Fig. 4. The proposed mechanism for the growth of different diameter CNTs in the thermal plasma jet system.

lytic particles will determine that of the CNTs. The proposed mechanism for the growth of different diameter CNTs in the TPJ system is shown in Fig. 4. According to this proposed mechanism, relatively larger diameter CNTs could be expected by introducing the carbon source through inlet (b) rather than inlet (a). This expectation agrees well with our results.

In summary, we have developed a new TPJ system to produce controlled CNTs in a continuous process. High-purity single-, double- and multi-walled carbon nanotubes have been synthesized selectively over Fe catalyst by varying the inlet location of carbon source and with or without dosing H_2 gas. Thus, it should be possible to achieve mass production of controlled carbon nanotubes using our new TPJ system.

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Jacobsen catalyst anchored onto an activated carbon as an enantioselective heterogeneous catalyst for the epoxidation of alkenes

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The chiral 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 by the Jacobsen and Katsuki groups in the early

nineties as very efficient catalysts in the asymmetric epoxidation of unfunctionalised alkenes [1,2]. Ever since, this system has gained importance due to its practical use in laboratory and industry scale and to the broad use of epoxides as intermediates in organic synthesis; they can be easily transformed into a large variety of compounds by means of regioselective ring opening reactions.

Therefore, currently, the heterogenisation of these homogeneous enantioselective catalysts on several supports is the object of intense research in order to make them recyclable as well as economical [3]. The anchoring of the Mn(III) *salen* complexes onto a support has also been found to increase the catalyst stability [3], since the main deactivation process observed in homogeneous phase, formation of inactive dimeric μ-oxo manganese(IV) species [1,2], is hindered by local site isolation of the complexes in a solid matrix [3]. The majority of the reports on the heterogenisation of Mn(III) *salen* catalysts have been centred on their covalent binding to organic polymers and on their encapsulation, entrapment, adsorption and covalent attachment to porous inorganic supports, such as zeolites, MCM-41, Al-MCM-41 and clays [3].

Activated carbons are porous, readily available and inexpensive materials, extensively used in heterogeneous catalysis as supports [4], which possess several types of oxygen surface groups, which may be selectively maximised by thermal and chemical processes [5], which can be used as building blocks for the covalent attachment of catalytic active species.

Despite of the few reports on the covalent attachment of homogeneous catalysts onto activated carbons, we started to develop procedures to prepare new carbon based heterogeneous catalysts using several strategies to covalently attach *salen* transition metal complexes onto activated carbon [6–9]. We applied some of this strategies on the anchoring of non-chiral Mn(III) *salen* complexes to the surface oxygen functional groups of modified activated carbons and yielded heterogeneous catalysts which were selective and reusable in the epoxidation of styrene using PhIO as oxidant in acetonitrile at room temperature [10,11]. Herein, we report the extension of these studies on the heterogenisation of Mn(III) *salen* complexes onto activated carbons to their chiral counterparts using a new and easy methodology.

The surface phenol groups of an air oxidised activated carbon (Cox) [5,6,8,9], prepared from a NORIT ROX 0.8 commercial activated carbon (C), were activated by reflux with an aqueous solution of sodium hydroxide 0.0138 mol dm^{-3} for an hour; a decrease in the pH of the aqueous solution was observed. This material (CoxONa) was washed with deionised water until constant pH (8) and then dried at 120 °C in an oven, under vacuum. Then 0.50 g of CoxONa was refluxed for 8 h with 100 cm^3 of an ethanolic solution

0.50 mol dm^{-3} in commercial (1R,2R)-Jacobsen catalyst (Fig. 1) [12]. The anchoring process was monitored by UV–vis spectroscopy and a decrease in intensity of the electronic spectra ($\lambda = 200$–800 nm) of the manganese(III) *salen* complex was observed. In order to remove physisorbed complex, the resulting material was purified by Soxhlet extraction with ethanol for 16 h. Finally, the carbon nanocomposite was dried in an oven at 120 °C for 13 h, under vacuum. All activated carbons were characterised by XPS and the manganese content of the final material was determined by ICP-AES.

