Activated carbons with immobilised manganese(III) *salen* complexes as heterogeneous catalysts in the epoxidation of olefins: influence of support and ligand functionalisation on selectivity and reusability

Ana Rosa Silva,[a] Joaquim Vital,[b] José Luís Figueiredo,[c] Cristina Freire*[a] and Baltazar de Castro[a]

[a] REQUIMTE, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal. E-mail: acfreire@fc.up.pt; Fax: +351 22 6082959; Tel: +351 22 6082890

[b] REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

[c] LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, 4150-123 Porto, Portugal

A manganese(III) N_2O_2 Schiff base complex functionalised with hydroxyl groups on the aldehyde moieties, [Mn(4-HOsalhd)CH$_3$COO], was immobilised onto a commercial activated carbon and on its air and acid oxidised forms: the unfunctionalised manganese(III) *salen* complex [Mn(salhd)Cl] was also immobilised onto the air oxidised activated carbon. All the materials were characterised by elemental analyses and by XPS and the type of oxygen functionalities present at the surface of the various activated carbons was characterised by TPD. The catalytic activities in the epoxidation of styrene of the manganese(III) *salen* complexes in homogeneous phase and heterogenised onto the activated carbon based materials were studied, using iodosylbenzene as oxidant and acetonitrile as solvent. All the heterogeneous catalysts are as chemoselective towards the styrene epoxide as their homogeneous counterparts, with the exception of the complex supported onto the nitric acid oxidised activated carbon, which exhibited the lowest values, a consequence of the catalytic role of the support. Catalyst reutilisation studies showed that the hydroxyl functionalised manganese(III) complex supported onto the two oxidised activated carbons kept the catalytic activity, contrasting with the hydroxyl functionalised manganese(III) complex supported onto the untreated activated carbon and the unfunctionalised manganese(III) complex supported onto the air oxidised activated carbon, for which a decrease in styrene epoxide yield was clearly observed. These results indicate that lack of oxygen functionality on the activated carbon or of complex functionalisation results in the deactivation of the manganese(III) *salen* based heterogeneous catalyst as a consequence of inefficient active phase anchoring. Conversely, the combination of support oxidation and of suitable complex functionalisation leads to the establishment of a covalent attachment of the hydroxyl functionalised Mn(III) complexes onto the carbon surface oxygen groups that retains an efficient site isolation of the complexes, both needed to produce very stable and reusable catalysts.

Introduction

Activated carbons are non-crystalline carbon-based materials prepared to present a high degree of porosity and an extended interparticulate surface area.[1] They are part of a long list of carbon materials that feature a high content of elemental sp^2-hybridised carbon atoms that exhibit at least two-dimensional order and can easily combine with other elements (*e.g.* oxygen) to form a variety of surface groups.[2]

Activated carbons and other carbon materials have been widely used in heterogeneous catalytic reactions as they satisfy most of the desirable requirements for a suitable support: stability, mechanical resistance, high surface area and optimum porosity. In addition to acting as catalysts, they are mainly used as supports for precious metals which are widely used as catalysts in the synthesis of high-value-added chemical products.[3] The adsorptive and catalytic performance of activated carbons are determined by their texture and surface chemistry,[3] which can be tailored by convenient thermal or chemical processes.[4]

Manganese(III) Schiff base complexes with a N_2O_2 coordination sphere, generally known in the literature as manganese(III) *salen* complexes, have been reported as efficient catalysts for the epoxidation of unfunctionalised alkenes in homogeneous phase,[5] using a wide range of oxidants: iodosylbenzene, sodium hypochlorite, *tert*-butylhydroperoxide, hydrogen peroxide, *etc.*[6] Furthermore, when chiral Mn(III) salen complexes are used they have been shown to be highly enantioselective.[6] This system has gained importance since epoxides are relevant intermediates in organic synthesis as they can be easily transformed into a large variety of compounds by means of regioselective ring opening reactions. For instance, styrene is one of the most important prochiral olefins and the corresponding epoxide is an extremely useful building block in the synthesis of chiral organic compounds.[7]

Currently, the heterogenisation of these complexes on several supports is the object of intense research in order to prepare recyclable and economical catalysts.[8–10] Furthermore, the anchoring of the Mn(III) *salen* complexes onto a support has been found to increase the catalyst stability,[9] since the

main deactivation process observed in homogeneous phase, formation of inactive dimeric μ-oxo manganese(IV) species,[8,9] is hindered by local site isolation of the complexes in a solid matrix.[8] Reports on the heterogenisation of chiral and non-chiral, symmetrical and unsymmetrical, Mn(III) *salen* catalysts have been centred on their covalent binding to organic polymers[10] and on their encapsulation, entrapment, adsorption and covalent attachment to porous inorganic supports, such as zeolites, MCM-41, Al-MCM-41 and clays.[9] Some of these heterogeneous catalysts have proved to be successful in the epoxidation of olefins, but information regarding their re-use and metal complex leaching is rarely provided.[8,9]

We have been developing strategies for chemical modification of the activated carbon surface in order to attach transition metal Schiff base complexes,[11–15] and recently we have reported the immobilisation onto an air oxidised activated carbon of two manganese(III) N_2O_2 Schiff base complexes bearing hydroxyl groups on the aldehyde moieties. The resulting catalysts have shown to be selective in the epoxidation of styrene, resistant to leaching and effective towards re-use.[16]

Herein we report the anchoring of two manganese complexes:[*N,N'-bis*(4-hydroxysalicylaldehyde)cyclohexanediaminate] manganese(III) acetate, [Mn(4-HOsalhd)CH$_3$COO](I), onto three activated carbons (a non oxidised, a nitric acid oxidised and an air oxidised activated carbon), and the unfunctionalised complex [*N,N'-bis*(salicylaldehyde)cyclohexanediaminate] manganese(III) chloride, [Mn(salhd)Cl] (II), onto an air oxidised activated carbon (Scheme 1). Catalytic activity and reusability of all the new materials in the heterogeneous epoxidation of styrene were also assessed. Data obtained provide insights into the influence of carbon surface chemistry and of complex functionalities on complex adsorption and catalytic efficiency of these novel carbons based heterogeneous catalysts. The surface chemistry of the various supports was characterised by TPD and all the materials were also characterised by elemental analysis and by X-ray photoelectron spectroscopy (XPS).

