-based heterogeneous catalysts have been evaluated as catalysts for alkene epoxidation.

In our previous works, we have exploited the surface properties of silica for covalent immobilization of Mn(II)-Shiff base ligands for alkene epoxidation with H_2O_2 (Scheme 1) [15, 16]. In general, the development of efficient heterogenised manganese catalysts that incorporate H_2O_2 has limitations due to competitive H_2O_2 dismutation by both the Mn-center (catalase-type-activity) and the SiO₂. The catalytic efficiency of the heterogenised catalysts reported in [15, 16] was shown to be switched-on by CH₃COONH₄ achieving remarkable effectiveness and selectivity towards epoxides providing 150-900 TONs and 10 h⁻¹-50 h⁻¹ TOFs. Nevertheless, these catalysts were not recyclable [16].

Insert Scheme 1

In the literature there are very few examples of Mn-based oxidation catalysts immobilized on activated carbon; their anchoring has been achieved either *via* adsorption [9,10,17], axial coordination to support [8, 18] or covalent attachment [11]. They have been evaluated for alkene oxidation using PhIO and NaOCl as oxidants, nevertheless, with rather poor efficiency, i.e. 0.1-47 TONs and 0.1 h^{-1} -11 h^{-1} TOFs. In the present work, we show that covalently anchored Mn(II)-Shiff base catalysts onto AC by the novel method described herein, achieve significant TONs and TOFs, and are recyclable.

The main findings of the present work are: (i) the AC-anchored Mn-catalysts are effective and selective towards epoxides, and, moreover (ii) they are re-usable and kinetically faster than the corresponding SiO₂-based catalysts which may be a considerable advantage in using such catalysts. Electron Paramagnetic Resonance [EPR] has been also used to study the coordination environment of the heterogeneous Mn-catalysts and the interaction between the active catalyst centre and the activated carbon support.

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 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 analyzer. 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 Brucker ER200D spectrometer at liquid N₂ temperature, equipped with an Agilent 5310A frequency counter. The spectrometer was running under a home-made software based on LabView. Thermogravimetric analyses were carried out by Shimadzu DTG-60 analyser using a heat rate of 5 K min⁻¹ and a flow rate of synthetic air carrier gas of 50 cm³ min⁻¹. 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 N₂ 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/Po) range of 0.05-0.30 and assuming a closely packed BET monolayer. H_2O_2 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).

Ligand Synthesis. Ligands L1 and L2 have been synthesized and characterized by the methods detailed in our recent works [15,19].

Oxidation of activated carbon. 5 gr of activated carbon (**AC**) was refluxed with 90 ml 65% v/v HNO₃ for 6h. The oxidized carbon (**ACox**) obtained was separated by filtration, washed exhaustively with distilled water until pH~7 and dried under reduced pressure at 40 °C for 12 h. DRIFTS-IR (cm⁻¹, selected peaks): 2955, 2869: v(C-H); 1708: v(C=O); 1586: v(C=C); 1251, 1214: v(C-O). Thermal analysis: the derivative thermogram of **ACox** shows a broad peak in the range of 130-420 °C assigned to the decomposition of –COOH surface groups with a 10.2 % weight loss

and an intense peak at 600 °C assigned to the combustion of carbon support. The observed weight loss of **ACox** sample in the temperature range of 20-700 °C was 100%. The formed –COOH groups are *ca*. 2.2 mmol g⁻¹ determined by thermogravimetric and elemental analysis. The **ACox** had an average surface area of *ca*. 687 m² g⁻¹, listed in Table 1.

Synthesis of Organosilane-ligands. (a) synthesis of organo-silanes L1-OS and L2-OS. 1.2 mmol of L1 or L2 and 1.0 mmol of (3-glycidyloxypropyl)trimethoxysilane or (3-chloropropyl)-trimethoxysilane respectively were stirred for 48 h in 10 ml of MeOH under N₂ at 60 °C in order to generate L1-OS and L2-OS silaneprecursors. (b) formation of modified carbon materials. The L1@ACox and L2@ACox materials were prepared through co-condensation of L1-OS or L2-OS precursors with the –OH functional groups of oxidised carbon ACox. Accordingly, 0.5 g oxidised carbon ACox and 5 ml EtOH were added to the precursor L1-OS or L2-OS solution, and the resulting slurry was stirred at 60 °C for 24 h. The obtained solids, L1@ACox and L2@ACox, were washed several times with MeOH and EtOH and dried under vacuum at 60 °C for 12 h.

L1@ACox: DRIFTS-IR (cm⁻¹, selected peaks): 2943, 2866: v(C-H); 1686: v(C=O); 1660: v(C=N); 1587, 1495: v(C=C); 1209: v(C-O). Thermal analysis provides a weight loss of 14.5 %, see Table 1, assigned to the decomposition of the anchored organic ligand **L1**. This material showed an average surface area of *ca*. 45 m² g⁻¹, see Table 1.

L2@ACox: DRIFTS-IR (cm⁻¹, selected peaks): 2962, 2873: v(C-H); 1690: v(C=O); 1663: v(C=N); 1587: v(C=C); 1215: v(C-O). Thermal analysis shows a weight loss of 20.3 % corresponds to the decomposition of the anchored organic ligand **L2**. This material had an average surface area of *ca*. 75 m² g⁻¹.