Comparison of the XPS chemical analyses of the (1R,2R)-[Mn (3,5-dtButsalhd)Cl]@CoxONa material with its precursor (CoxONa) showed the presence of manganese besides a significant decrease of sodium content. These results suggest that the manganese(III) *salen* complex was anchored onto the surface of the activated carbon through axial coordination of the phenolate activated carbon groups to the manganese(III) centre, as represented in Fig. 1. However, the manganese content obtained by ICP-AES is lower (0.107 mmol g^{-1} material) than that obtained by XPS (0.692 mmol g^{-1} material, Table 1), indicating that the manganese(III) *salen* complex is mainly anchored at the external surface of the activated carbon matrix, which might be a consequence of the large dimensions of the molecule.

The catalytic activity in the epoxidation for styrene of the new material (0.100 g) was accessed in dichloromethane using 3-chloroperoxybenzoic acid (m-CPBA) as oxygen source in combination with 4-methylmorpholine N-oxide (NMO), at temperatures approximately −5 °C (ice bath with saturated solution of sodium chloride). The experimental conditions were typical of those reported in the use of soluble Jacobsen catalyst [13] and the yield and enantiomeric excesses (%ee) of the epoxidation were determined by gas chromatography.
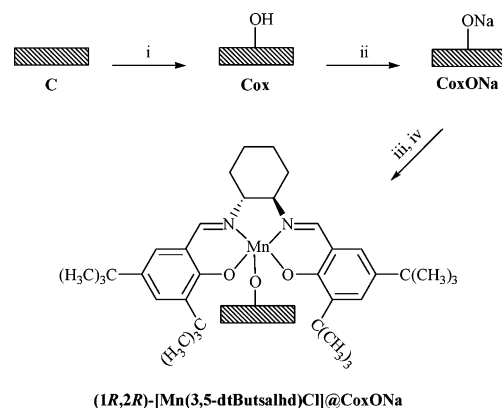

(1R,2R)-[Mn(3,5-dtButsalhd)Cl]@CoxONa

Fig. 1. Reagents and procedures used in the anchoring of the Jacobsen catalyst onto an activated carbon: (i) 5% air, 698 K, 10 h [5,6,8,9]; (ii) NaHO (aq), reflux, 1 h; (iii) commercial (1R,2R)-[Mn(3,5-dtButsalhd)Cl], ethanol, reflux, 8 h; (iv) ethanol, reflux, 16 h.

Table 1
XPS elemental analyses of the carbon based materials[a]

Material	C	O	Na	Mn
C	92.08	6.10	0.90	
Cox	89.28	9.94	0.94	
CoxONa	83.73	10.83	2.18	
(1*R*,2*R*)-[Mn(3,5-dtButsalhd)Cl]@CoxONa	83.96	11.19	0.99	0.87 (0.692)[b]

[a] Atomic percentages.

[b] The value in parenthesis is in mmol g^{-1}. The value was calculated using the formula: mmol Mn/weight of sample = at% Mn/[at% Mn × Ar(Mn) + at% C × Ar(C) + at% O × Ar(O) + at% C × Ar(C) + at% Na × Ar(Na)].