Experimental

Materials

The starting carbon material was a NORIT ROX 0.8 activated carbon (rodlike pellets with 0.8 mm diameter and 5 mm length). This material has a pore volume of 0.695 cm^3 g^{-1} determined by porosimetry (corresponding to meso- and macropores), a micropore volume of 0.359 cm^3 g^{-1} and mesopore area of 122 m^2 g^{-1} determined by N$_2$ adsorption at 77 K (*t*-method),[11–16] an ash content of 2.6% (w/w), an iodine number of 1000 and mercury and helium densities of 0.666 and 2.11 g cm^{-3}, respectively. The activated carbon was purified by Soxhlet extraction with HCl 2 mol dm^{-3} for 6 h, washed with deionised water until pH 6–7 and then dried in an oven, under vacuum, at 150 °C for 13 h (C1).

The reagents and solvents used in the synthesis of the Schiff base complex, in the modification of the activated carbon surface, in the anchoring of the metal complexes and in the

catalytic experiments were used as received, except for 1,2-diaminocyclohexane which was purified by distillation. Salicylaldehyde, 4-hydroxysalicylaldehyde, 1,2-diaminocyclohexane, manganese(II) acetate tetrahydrate, styrene, chlorobenzene, benzaldehyde and styrene epoxide were from Aldrich, manganese(II) chloride tetrahydrate from Sigma, and all solvents from Merck (*pro analysi*), except the acetonitrile used in the catalytic experiments, which was from Romil (HPLC grade). Iodosylbenzene (PhIO) was synthesised according to procedures described in the literature.[17]

Synthesis of the schiff bases and Mn(III) *salen* complexes

The ligands N,N'-*bis*(salicylaldehyde)cyclohexanediamine, H$_2$(salhd), and N,N'-*bis*(4-hydroxysalicylaldehyde)cyclohexanediamine, H$_2$(4-HOsalhd), were synthesised by refluxing an ethanolic solution of 1,2-cyclohexanediamine with either salicylaldehyde or 4-hydroxysalicylaldehyde.[18] Typically, 0.037 mol of diamine were refluxed with 0.075 mol of salicylaldehyde in 100 cm^3 of ethanol for 1–2 h. The precipitated ligands were collected by filtration and dried under vacuum for several days; yield: 75–90%.

H$_2$(salhd): C$_{20}$H$_{22}$N$_2$O$_2$. ^{1}H-NMR (d$_6$-DMSO, 200 MHz, 297 K), δ (ppm): 13.5, 13.3 (s, 2H, HO), 8.3, 8.2 (s, 2H, N=CH), 7.3–7.1 (m, 4H, aromatic), 6.9–6.7 (m, 4H, aromatic), 3.6, 3.4–3.2 (m, 2H, CH$_2$), 1.9–1.4 (m, 8H, CH$_2$); UV-Vis, λ_{max}/nm: 248, 303, 335, 398 (sh); FTIR, v/cm^{-1}: 2933 m, 2924 m, 2897 m, 2868 m, 2858 m, 2850 m, 1628 vs, 1608 (sh), 1579 vs, 1500 s, 1460 s, 1448 m, 1419 s, 1388 m, 1350 w, 1342 w, 1311 vw, 1280 s, 1248 m, 1213 m, 1203 m, 1144 s, 1115 m, 1095 m, 1080 m, 1057 w, 1045 w, 1030 w, 1001 w, 982 s, 953 w, 935 w, 926 w, 908 w, 893 w, 876 m, 850 s, 827 m, 802 vw, 768 vs, 758 vs, 677 vw, 661 m, 631 w, 557 w, 496 w, 482 w, 467 w, 449 w, 438 w, 420 w, 407 w.

H$_2$(4-HOsalhd): C$_{20}$H$_{22}$N$_2$O$_4$. ^{1}H-NMR (d$_6$-DMSO, 200 MHz, 297 K), δ/ppm: 13.6 (s, 2 H, OH), 8.2 (s, 2 H, N=CH), 7.1 (d, 2 H, aromatic), 6.3–6.1 (m, 4 H, aromatic), 1.9–1.4 (m, 8 H, CH$_2$); UV-Vis, λ_{max}/nm: ≈250 (sh), 276, 354, ≈490 (sh); FTIR, v/cm^{-1}: 1631 vs, 1595 vs, 1543 w, 1508 w, 1473 m, 1406 w, 1367 m, 1352 w, 1294 m, 1242 s, 1223 s, 1180 s, 1120 w, 1072 w, 1028 w, 976 w, 941 w, 850 m, 800 w, 760 vw, 748 vw, 669 w, 644 w, 623 w, 594 w, 573 w, 536 w, 523 w, 507 w, 490 w, 467 w, 415 w.

The manganese(III) complexes, [Mn(salhd)Cl] and [Mn(4-HOsalhd)CH$_3$COO] (Scheme 1) were prepared by a procedure adapted from the literature, by refluxing ethanolic solutions of equimolar quantities of manganese(II) chloride tetrahydrate or manganese(II) acetate tetrahydrate with the ligand for 1–2 h.[19] The complexes were re-crystallised from acetonitrile; yield: 30–75%.