Anchoring of Mn-complexes. (a) organo-silanes metalation. The L1-OS and L2-OS silane-precursors were formed according to the procedure described in the previous paragraph. Then after cooling at room temeperature (26⁰C), 1.2 mmol of MnCl₂.4H₂O in 10 ml MeOH, were added to this solution. The obtained solution was stirred overnight at room temperature leading to metalated precursors Mn^{II}-L1-OS and Mn^{II}-L2-OS. (b) formation of carbon-based materials. The Mn^{II}-L1@ACox and Mn^{II}-L2@ACox materials were prepared through co-condensation of Mn^{II}-L1-OS or Mn^{II}-L2-OS precursors with the –OH functional groups of oxidised carbon ACox.

For this, 0.5 g oxidised carbon ACox and 5 ml EtOH were added to the precursor Mn^{II}-L1-OS or Mn^{II}-L2-OS solution, and the resulting slurry was stirred at 60 °C for 24 h. The filtered solids, herein called Mn^{II}-L1@ACox and Mn^{II}-L2@ACox, were washed several times with MeOH and EtOH and dried under vacuum at 60 °C for 12 h.

Mn^{II}-L1@ACox: Metal loading: 0.30 mmol g⁻¹. DRIFTS-IR (cm⁻¹, selected peaks): 2941, 2871: v(C-H); 1690: v(C=O); 1665: v(C=N);1587, 1493: v(C=C);1214: v(C-O). Thermal analysis provides a weight loss of 18.5 %, see Table 1, assigned to the decomposition of the anchored organic ligand L1. This material showed an average surface area of *ca*. 2 m² g⁻¹, see Table 1.

Mn^{II}-L2@ACox: Metal loading: 0.40 mmol g⁻¹. DRIFTS-IR (cm⁻¹, selected peaks): 2962, 2873: v(C-H); 1693: v(C=O); 1665: v(C=N); 1587: v(C=C);1215: v(C-O). Thermal analysis shows a weight loss of 20.4 % corresponds to the decomposition of the anchored organic ligand **L2**. This material had an average surface area of *ca*. 21 m² g⁻¹. All parameters are listed in Table 1.

Catalytic Conditions. The catalytic experiments were performed in acetone/MeOH (450 µl /400 µl) solvent mixture containing alkene (as substrate, 1 mmol), acetophenone or bromobenzene (as internal standard, 1 mmol), catalyst (1 μ mol of Mn-complex) and CH₃COONH₄ additive (1 mmol). H₂O₂ (2 mmol) was added by a digitally controlled syringe pump [SP101IZ WPI] over 30 min to the catalytic solution. This corresponds to [catalyst : H_2O_2 : alkene : CH_3COONH_4] = [1:2000:1000:1000 µmol]. 1 µmol of Mn^{II}-L1@ACox and Mn^{II}-L2@ACox weights 5 mg and 6 mg respectively based on the catalysts' loading and their molecular weights. The total volume of the catalytic reaction was 1 ml. Reactions were complete within 5 h for Mn^{II}-L1@ACox and within 1.5 h for the Mn^{II}-L2@ACox catalyst. The progress of the reaction was monitored by GC-MS, for 20µl samples periodically taken from the reaction mixture. Quantitative analysis of the GC data was done by comparing the integrals of the GC peaks vs. the internal standard integral, thus providing the substrate conversion and product yield. When alcohol and ketone are detected as allylic oxidation products, the sample was treated with PPh₃ and measured again by GC-MS according to Shul'pins' procedure [20]. To establish the identity of the epoxide product unequivocally, the retention time and spectral data were compared to those of commercially available compounds. Blank experiments showed

that without Mn-catalyst or CH₃COONH₄, oxidation reactions do not take place. Control experiments were performed to substantiate that the observed catalytic results are derived by the heterogeneous catalysts e.g. no leaching of the active component or demetallation occurs during the catalytic processes. Thus, in typical catalytic experiments, a) the solid catalysts were filtered after 1 h of reaction and b) the catalytic reaction of the filtrate's solution was monitored by GC [16]. The data showed that no evolution of the studied reactions was observed in the filtrate ensuring that no leaching of the active supported Mn(II)-component occurs.

Recycling experiments. For recycling experiments, the heterogeneous catalysts were tested with cyclohexene as substrate, for [catalyst:H₂O₂:cyclohexene:CH₃COONH₄] = [1:2000:1000:1000 μ mol], using the experimental conditions of the catalytic experiments described above. After the end of each oxidation reaction, 5 h for reactions catalysed by **Mn^{II}-L1@ACox** and 1.5 h for reactions by the **Mn^{II}-L2@ACox**, the solid catalyst was separated from the reaction mixture by centrifugation, washed three times with MeOH and dried under vacuum (40 °C, 12 h). The mass of the recovered solid was estimated by mass-weighting. Importantly, we underline that in reuse experiments, it has to be ensured that exactly the same mass of solid is used in each cycle. In our experiments this was done for every material by running 5 identical catalytic batches followed by washing/drying as detailed above. Thus for the next use we could weigh exactly 5 or 6 mg of each material. Subsequently the recovered solid catalyst was reused for a new oxidation reaction under the same catalytic conditions.