[Mn(salhd)Cl], chloro-[*N,N'-bis*(salicylaldehyde)cyclohexanediaminate] manganese(III): MnC$_{20}$H$_{20}$N$_2$O$_2$Cl. FAB-HRMS, m/z: calculated ([MnC$_{20}$H$_{20}$N$_2$O$_2$–Cl]$^+$) 375.0905, experimental 375.0920. UV-Vis, λ_{max}/nm: 212, ≈276 (sh), 298, 352, 395, ≈455 (sh), ≈686 (sh), 557; FTIR, v/cm^{-1}: 2933 m, 2926 m, 2870 (sh), 2858 m, 1622 vs, 1599 vs, 1543 s, 1470 m, 1446 s, 1394 m, 1350 m, 1336 (sh), 1319 s, 1309 s, 1277 s, 1246 w, 1217 m, 1200 m, 1149 s, 1124 w, 1051 w, 1030 w, 1010 w, 906 m, 862 w, 848 w, 808 m, 750 s, 686 w, 623 m, 605 w, 569 m, 515 w, 459 w, 426 m.

[Mn(4-HOsalhd)CH$_3$COO], carboxylate-[*N,N'-bis*(4-hydroxysalicylaldehyde)cyclohexanediaminate] manganese(III): MnC$_{22}$H$_{23}$N$_2$O$_6$. FAB-HRMS, m/z: calculated ([MnC$_{20}$H$_{20}$N$_2$O$_4$–CH$_3$COO]$^+$) 407.0804, experimental 407.0808. UV-Vis, λ_{max}/nm: 209, 222, 286, 323, ≈370, ≈447 (sh), 557; FTIR, v/cm^{-1}: 1597 vs, 1535 vs, 1494 m, 1446 m, 1394 w, 1340 w, 1400 w, 1311 w, 1234 vs, 1174 m, 1122 m, 1024 m, 983 m, 875 w, 845 m, 804 m, 762 m, 658 m, 636 s, 540 w, 511 w, 458 w, 415 m.
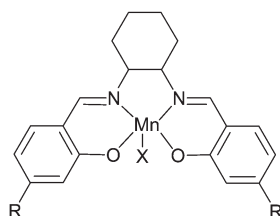
Scheme 1 Mn(III) *salen* catalysts: [Mn(4-OHsalhd)CH$_3$COO] (R = OH, X = CH$_3$COO) and [Mn(salhd)Cl] (R = H, X = Cl).

Activated carbon oxidation

The activated carbon (C1) was oxidised either (a) with a mixture of N_2 and air (5% O_2) at 698 K for 10 h (C2)-burnoff = 11%,[4,11,13] or (b) with a 5 mol dm^{-3} nitric acid solution at reflux for 6 h (1 g/30 cm^3) washed with deionised water until pH 6–7 and then dried under vacuum in an oven at 110 °C for 13 h (C3).[4,12,14]

Preparation of the heterogeneous catalysts

The heterogeneous catalysts were prepared by adsorption, onto the pre-dried activated carbons, of N,N'-dimethylformamide (dmf) solutions of [Mn(4-HOsalhd)CH$_3$COO] or dichloromethane solutions of [Mn(salhd)Cl]. For the preparation of [Mn(4-HOsalhd)]@C1, [Mn(4-HOsalhd)]@C2 and [Mn(salhd)]@C2 (the anions are omitted for simplicity), solutions containing 184 μmol of complex per gram of activated carbon were refluxed for 6 h. For the preparation of [Mn(4-HOsalhd)]@C3, a solution of 16 μmol of complex per gram of activated carbon was kept at about 100 °C for 23 h. The adsorption processes were monitored by ultraviolet–visible spectroscopy. The catalysts were collected by filtration and purified by Soxhlet extraction for 8 h sequentially with 150 cm^3 of dmf, and then with 150 cm^3 of acetonitrile for the [Mn(4-HOsalhd)CH$_3$COO] based catalysts or with 150 cm^3 of dichloromethane for [Mn(salhd)Cl] based catalyst. Finally, they were dried under vacuum in an oven at 120 °C for 13 h.

Physical measurements

^{1}H NMR spectra were recorded with a Bruker AC 200 at 25 °C, using SiMe$_4$ as internal reference. FTIR spectra were obtained as potassium bromide pellets in the range 400–4000 cm^{-1} with a Biorad FTS 155, and diffuse reflectance electronic spectra on a Shimadzu UV-3101 PC in the range 1600–200 nm, using barium sulfate as reference. Elemental analysis (C, N, H and Mn) was carried out at 'Laboratório de Análises', IST, Lisboa (Portugal).

X-ray photoelectron spectroscopy was performed at 'Centro de Materiais da Universidade do Porto' (Portugal), in a VG Scientific ESCALAB 200A spectrometer using non-monochromatized Mg Kα radiation (1253.6 eV). In order to correct for possible deviations caused by electric charge of the samples, the graphitic C 1s band at 284.6 eV was taken as internal standard.[20,21]

Temperature programmed desorption (TPD) was carried out using a Micromeritics TPD/TPR 2900 instrument, with the evolution of CO (m/z 28) and CO$_2$ (m/z 44) being monitored by mass spectrometry using a Fisons MD800 instrument. Prior to analysis, the sample (ca. 50 mg) was placed in a fixed bed U-shaped quartz tubular micro-reactor and dried overnight at 383 K under a stream of helium. The temperature was then increased at a rate of 5 K min^{-1} to 1200 K under helium (25 cm^3 min^{-1}, 0.1 MPa).

The adsorption/desorption of [Mn(4-HOsalhd)CH$_3$COO] or [Mn(salhd)Cl] remaining in solution was monitored by UV-Vis spectroscopy using a Unicam UV300 spectrometer in the range 250–800 nm, using quartz cells with a 1 cm optical path. Aliquots of 1.00 cm^3 from the reaction mixture, diluted to 10.00 cm^3, were used to record the spectra.

GC-FID chromatograms were obtained with a Varian CP-3380 gas chromatograph using helium as carrier gas and a fused silica Varian Chrompack capillary column CP-Sil 8 CB Low Bleed/MS (30 m × 0.25 mm id; 0.25 μm film thickness). Conditions used: 60 °C (3 min), 5 °C min^{-1}, 170 °C (2 min), 20 °C min^{-1}, 200 °C (10 min); injector temperature, 200 °C; detector temperature, 300 °C.

Catalysis experiments

The activity of the catalysts in the epoxidation of styrene was studied at room temperature using 0.500 mmol of styrene (substrate), 0.500 mmol of chlorobenzene (GC internal standard), 0.100 g of heterogeneous catalyst and 0.250 mmol of iodosylbenzene (PhIO) as oxidant in 5.00 cm^3 of acetonitrile, under stirring conditions. During the experiment 0.1 cm^3 aliquots were taken from solution with a hypodermic syringe, filtered through 0.2 μm syringe filters, and directly analysed by GC-FID. When all the iodosylbenzene (PhIO) had disappeared from solution and the ratio of the areas of iodobenzene and of chlorobenzene in the chromatogram was constant, the solution was withdrawn with a hypodermic syringe and filtered through 0.2 μm syringe filters to a new flask, to which 0.250 mmol of PhIO were added. This procedure ensures that there was no leaching of the metal complex to the reaction medium and thus the epoxidation was catalysed heterogeneously. The catalysts were then washed sequentially by Soxhlet extraction with 150 cm^3 of methanol and 150 cm^3 of acetonitrile, for 1–2 h, and dried under vacuum in a horizontal oven at 120 °C for 13 h. They were reused twice using the same experimental procedure.

To provide a framework for the results obtained using the heterogenised complexes, styrene epoxidation was also carried out under experimental conditions comparable to those described above (a) in homogeneous media using the same amount of Mn(III) catalyst, and (b) using the activated carbon without any added Mn(III) complex.

Results and discussion

Activated carbon oxidation

The TPD profiles provide qualitative and quantitative information about the surface oxygen groups of activated carbons, since they evolve as carbon monoxide and carbon dioxide at different temperatures when heated in an inert atmosphere.[4,11–14] The hydroxyl, carbonyl and ether groups decompose as carbon monoxide at high temperatures, whereas carboxylic acid and lactone groups decompose as carbon dioxide; carboxylic anhydride groups decompose as CO and CO$_2$.[4]

By comparing the TPD profiles of carbon monoxide (m/z = 28) and carbon dioxide (m/z = 44) fragments of the parent activated carbon and oxidised samples (Fig. 1), it is clear that both oxidation treatments increase the content of oxygen functional groups. The carbon sample oxidised with nitric acid (C3) exhibits the largest evolution of CO$_2$ and CO, showing clearly that this sample has the highest oxygen content. Its CO$_2$ TPD profile suggests a very high content in free carboxylic acid (553 K) and carboxylic anhydride groups. This feature is in striking contrast with what is observed for the air oxidised carbon sample (C2), as its CO$_2$ TPD profile reveals an almost complete absence of free carboxylic acid and anhydride functional groups; CO evolution is only observed in the high temperature range (700–1000 K) and is likely to be due to decomposition of lactone groups.[4,11] CO evolution in C2, although smaller than that in C3, is also relatively intense, suggesting that phenol (976 K) and carbonyl (1094 K) groups are the predominant surface oxygen functional groups.

The above observations are also in agreement with those inferred from elemental and XPS analyses (Table 1): oxidation of carbon C1 increases the surface and total oxygen content of the activated carbon,[4,12,13] and this increase is larger for nitric acid oxidation than for air oxidation (Fig. 1).

Further insights on chemical surface modifications of the materials can be obtained by careful inspection of the high resolution XPS profile spectra in the C 1s and O 1s regions. All samples show an intense asymmetric band in the C 1s region, centred at 284.6 eV, due to the graphitic
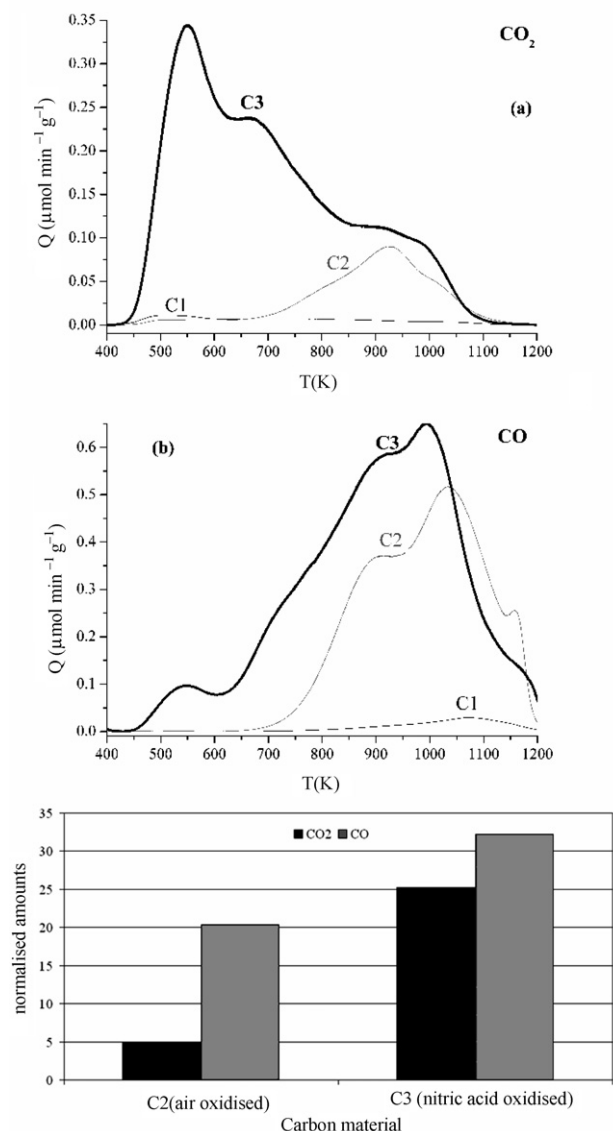
Fig. 1 TPD profiles for the (a) CO_2 and (b) CO fragments of the untreated (C1), air oxidised (C2) and nitric acid oxidised (C3) NORIT ROX 0.8 activated carbon and (c) the C2 and C3 amounts of CO and CO_2 normalised by the corresponding amounts in C1.