Simulation of the EPR spectra: Numerical calculations of EPR spectra for ${}^{55}Mn^{2+}$ (S=5/2, I=5/2) were performed assuming a Spin Hamiltonian has the form:

$H = g\beta B \cdot S + S \cdot D \cdot S + I \cdot A \cdot S \qquad [1]$

where the first term is the Zeeman energy, the following two are the zfs (zero-field splitting) interaction determined by D and E, the axial and rhombic zfs tensor parameters respectively, the last term is the manganese hyperfine interaction. The six main lines resolved in the EPR spectra centered at g=2.0, indicate that the zfs (parametrized by D) of the Mn^{II}-complex is relatively small $|D| \ll g\beta B_0$ (where the resonant microwave quantum energy, hv, at X-band is ≈ 0.33 cm⁻¹). The numerical spectra were calculated using the EasySpin software version 4.5.5, running in a

desktop computer [21]. After a systematic survey, we found that the spectral lineshapes of our Mn-catalysts are determined by the value of the zero-field parameter *D* in combination with *D*-strain. The notion of *D*-strain can be understood as follows: small variations in metal–ligand coordination, bond-lengths/angles/strength may result in a distribution of orbital energy levels, and in turn, a distribution in the zero-field splittings, referred to as *D*-strain [22]. In our calculations *D*-strain was allowed to span values between 20-200Gauss.

3. Results and discussion

Synthesis of the catalysts: The methodology applied here for anchoring of Mn^{II} -L1 and Mn^{II} -L2 catalysts onto activated carbon uses silvlation reaction of silaneprecursors, depicted in Scheme 2 (A and B). The key concept of the present method is, first, a reaction of bifunctional, commercially available, alkoxy-silanes with our ligang L1 or L2 producing a <L-silane> precursor which has the alkoxy-moiety intact, and, second, silvlation reaction of the so obtained <L-silane> with the surfacial –OH groups of the activated carbon. This stepwise procedure avoids putative undesirable side-reactions of bifunctional alkoxy-silanes with the activated carbon surface groups.

Overall, the present synthetic procedure involves: (i) oxidation of the activated carbon AC with concentrated HNO₃; (ii) derivatization of the ligands L1 and L2 to form <silane-L1>, <silane-L2> compounds; (iii) their metalation with Mn^{II} -ionic salts; and (iv) anchoring of the metalated silane-precursors <silane-L-Mn> to the oxidised activated carbon ACox.

Derivatization occurs *via* reaction of L1 and L2 with (3-glycidyloxypropyl)- or (3-chloropropyl)-trimethoxysilane to generate L1-OS and L2-OS silane-precursors respectively. Subsequently, their metalation results in Mn^{II} -L1-OS and Mn^{II} -L2-OS. The propyl-trimethoxysilane moieties of Mn^{II} -L1-OS and Mn^{II} -L2-OS allows their covalent attachment on the oxidize carbon ACox surface via hydrolysis and co-condensation with the –OH functionalities of the ACox.

Insert Scheme 2

Alternatively, if the metalation step is detoured, the modified materials L1@ACox and L2@ACox are obtained which bear the ligands L1 and L2 covalently attached onto the ACox. However, we found that, that metalation of L1@ACox and L2@ACox materials with Mn^{II}-compounds results in totally inactive materials in

catalytic epoxidations. This is attributed to Mn^{II} -spoliation by the free –COOH groups of the **ACox** blocking the desirable Mn^{II} -complexation with the ligands **L1** and **L2** in order to form the active catalytic centre.

The DRIFTS-IR spectra of the Mn^{II} -L1@ACox and Mn^{II} -L2@ACox show several bands corresponding to various structural units of the solid support as well as from the ligands L1 and L2. More specifically, the bands at 1690 and 1693 cm⁻¹ are attributed to v(C=O) stretching vibrations while the bands observed for both samples, at ~1665 cm⁻¹ are attributed to the v(C=N) stretching of the organic ligands. These vibrations are clearly shifted when compared with the non-metalated materials L1@ACox and L2@ACox indicating coordination of the Mn^{II} with the iminenitrogen and keto-oxygen of the attached ligands L1 and L2 [15,16].

The derivative thermogram for $\mathbf{Mn^{II}}$ -L1@ACox shows a 28.7 % weight loss, in the range 130-400 °C, which corresponds to a loss of anchored organic moieties and surface oxidised functionalities. Taking into account that the parent ACox material bears 10.2 % [w:w] –COOH surface groups which are decomposed in the same temperature region, the additional weight loss of 18.5% is assigned to the decomposition of the anchored organic ligand L1. The ligand-loading achived is *ca*. 0.30 mmol g⁻¹, listed in Table 1. The thermogram exhibits also an intense peak at 460 °C assigned to the combustion of carbon support which is shifted to lower temperature for the modified material $\mathbf{Mn^{II}}$ -L1@ACox. The total weight loss of $\mathbf{Mn^{II}}$ -L1@ACox observed in the temperature range of 20-700 °C where all the carbon has been combusted was 95.8%. The obtained solid residue of 4.2% corresponds to SiO₂ and MnO₂ oxides, identified by IR spectroscopy with comparison to reference SiO₂ and MnO₂ samples. Since the Mn-loading determined by FAA spectroscopy found to be 0.30 mmol g⁻¹ (2.6%), it allows us to calculate Si-loading of 0.27 mmol g⁻¹.

The derivative thermogram for $\mathbf{Mn^{II}}$ -L2@ACox exhibits a 30.6% weight loss in the range of 130-400 °C, which is assigned to a loss of anchored organic moieties and surface oxidised functionalities. Since the parent ACox material bears 10.2 % [w:w] – COOH surface groups, which are decomposed in the range of 130-400 °C, the difference weight-loss of 20.4 % corresponds to the decomposition of the anchored organic ligand L2 resulting in ligand-loading of 0.45 mmol g⁻¹, see Table 1. The thermogram shows also an intense peak at 450 °C that resembles that of the parent

sample **ACox**, but with the maximum shifted to lower temperature for the modified material **Mn^{II}-L2@ACox**; this peak is assigned to the combustion of the carbon support. The observed weight loss of **Mn^{II}-L2@ACox** sample in the temperature range 20-700 °C was 93.8 %. The solid residue, SiO₂ and MnO₂, corresponds to 6.2 %. Taking into account that Mn-loading determined by FAA spectroscopy found to be 0.40 mmol g⁻¹ (3.5%), the Si-loading achived is *ca*. 0.45 mmol g⁻¹. All these data are summarised in Table 1.

Insert Table 1

Noticeably, after grafting, the resulting material shows a dramatic collapse of the specific surface area, see BET values in Table 1. This shows that the Mn^{II} -L@ACox hybrids should be conceptualised as compact blocks of compacted carbon layers with practically zero porosity. Thus all the grafted Mn-L centers are localised on the surface of the particles, since there are no pores available, thus making them readily accessible to the catalytic substrate and the oxidant. As we argue in the following this, characteristic might be correlated with the observed dramatic acceleration of the catalytic performance of the Mn^{II} -L@ACox catalysts e.g. compared with the Mn^{II} -L@ACox catalysts e.g. compared with the Mn^{II}-L@ACox catalysts

Catalytic Epoxidation with H_2O_2 : To evaluate the catalytic behaviour of the prepared catalysts, oxidations of several alkenes have been carried out at room temperature. As shown before for the parent homogeneous systems and the corresponding silica-based heterogeneous systems [15-16,19], the present carbon-based heterogeneous catalysts required also ammonium acetate as additive to generate efficient catalytic system.

Catalytic Yield and TONs: According to Table 2, epoxidation of a wide range of olefins proceeds with high conversion and selectivity for the epoxide product (the mass balance is 98-100%) in most of the cases (Table 2). For example, oxidation of cyclooctene provides a 100% selectivity for *cis*-cyclooctene epoxide with 61.0% and 52.0% yield and 100% m.b. catalysed by **Mn^{II}-L1@ACox** and **Mn^{II}-L2@ACox** respectively (see Figure 1). Cyclohexene achieves moderate epoxide yields, ranging from 45.6 to 56.0% catalysed by **Mn^{II}-L1@ACox** and **Mn^{II}-L2@ACox** respectively. In the case of **Mn^{II}-L1@ACox**, allylic oxidation has also occurred in some extent,

with the formation of 2-cyclohexene-1-ol and 2-cyclohexene-1-one. It is noticed that the detected amounts of 2-cyclohexene-1-ol and 2-cyclohexene-1-one are identical to that for PPh₃-treated sample following the Shul'pins' procedure [20]. This indicates that if any hydroperoxide has been formed, as primary-product, this has been completely transformed into the alcohol- and ketone-oxidation products [20, 23]. Hexene-1 is a rather hard oxidation substrate showing epoxide yields 7.6 and 8.5% and selectivity 100% for the *cis*-epoxide.

Insert Table 2 Insert Figure 1

Styrene oxidation produces only epoxide (100% selectivity) with 42.4% and 47.6% yields. The catalysts showed analogous ability towards the oxidation of *trans*β-methylstyrene (51.0 and 38.3% epoxide yield by Mn^{II} -L1@ACox and Mn^{II} -L2@ACox respectively). The major products detected from oxidation of limonene, were two epoxides (cis- and trans-) derived from epoxidation of the electron-rich double bond in 1,2-position. Additionally, small amounts of products formed by allylic oxidation of the limonene ring have been observed. These were identified as the corresponding derivatives of cyclohexene-1-ol and cyclohexene-1-one. Epoxides derived from the more accessible but less electron-rich double bond in 8,9-position have not detected. The total yield of 1,2-epoxides was 76.7% and 64.9% catalyzed by Mn^{II}-L1@ACox and Mn^{II}-L2@ACox respectively. The corresponding cyclohexene-1-ol was detected from 12.9-14.5% and the corresponding cyclohexene-1-one 0.8% in the case of Mn^{II}-L2@ACox. Thus, the epoxidation was clearly the main reaction path resulting mainly in 1,2-epoxides (see Table 2, Figure 1). In the oxidation of cisstilbene catalysed by Mn^{II}-L1@ACox, the major product was *cis*-epoxide with selectivity of 80% and yield 40.5%, while considerable amounts of trans-stilbene epoxide (11.0%) has been also detected. Oxidation of *cis*-stilbene catalysed by Mn^{II}-L1@ACox provides only *cis*-epoxide with 50.1 % yield and 100% selectivity.