533.2 eV, respectively, with a low energy shoulder at 531.6 and 531.5 eV, respectively. The shoulders correspond to C=O containing groups (ketone, lactone and carbonyl) and the intense bands to C–OH and/or C–O–C groups.[4,11,13,20,21]

Immobilisation of manganese(III) *salen* complexes

For all materials, a decrease in the intensity of the brown colour of the complex solutions was observed during the reflux with the oxidised activated carbons, which was paralleled by a progressive decrease in absorbance of the electronic bands in the UV-Vis spectra. After Soxhlet extraction the solutions used in the purification were colourless, with no electronic bands due to the complexes, indicating that the manganese(III) *salen* complexes were immobilised onto the surface of the oxidised activated carbon and did not leach from the support under the experimental conditions used.

When compared with the parent materials, all manganese based materials show an increase in nitrogen content, both in the elemental and XPS analyses (Table 1), due to the nitrogen atoms of the Schiff base ligands. The manganese content in [Mn(4-OHsalhd)]@C1, [Mn(4-OHsalhd)]@C2 and [Mn(4-OHsalhd)]@C3 is 55, 142 and 10 μmol of manganese per gram of activated carbon, respectively. These values correspond to adsorption efficiencies (amount of adsorbed complex/amount of complex in the original solution × 100) of 30%, 77% and 62%, respectively, which supports the conclusion that oxidation of the activated carbon approximately doubles metal loading, notwithstanding the different adsorption conditions used in the preparation of [Mn(4-OHsalhd)]@C3 (see experimental section).

Recently, we have reported the direct anchoring of Cu(II)[13] and Ni(II)[15] *salen* complexes bearing hydroxyl groups in the aldehyde moieties onto an air oxidised activated carbon, by reaction of the ligand hydroxyl groups with the carbonyl and carboxylic type oxygen surface groups (anhydride), and the immobilisation procedure has proved to be very effective against complex leaching. We propose that the anchoring process for the manganese complex with hydroxyl groups in the aldehyde moieties in C2 and C3 occurs by the same reaction of the homologous copper(II) and nickel(II) complexes.[13,15] This is sustained by the observation that the highest adsorption efficiency was obtained for the oxidised activated carbons, for which the amount of surface oxygen groups is larger (Table 1, Fig. 1), thus facilitating the reaction of the ligand hydroxyl functionalities with carbon surface carbonyl and carboxylic type groups.

For [Mn(4-OHsalhd)]@C1, for which the quantity of accessible oxygen surface groups in the support is very small, such a reaction does not occur extensively and the anchoring process must occur mostly by π–π interactions between the delocalised π system of the complex and graphitic aromatic rings.[22] As physical adsorption is supposed to be less effective than chemical binding to carbon surface through ligand functionalities,

structure, which tails into the high binding energy region (Fig. 2).[4,11–15,20,21] For C3, a large band centred at about 288.5 eV is also observed in this region, which has been attributed to surface carboxylic acid groups (Fig. 2).[20,21]

In the O 1s region (Fig. 3), carbon C1 shows an apparent symmetric broad band centred at 532.2 eV, whereas carbons C2 and C3 show asymmetric bands centred at 533.5 and

Table 1 Elemental and XPS analyses of the carbon based materials

Material	Elemental analysis (wt.%)					XPS (at.%)			
	N	C	H	Mn	O[a]	N	C	Mn	O
C1	0.58	91.20	1.18	—	7.04	0.38	92.08	—	6.10
[Mn(4-HOsalhd)]@C1	0.98	90.02	0.47	0.30	8.23	1.90	75.61	0.81	17.42
C2	0.62	86.57	1.14	—	11.67	0.35	89.28	—	9.94
[Mn(4-HOsalhd)]@C2	1.82	83.16	0.88	0.78	13.36	2.43	84.26	0.49	12.42
[Mn(salhd)]@C2	0.82	83.49	0.80	0.47	14.42	0.62	88.02	0.08	10.61
C3	1.02	75.11	0.88	—	22.99	0.80	81.39	—	17.62
[Mn(4-OHsalhd)]@C3	2.99	77.97	1.06	0.06	17.92	2.81	83.40	[b]	13.58

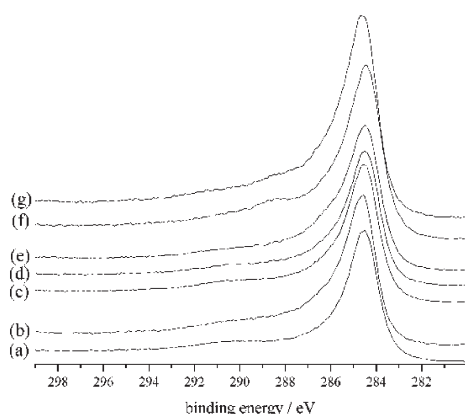[a] Determined using the expression: 100 − (N% + C% + H% + Mn%). [b] Below the detection limit.

Fig. 2 High resolution XPS C 1s spectra of the carbon based materials: (a) C1, (b) [Mn(4-OHsalhd)]@C1, (c) C2, (d) [Mn(salhd)]@C2, (e) [Mn(4-OHsalhd)]@C2, (f) C3 and (g) [Mn(4-OHsalhd)]@C3.

lower metal complex loadings are obtained. On the other hand, [Mn(salhd)]@C2 contains 86 μmol of manganese per gram of activated carbon (Table 1), corresponding to an adsorption efficiency of 47%, which is less than that obtained for [Mn(4-OHsalhd)]@C2. Thus, absence of complex functionalisation results in low metal complex loadings even in the presence of an oxygen rich carbon surface, and therefore we propose that the unfunctionalised manganese(III) complex may be immobilised onto the activated carbon through the acidic groups by ionic exchange or by π–π interactions between the metal complex delocalised π system and graphitic aromatic rings of the activated carbon, as in [Mn(4-OHsalhd)]@C1.

For all the manganese based carbon materials there is a slight increase in intensity in the XPS O 1s region of lower binding energy (531–532 eV) (Fig. 3), as in copper(II) and nickel(II) homologous complexes.[11,13,15] As the manganese(III) complexes have two bands in the O 1s region, one in the range 531.5–532.0 and the other at 534.0 eV, which correspond respectively to the ligand oxygen atoms coordinated to the metal and those from the hydroxyl groups in the aldehyde moieties (Scheme 1),[11,13,15] the intensity increase in the low energy shoulder in the XPS spectra of the carbon materials can be attributed to the presence of the oxygen atoms associated to the metal complexes. The XPS of all materials show, in the N 1s region, a band at about 400 eV due to the imine group of the Schiff base (Scheme 1), as well as a very large band at about 642 eV, with low signal/noise ratio, in the Mn $2p_{3/2}$ region, due to the presence of the metal, in agreement with the values reported for manganese(III) complexes with *salen*[23] and porphyrinic[24] ligands.

XPS data in the C 1s region is dominated by the carbon matrix band at 284.6 eV. For [Mn(4-OHsalhd)]@C1 and [Mn(salhd)]@C2, the spectra are virtually identical to that of
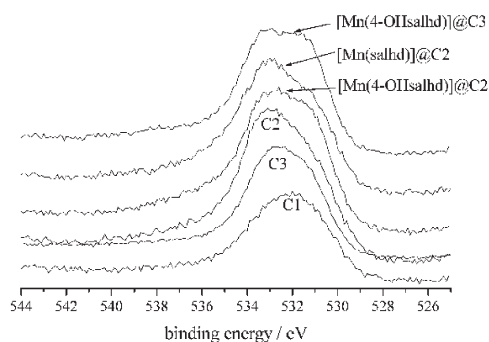

Fig. 3 High resolution XPS O 1s spectra of the C1–C3 activated carbons and correspondent [Mn(4-OHsalhd)CH₃COO] based catalysts.

the starting material, C1, thus providing evidence that the interaction of the adsorbed complexes does not change the carbon framework. For [Mn(4-OHsalhd)]@C3 is observed a decrease in the intensity of the band at 288.5 eV (Fig. 2), which is assigned to free carboxylic acid, anhydride and lactones groups, thus suggesting that these groups have been changed/removed, probably by the reaction with the ligand hydroxyl functionalities of the manganese complexes. In the case of [Mn(4-OHsalhd)]@C2, the anchoring reaction has occurred mainly by carbonyl surface groups, as observed in the homologous copper(II) and nickel(II) complexes, as in this activated carbon no low temperature stable groups (such as carboxylic acid and anhydride groups) exist; however, no changes on surface carbonyl groups can be detected in the C 1s region.

Catalysis experiments

The results obtained in the epoxidation of styrene at room temperature using the manganese(III) *salen* based materials as heterogeneous catalysts, and PhIO as oxidant in acetonitrile, are summarised in Table 2 and Fig. 4, in which data from homogeneous phase and blank experiments run under comparable conditions are also included.

All new manganese(III) *salen* based materials show high styrene epoxide chemoselectivities that are comparable to those of the corresponding homogeneous phase catalysts (Table 2), with the exception of [Mn(4-OHsalhd)]@C3 for which a significant decrease in chemoselectivity is observed. Moreover, after removal of the heterogeneous catalysts, no further activity was observed in the filtrates, sustaining the idea that the epoxidation of styrene was only catalysed heterogeneously.

For all heterogeneous catalysts the reaction profiles reveal a levelling off of the chemoselectivities, whereas in homogeneous phase a decrease in selectivity is observed with time, due to catalyst deactivation by formation of dimeric μ-oxo Mn(IV) species.[15,25] This observation clearly indicates that the metal complexes are stabilised upon immobilisation onto the activated carbons as dimer formation is prevented by site isolation in the carbon matrix.