When we compare the TONs achieved by the present carbon-based heterogeneous catalysts Mn^{II} -L1@ACox and Mn^{II} -L2@ACox *vs.* the corresponding silica-based heterogeneous catalysts Mn^{II} -L1@SiO₂ and Mn^{II} -L2@SiO₂ we notice that Mn^{II} -L1@ACox achieves TON's equivalent-to/or for certain substrates (e.g. cyclohexene) outcompetes Mn^{II} -L1@SiO₂ (Table 1 and Figure 2A). On the other hand Mn^{II} -L2@ACox is equivalent-to/or outcompetes Mn^{II} -L2@SiO₂ for certain substrates (e.g. cis-stilbene, *trans*- β -methylestyrene) (Table 1 and Figure 2B).

Insert Figure 2

Catalytic Kinetics, TOFs: The oxidation reactions catalysed by the carbon-based catalysts were much faster than those catalysed by the corresponding silica-based catalysts. Reactions catalysed by Mn^{II} -L1@ACox were practically accomplished within 5 h and reactions catalysed by Mn^{II} -L2@ACox were accomplished within 1.5 h. For comparison, reactions catalysed by the corresponding silica-based Mn^{II} -L1@SiO₂ and Mn^{II} -L2@SiO₂ catalysts were accomplished within 24 h and 18 h respectively [15,16]. Taking into account these data, the carbon-based heterogeneous catalysts show remarkably higher TOFs vs. the corresponding silica-based catalysts (Figure 3A and B).

Insert Figure 3

Moreover, the present carbon-based heterogeneous catalysts show even higher TOFs than the corresponding homogeneous systems: for homogeneous Mn^{II} -L1 catalyst, TOFs ranged from 7.9 h⁻¹-30 h⁻¹ [15], while TOFs 15 h⁻¹-182 h⁻¹ (present data, see Table 2) were achieved by Mn^{II} -L1@ACox; in a similar way, the homogeneous Mn^{II} -L2 system showed TOFs from 54 h⁻¹-257 h⁻¹ [19], while Mn^{II} -L2@ACox achieves TOFs 57 h⁻¹-519 h⁻¹ (Table 2). This clearly reveals that the activated carbon support ACox has a beneficial influence on the anchored Mn-catalysts studied herein, by decreasing dramatically the reaction time. We notice that -after grafting- the resulting ACox shows a dramatic collapse of the specific surface area e.g. from 687 m²g⁻¹ becomes 2 m²g⁻¹ and 21 m²g⁻¹ for Mn^{II}-L1@ACox and Mn^{II}-L2@ACox materials respectively. Thus Mn^{II}-L@ACox hybrids consist of compacted carbon layers with practically zero porocity (Scheme 3), which renders all the grafted Mn-L active catalytic centers readily accessible to H₂O₂/CH₃COONH₄ and substrate. This characteristic could be correlated with the observed dramatic acceleration of the catalytic performance of the Mn^{II}-L@ACox catalysts.

Insert Scheme 3

Catalyst Recycling: The recyclability of the heterogeneous Mn^{II} -L1@ACox and Mn^{II} -L2@ACox catalyst was examined by repeated recovering and reusing of the solid catalyst for the oxidative catalysis of cyclohexene. A [catalyst:H₂O₂:substrate]=[1:2000:1000] molar ratio was used in an acetone/MeOH (450 µl /400 µl) solvent mixture. After each catalytic run, the catalyst was recovered

by centrifugation, washed, dried and reused under the same experimental conditions as in Table 2. The catalytic data for Mn^{II}-L1@ACox and Mn^{II}-L2@ACox are displayed in Figure 4.

Insert Figure 4

According to Figure 4, **Mn^{II}-L1@ACox** presented very good reusability i.e., <7% loss of the catalytic activity during the 2nd run and ~35% loss of the activity for each of the following runs, that is, it worked with one third of its activity in a 4th reuse. In total, **Mn^{II}-L1@ACox** provided more than 2000 TONs for cyclohexene oxidation. **Mn^{II}-L2@ACox** presented analogous reusability and worked with 35% of its activity in the 4th catalytic run. Thus **Mn^{II}-L1@ACox** and **Mn^{II}-L2@ACox** are more stable than the corresponding silica-based **Mn^{II}-L1@SiO₂** and **Mn^{II}-L2@SiO₂** catalysts indicating that activated carbon support **ACox** protects the catalyst centers against oxidative destruction.

Mechanistic Studies: [A] Redox: The time-course profiles of the Mn^{II} -L1@ACox- and Mn^{II} -L2@ACox-catalysed oxidations of cyclohexene, in conjunction with the observed redox potential of solution E_h (versus standard hydrogen electrode SHE) are shown in Fig. 5. At the beginning of the reaction catalysed by Mn^{II} -L1@ACox, E_h was +372 mV; after 1h, it dropped at +300 mV with a 45.7% total oxidation yield and finally, after 5 h reaction time, it approached a E_h =+279 mV with a 60.5% yield. In the case of Mn^{II} -L2@ACox-catalysed oxidation, at t=0, E_h was +394 mV, then decreased to +273 mV (t=1 h), providing a product yield of 49%, then E_h =+265 mV (t=1.5 h) with a 56% cyclohexene epoxide formation. Similar time course profiles of the carbon-based catalysts have been observed for all the substrates used herein.

Insert Figure 5

The present redox data show that during these catalytic reactions oxidative equivalents are consumed in both systems. Interestingly, the kinetics of E_h evolution correlate with the kinetics of the catalysis i.e. the **Mn^{II}-L1@ACox** system accomplishes the catalytic reactions within 1.5 h while **Mn^{II}-L2@ACox** needs 5 h. This shows that the same rate limiting steps are implicated in the redox events and in catalysis.

[B] EPR spectroscopy: The EPR spectrum of **ACox** powder material bears radical signals at $g\sim2$ whose linewidth (Δ H=8 Gauss and $g_{iso}=2.0024$) are characteristic of

radicals (S=1/2) in amorphous carbon matrices with mixed sp^2/sp^3 hybridization [24-26]. Spin counting using DPPH as spin standard [24-26] shows that the materials contain 110±20 µmoles of C-based radicals per gram of material. We underline the acid-treated **ACox** powder was free of any EPR-detectable paramagnetic impurities i.e. such as adventitious Fe^{III} or Mn^{II} (data not shown).

Figure 6 shows 77K EPR spectra of $\mathbf{Mn^{II}}$ -L2@ACox material in 1:1 acetone:MeOH. Spectrum (a) is the EPR for $\mathbf{Mn^{II}}$ -L2@ACox in the presence of 20µM H₂O₂ (E_h=360mV vs. SHE). The lineshape is typical for mononulcear $\mathbf{Mn^{2+}}(S=5/2, I=5/2)$ centres with well resolved allowed ⁵⁵Mn(S=5/2, I=5/2) hyperfine splittings e.g. due to the well understood m_I dependence of the Mn⁵⁵-splittings [27-29]. Noticeably the Mn^{II}-L2@ACox material bears no-radical EPR signals. This shows that grafting of the Mn^{II}-L2 complexes results in quenching of all surface radicals. This may be correlated with the observed structural modification e.g. compacting of the carbon matrix after grafting as evidenced by the collapse of the specific surface area, see BET values in Table 1.

The EPR lineshape for the Mn^{II} -L2@ACox material is comparable to the EPR spectrum analyzed previously by our group [19] for the homogeneous Mn^{II} -L2 complex as well as for the Mn^{II} -L2@SiO₂ heterogeneous catalyst [16]. The *A* and *D* values for **Mn^{II}**-L2@ACox derived by computer simulation are A=-94Gauss, D=161 Gauss material, are comparable with the those previously reported for the homogeneous **Mn^{II}**-L2 complex [19] indicating that the grafting protocol that we describe herein resulted in successful attachment of the Mn-L2 complex on the ACox matrix.

Insert Figure 6

To better understand the structural significance of the spectral change observed in Figure 6, we refer to the theoretical EPR spectra that are pertinent for our systems studied herein. Figure 7A shows that for a *D*-strain=200Gauss, the EPR spectral features are sensitive to the *D*-value in when $D \ge D_{\text{-strain}}$. Physically, this corresponds to Mn^{II} complexes where the local ligand field shows strong heterogeneity.

Insert Figure 7

The theoretical spectra in Figure 7 reveal that for high *D*-strain systems, by increasing the zero-field splitting parameter *D*, the spectrum undergoes two main changes [i] the

outermost low-field and higher-field transitions are decreasing faster than the other peaks. [ii] a broad bump [marked by the dashed lines and the vertical arrows] is shifting downfield proportionally to the increasing D-value.

The effect of D on the relative intensities of the m_I-transitions of 65 Mn²⁺(S=5/2, I=5/2) has been originally analyzed by Allen [29], who suggested a quite useful practical rule based on the intensity ratio $I_{5/2}/I_{3/2}$ to get a reasonable estimate of D with no use of computer simulations. Our present full-numerical calculations reveal that D-strain may strongly affect the line intensities. On the other hand the observation of the lowfield bump may serve as a practical diagnostic tool for the variations in D-value is systems with non-negligible D-strain. A full-detailed discussion of the spin physics of this effect is out of the scope of the present paper, and will be analyzed in another publication. Here, we focus on the use of the experimental EPR spectra, shown in Figure 6, to understand the evolution of the Mn-coordination during the catalytic cycle. Accordingly, after addition of the co-catalyst CH_3COONH_4 , at t=1min, the spectral changes i.e. decrease of the outermost sharp features at high- and low-field, as well as the downshift of the low-field bump [see zoomed inset in figure 6], are attributed to an increase of D to 185Gauss. Then at reaction times t=5min up to 30min, the Mn²⁺ spectral intensity decreases monotonically, indicating formation of higher-oxidation Mn-states, as observed previously for the homogeneous Mn-L2 system under similar conditions [19]. After t=30min the Mn spectrum remains unaltered. Importantly, at close inspection of the t=30min spectrum shows that this is similar to the initial spectrum before addition of the co-catalyst.