With the heterogeneous catalysts, the reaction time increases and styrene conversion decreases, when compared with the homogeneous counterparts (Table 2). The first is a general effect that arises upon immobilisation of metal complex catalyst in porous matrices and has been attributed to diffusional constraints imposed on substrates and reactants by the porous network of the matrix. The diffusion of the reactants to the metal centre can be particularly hindered for PhIO, a solid with low solubility in acetonitrile and whose solubilisation is controlled by its rate of consumption.[26] The latter effect, lower styrene conversion, must be due to consumption of PhIO in competing reactions. On the one hand, PhIO is homolytically degraded to iodobenzene, both in homogeneous and heterogeneous media.[5,15] On the other hand, all heterogeneous catalysts, after being used for three catalytic cycles, exhibit an increase in the band at 288.5 eV in their XPS C 1s region, which may be attributed to newly formed high oxidation state carbon groups (carboxylic acid, lactone and carboxylic anhydride groups) that result from carbon oxidation by PhIO.[15] To circumvent this problem we have also tried to use sodium hypochlorite as the oxygen source, which is commonly used in epoxidation reactions, but with limited success, because it promoted leaching of the active phase, deactivation of the heterogeneous catalysts, and a lowering of epoxide selectivity.[15]

Influence of support surface chemistry and complex functionalities

The use of Mn(III) *salen* complexes anchored onto the activated carbon was also found to affect the amount of compounds other that styrene epoxide that are produced: the only

Table 2 Epoxidation of styrene catalysed by the manganese(III) *salen* based catalysts[a]

Entry	Catalyst	Run	Mn (mol%)[b]	t/h[c]	C (%)[d e]	Selectivity (%)[e f]			TON[g]	TOF/h^{-1}[h]
						SE	B	O		
1	[Mn(4-OHsalhd)CH$_3$COO]		4.0	3.5	56	89 (50)	6	5	5	2
2			2.8	5	62	85 (53)	5	9	8	2
3			1.1	8	60	81 (49)	9	10	19	2
4			0.2	48	54	79 (43)	15	6	46	1
5	[Mn(salhd)]		1.7	4	68	86 (58)	7	7	14	4
6	C1			70	30	48 (14)	53	0		
7	[Mn(4-OHsalhd)]@C1	1st	1.1	70	42	89 (37)	11	0	9	0.1
8		2nd	1.1	70	31	88 (27)	12	0	7	0.1
9		3rd	1.1	70	31	82 (25)	17	1	4	0.06
10	C2			48	18	38 (7)	62	0		
11				25	15	45 (7)	55	0		
12	[Mn(4-OHsalhd)]@C2	1st	2.8	48	42	81 (34)	19	0	4	0.08
13		2nd	2.8	48	41	76 (31)	22	2	4	0.08
14		3rd	2.8	48	42	79 (33)	21	0	6	0.1
15	[Mn(salhd)]@C2	1st	1.7	25	47	83 (39)	15	2	6	0.2
16		2nd	1.7	25	43	79 (34)	20	1	5	0.2
17		3rd	1.7	25	36	79 (28)	21	0	5	0.2
18	C3			24	31	0 (0)	88	12		
19	[Mn(4-OHsalhd)]@C3	1st	0.2	24	26	56 (15)	42	2	4	0.2
20		2nd	0.2	24	28	63 (18)	35	2	7	0.3
21		3rd	0.2	24	30	64 (19)	34	2	9	0.4

[a] In acetonitrile, room temperature, molar ratio styrene/PhIO = 2 : 1. [b] Relative to styrene. [c] Time needed for complete consumption of the oxidant. [d] Styrene conversion corrected for the limiting reactant PhIO. [e] Determined by GC-FID against internal standard (chlorobenzene); values between brackets refer to the yield. [f] SE = styrene epoxide, B = benzaldehyde and O = other reaction by-products. [g] Total TON = mmol epoxide/mmol Mn. [h] TOF = TON/time reaction.

by-product detected was benzaldehyde, which must be contrasted with that observed in the homogenous catalytic reaction (Table 2), for which small quantities of benzaldehyde and other products were formed. The large yields of benzaldehyde observed in the heterogeneous reactions must be due to a different catalytic pathway involving the carbon matrix.

Styrene conversion and chemoselectivities can be correlated with the activated carbon surface chemistry. The blank experiments performed with the three supports show that all the activated carbons are not inert in styrene oxidation, although yielding relatively small styrene conversions (Table 2). After 70 h of reaction, the untreated activated carbon, C1, produces 14% of styrene epoxide and 16% benzaldehyde; after 48 h of reaction, C2 produces 7% of styrene epoxide and 11% benzaldehyde; and after 24 h of reaction, C3 produces, 0% of styrene epoxide and 27% benzaldehyde. The C3 support has a large amount of surface carboxylic acids (which are practically absent in C1 and C2) that are likely to be responsible for the absence of styrene epoxide, as they induce the ring opening of the epoxide; moreover, these surface groups may also increase the rate of homolytic degradation of the PhIO, thus ending the catalytic reaction at shorter reaction times. In this context, as C1 and C2 have low concentration surface carboxylic acids, [Mn(4-OHsalhd)]@C1, [Mn(4-OHsalhd)]@C2 and [Mn(salhd)]@C2 exhibit styrene epoxide selectivities similar to those of their respective homogeneous reactions, whereas [Mn(4-OHsalhd)]@C3 shows the lowest values.

Reutilisation is one of the great advantages of heterogeneous catalysts, and its study is also important as can provide insights into the anchoring process involved with each complex, and thus catalyst stabilisation during the catalytic cycle.

From data in Table 2 and Fig. 4 it is clear that [Mn(4-OHsalhd)]@C2 and [Mn(4-OHsalhd)]@C3 do not lose their efficiency (similar styrene conversion, yield of styrene epoxide and TON) after three catalytic cycles, suggesting that the anchoring process of the complexes through the ligand functionalities is very effective, not only preventing complex deactivation, but also leaching by fixing them strongly to the support surface. Curiously, the [Mn(4-OHsalhd)]@C3 catalyst shows better yields of styrene epoxide and TON after reuse, which may be due to partial deactivation of the acidic surface groups during the catalytic cycles (Table 2, Fig. 4).