These observations are interpreted as follows:[1] addition of H_2O_2 only, causes small- structural changes on the ligand field around the Mn^{2+} center, however nocoordination or-redox advancement takes place. Thus, no catalytic evolution takes place and the EPR spectrum remains unchanged (data not shown). [2] Addition of the CH₃COONH₄ triggers a more important structural modification of the ligand field around the Mn center e.g. increase in *D*, thus increase in ligand field strength. Now the loss of Mn^{II} signals indicates rapid evolution towards Mn³⁺/Mn⁴⁺ states, becoming EPR undetectable, and this results in decrease of the Mn²⁺ EPR intensity. [3]. Centres that did not interact with H₂O₂/CH₃COONH₄ remain unchanged/inactive thus, at 30min their spectrum is the only part resolved in the EPR spectrum. The EPR data show that these centers account for 20% of the total Mn²⁺ present.

Thus CH₃COONH₄ plays a multiple role in the Mn^{II}/H_2O_2 system, as reported many times previously [15-16, 19, 30-32]. This can be attributed to a dual acid-base role for CH₃COONH₄ able to act as proton-donor and proton-acceptor [19]. An analogous beneficial role of CH₃COONH₄ has been clearly demonstrated in Mn-Porphrin/H₂O₂ systems also [20, 33-34].

Herein, taking into account all the data we suggest a catalytic mechanism, schematically depicted in Scheme 4, as follows: [i] CH_3COO^- abstracts proton from H_2O_2 promoting its coordination to Mn^{II} and formation of Mn^{II} -OOH species (Scheme 4) and b) [ii] subsequently, NH_4^+ , by acting as a proton-donor to Mn^{II} -OOH, accelerates heterolytic O-O cleavage forming the active $Mn^{IV}=O$ species which [iii] catalyzes alkene epoxidation (Scheme 4).

Insert Scheme 4

4. Conclusion

A new synthetic methodology to covalently anchor our Mn(II)-Shiff base catalysts onto activated carbon has been applied resulting in heterogeneous Mn^{II}-L@ACox materials. This procedure involves functional <L-silane> precursors-which have been pre-formed- and reaction of their alkoxy-groups with surface -OH from activated carbon via the sol-gel chemistry. The, so obtained, carbon-based heterogeneous catalysts [Mn^{II}-L@ACox] are effective and selective towards epoxides with H₂O₂ in the presence of CH₃COONH₄ providing TONs equivalent-to/or outcompetes Mn^{II}-L@SiO₂ catalysts for certain substrates. Moreover, Mn^{II}-L(a)ACox catalysts are kinetically faster than the corresponding Mn^{II}-L(a)SiO₂ catalysts. BET data shows that after grafting the ACox matrix shows a dramatic collapse of the specific surface with practically zero porosity. This feature could be correlated with the observed dramatic acceleration of the catalytic performance of the Mn^{II}-L@ACox catalysts which results in extremely higher TOFs compared vs. the corresponding Mn^{II}-L@SiO₂ catalysts probably by rendering all the grafted Mn-L active catalytic centers readily accessible to H₂O₂, CH₃COONH₄ and substrate. Moreover, Mn^{II}-L@ACox catalysts present very good reusability indicating that they are more stable against oxidative destruction than the corresponding Mn^{II} -L@SiO₂ catalysts which were no recyclable.

Overall, by combining catalytic and EPR spectroscopic data we suggest a consistent catalytic mechanism which involves a) H-abstraction from H_2O_2 by

 CH_3COO^- and Mn^{II} -OOH formation and b) H-donation from NH_4^+ to Mn^{II} -OOH triggering Mn^{IV} =O generation which realizes alkene epoxidation.

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Figure 1. Distribution of oxidation products catalyzed by Mn^{II} -L1@ACox and Mn^{II} -L2@ACox in the presence of H₂O₂. Reaction performed in CH₃COCH₃/CH₃OH (0.45:0.40 ml). See Table 2 for further details.



Figure 2. Total turnover numbers for alkene epoxidations catalyzed by Mn^{II} -L1@ACox / Mn^{II} -L1@SiO₂ (A) and Mn^{II} -L2@ACox/ Mn^{II} -L2@SiO₂ (B) in the presence of H₂O₂. See Table 2 for further details.



Figure 3. TOF for alkene epoxidations catalyzed by Mn^{II} -L1@ACox / Mn^{II} -L1@SiO₂ (A) and Mn^{II} -L2@ACox/ Mn^{II} -L2@SiO₂ (B) in the presence of H₂O₂. See Table 2 for further details.



Figure 4. Recyclability of Mn^{II}-L1@ACox and Mn^{II}-L2@ACox for cyclohexene oxidation with H₂O₂.



Time dependence of cyclohexene epoxidation and solution redox potential for the same reaction catalysed by $Mn^{II}-L1@ACox$ [blue line, \blacksquare] and $Mn^{II}-L2@ACox$ [green line, \blacktriangle].



Figure 6. Experimental EPR spectra for Mn^{II} -L2@ACox in (a) Acetone / MeOH 1/1 (v/v), with addition H₂O₂, 1:2000 [Mn:H₂O₂] (b, c, d) after addition of CH₃COONH₄, [Mn:H₂O₂: CH₃COONH₄=1:2000:1000]. at reaction time t=1min (a), 5min (b), and 30mi (c) *Inset* : zoom of spectra (a, b): increase of the *D* parameter is manifested as a shift in the low-field bump marked by the arrows. Experimental Conditions: Temperature 77 K, modulation amplitude 4 G, microwave power 12.5mW.



Figure 7. Theoretical EPR spectra for $Mn^{II}(S=5/2, I=5/2)$ calculated by Easy spin using the spin Hamiltonian (1) for A_{iso} =-94Gauss, E/D=0.01 and D-stain=200Gauss. The spin package linewidth Iw was 1.3Gauss. By increasing the zero-field splitting parameter D, the spectrum undergoes two main changes [i] the outermost low-field and higher-field transitions are decreasing faster than the other peaks. [ii] a broad bump [marked by the dashed lines and the vertical arrows] is shifting downfield proportionally to the increasing D-value.



Scheme 1. Molecular structure of our Shiff base ligands covalently immobilised on silica surface.



Scheme 2A



Scheme 2. Schematic representation of the synthesis of Mn^{II} -L1@ACox (A) and Mn^{II} -L2@ACox (B) catalysts



Scheme 3: Morphological representation of Mn^{II}-L@ACox catalysts showing compact blocks of carbon layers supports.



Scheme 4: Suggested co-catalytic reaction mechanism of CH_3COONH_4 for the studied Mn^{II} -catalysts.

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entry	material	$\begin{array}{c} \boldsymbol{A}_{\mathbf{BET}} \\ (\mathbf{m}^2 \mathbf{g}^{-1}) \end{array}$	-COOH loading	ligand loading	Si-loading (mmol g ⁻¹)	Mn- loading			
			$(\text{mmol } g^{-1})$	$(\text{mmol } \mathbf{g}^{-1})$		$(\text{mmol } \mathbf{g}^{-1})$			
1	AC	856		-	-	-			
2	ACox	687	2.20	-	-	-			
3	L1@ACox	45		0.23	0.18	-			
4	L2@ACox	75		0.45	0.43				
5	Mn ^{II} -L1@ACox	2		0.30	0.27	0.30			
6	Mn ^{II} -L2@ACox	21		0.45	0.45	0.40			

Table1. Characterization of	` Mn ^{II} -catalys	ts and paren	t materials.
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Table 2.

Substrate	Products	Mn ^{II} -L1@ACox		Mn ^{II} -L1@SiO ₂		Mn ^{II} -L2@ACox			Mn ^{II} -L2@SiO ₂				
Substitute	Troducts	Yield (%) ^c	TON ^d	TOF $(h^{-1})^e$	Yield (%) ^c	TONd	TOF $(h^{-1})^e$	Yield (%) ^c	TON ^d	TOF $(h^{-1})^e$	Yield (%) ^c	TON^d	TOF $(h^{-1})^e$
Cyclohexene	<i>cis</i> -epoxide 2-Cyclohexenone	45.6 3.5			35.8 -			56.0 -			40.5 2.5		
	2-Cyclohexenol <i>cis</i> -diol	11.4 -	605	121	-	358	14.9		560	373	1.1 1.4	474	26.3
Cyclooctene	cis-epoxide	61.0	610	122	65.0	650	27.1	52.0	520	347	58.6	586	32.6
Hexene-1	cis-epoxide	7.6	76	15.2	11.0	110	4.6	8.5	85	57	9.5	95	5.3
Styrene	Epoxide	42.4	424	84.8	23.6	236	9.8	45.5	455	303	47.6	476	26.4
trans-Methyl-styrene	<i>trans</i> -epoxide <i>trans</i> -methyl-ketone	51.0	510	102	53.0	530	22.1	38.3	383	255	22.5 1.6	241	13.4
Limonene ^f	1,2-epoxides (<i>cis-/trans-</i>) 8.9-epoxides	76.7 (42.2/34.5)		81.4 (46.1/35.3) 15.9		64.9 (35.6/29.3)			50.8 (27.9/22.9) 10.1				
	-alcohol -ketone	14.4 -	911	182.2	-	973	40.5	12.9 0.8	778	519	0.7 0.8	624	34.7
<i>cis</i> -Stilbene	<i>cis</i> -epoxide <i>trans</i> -epoxide -ketone	40.5 11.0	515	103	60.0 2.7	600	25.0	50.1	501	334	10.2 1.3 3.2	124	6.9

^{*a*} Conditions- ratio of catalyst : H_2O_2 : CH_3COONH_4 : substrate=1:2000:1000:1000; equivalent of catalyst = 1µmol in 0.85 ml CH_3COCH_3 : CH_3OH_4 (0.45:0.40). ^{*c*} Yields based on starting substrate and products formed. The mass balance is 98-100%. ^{*d*} TON :total turnover number, moles of products formed per mole of catalyst. ^{*e*} TOF : turnover frequency which is calculated by the expression [epoxide]/[catalyst] x time (h^{-1}). ^{*f*} 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.



Highlights

- ► Mn-catalysts were synthesized by covalent grafting onto activated carbon.
- ► These catalysts are effective and selective towards epoxides with H₂O₂ and CH₃COONH₄.
- ► They are re-usable and provide considerably high TOFs.
- ▶ The function of CH₃COONH₄ which is determinant for the catalysis is proposed.