Contrastingly, [Mn(4-OHsalhd)]@C1 and [Mn(salhd)]@C2 show a systematic decrease in epoxide yield and TON after each consecutive catalytic reaction, suggesting partial deactivation of the active manganese complexes. As mentioned above, in these catalysts the Mn(III) complexes may be physically adsorbed *via* π–π or ionic interactions, and due to their mobility (migration) close molecules can dimerise originating dimeric μ-oxo manganese(IV) species, which are catalytically inactive, as observed in homogeneous phase.[8,9]

These results indicate that lack of oxygen functionalities on the activated carbon and complex functionalisation result in the deactivation of the manganese(III) *salen* based heterogeneous catalyst as a consequence of inefficient immobilisation; conversely, support oxidation coupled to suitable complex functionalisation leads to very stable and reusable catalysts which may probably be correlated with efficient site isolation of the hydroxyl functionalised manganese(III) *salen* complex, sustaining the covalent attachment onto the oxygen functionalities.

Conclusions

New heterogeneous catalysts were prepared by heterogenisation of a non-chiral manganese(III) N$_2$O$_2$ Schiff base complex functionalised with hydroxyl groups, [Mn(4-HOsalhd)CH$_3$-COO], onto activated carbons with different surface chemical properties. Oxidation of the support enhanced metal complex adsorption efficiency and catalyst stabilisation, but the acidity of the carbon surface has a pernicious effects on the styrene epoxide chemoselectivities. However, with the exception of the catalyst anchored onto the support with the highest percentage of acidic groups (C3, nitric acid oxidized carbon), all other
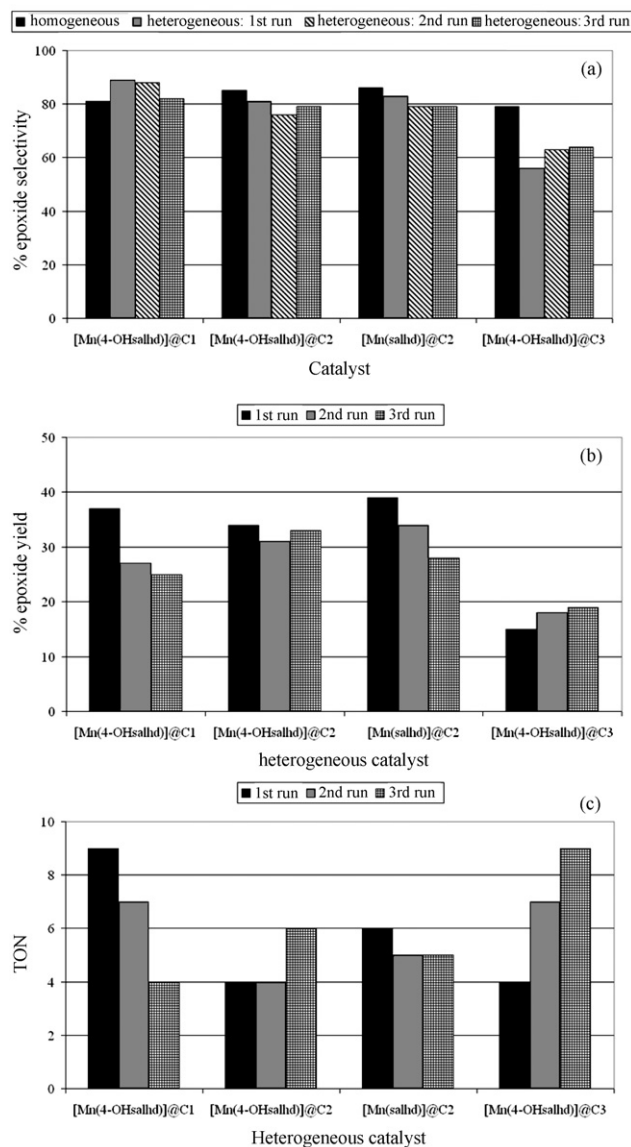
Fig. 4 Epoxidation of styrene catalysed by the [Mn(4-OHsalhd)CH₃-COO] complex in homogeneous phase and heterogenised onto untreated (C1), air oxidised (C2) and nitric acid oxidised (C3) NORIT ROX 0.8 activated carbon, and by the [Mn(salhd)Cl] complex in homogeneous phase and heterogenised onto the air oxidised activated carbon: (a) % epoxide selectivity = f (catalyst), (b) % epoxide yield = f (heterogeneous catalyst) and (c) % TON = f (heterogeneous catalyst).

functionalisation (hydroxyl functionalised manganese(III) *salen* complex) allow for covalent bonding (grafting) of manganese complexes to some of the oxygen carbon surface groups (efficient site isolation), being very resistant against deactivation.

Thus, to obtain a selective and reusable epoxidation heterogeneous catalyst it becomes necessary to adequately functionalise both the activated carbon and manganese(III) Schiff base complex.

Acknowledgements

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catalysts exhibit epoxide selectivities similar to that observed for their homogeneous counterparts.

The catalysts prepared by immobilisation of the hydroxyl functionalised manganese(III) *salen* complex onto the acid and air oxidised supports could be used at least three times without loss of efficiency. On the other hand, those prepared using either untreated activated carbon with functionalised complex or oxidised carbon with an unfunctionalised complex [Mn(salhd)Cl] show a decrease in catalyst performance with reuse. The different behaviour results from the complex immobilisation process: in the absence of carbon surface groups or of complex functionalisation, the manganese(III) *salen* complex must be immobilised by π–π interaction or ionic exchange, and are susceptible to active phase deactivation, whereas the presence of carbon surface groups and the appropriate complex