Table 2
Styrene epoxidation results using the homogeneous and heterogeneous catalyst with 2 mol% of manganese relative to alkene[a]

Entry	Catalyst	Oxidant/temperature[b]	Cycle	*t* (h)	%C	TON[c]	TOF (h^{-1})[d]	%ee
1	(1*R*,2*R*)-[Mn(3,5-dtButsalhd)Cl]	*m*-CPBA/−5 °C		0.5	100	48	95	47
2		PhIO/rt		1	60	28	28	12
4	(1*R*,2*R*)-[Mn(3,5-dtButsalhd)Cl]@CoxONa	*m*-CPBA/−5 °C	1st	4	94	46	11	44
5			2nd	4	60	30	8	16
6		PhIO/rt	1st	23	77	38	2	12
7			2nd	24	49	26	1	8

[a] Experimental conditions: 0.500 mmol of styrene, 0.500 mmol chlorobenzene (internal standard), 0.100 g of heterogeneous catalyst and 0.250 mmol of PhIO (oxidant), in acetonitrile, or 1.000 mmol of *m*-CPBA/2.500 mmol NMO (oxidant system), in dichloromethane.

[b] Alkene: styrene; oxidant: *m*-CPBA = 3-chloroperoxybenzoic acid and PhIO = iodosylbenzene.

[c] Total TON based on the styrene conversion.

[d] TOF = TON/reaction time.

Since in our previous paper on the carbon based catalysts with non-chiral manganese(III) *salen* counterparts [10,11], we have shown that these materials behave as stable and reusable catalysts in the epoxidation of styrene using PhIO as the oxygen source, we have also tested this oxidant in this work, using the reported experimental conditions. The results obtained are collected in Table 2.

The (1*R*,2*R*)-[Mn(3,5-dtButsalhd)Cl]@CoxONa catalyst acted as an enantioselective heterogeneous catalyst in the epoxidation of styrene using *m*-CPBA as oxidant and NMO as co-oxidant (entry 4), with comparable enantiomeric excess, conversion and turnover number as the reaction run with the homogeneous counterpart (entry 1), under similar experimental conditions, and with similar enantiomeric excess percentage (%ee) to the ones reported in the literature by Jacobsen with this catalyst [13]. The reaction run with PhIO gave much lower %ee (entry 6) than with *m*-CPBA/NMO (entry 4), but nevertheless equal %ee to that of homogeneous phase reaction and with better styrene conversion and, consequently, turnover number (entry 2). Hence the axially coordination of the manganese(III) *salen* homogeneous catalyst onto the surface phenolate groups of the activated carbon does not result in significant loss in enantiomeric excess in the case of styrene.

With the heterogeneous catalysts, the reaction time increases when compared with the homogeneous counterparts (Table 2). This 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 that has low solubility in acetonitrile and whose solubilisation is controlled by its rate of consumption. As a consequence the TOF values for the heterogeneous reactions are lower than those of homogeneous ones (Table 2).

The catalyst was also reutilised using the same epoxidation procedures, after convenient purification process (i.e. Soxhlet extraction with dichloromethane and ethanol, 4 h each, and then drying in an oven at 120 °C for 13 h, under vacuum). Reutilisation of the (1*R*,2*R*)-[Mn(3,5-dtButsalhd)Cl]@CoxONa heterogeneous catalyst resulted in loss of catalytic activity and enantioselectivity. ICP-AES manganese analysis of the heterogeneous catalyst after two successive catalytic cycles (0.091 mmol g^{-1} material) showed that no significant loss of the manganese(III) complex took place during the experiments. Thus, metal leaching is not responsible for the deactivation of the heterogeneous catalyst, and probably is due to ligand degradation under the experimental conditions, as already reported in the literature for other heterogenised chiral manganese(III) *salen* complexes onto several supports [3,14,15].

This is more evident for the experiments where *m*-CPBA is used as oxygen source, since the experiment performed with PhIO as oxygen gave lower styrene epoxide enantiomeric induction than with *m*-CPBA,

but resulted in lower loss of activity when the catalyst was reused (Table 2). This may be due to the lower stability of the manganese(III) *salen* complexes under the epoxidation conditions with *m*-CPBA, than in the case with PhIO, since we have reported stable and reusable carbon base catalysts with manganese(III) *salen* complexes [10,11].

Acknowledgments

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Catalytic chemical vapor deposition of vertically aligned carbon nanotubes on iron nanoislands formed from Fe+-implanted SiO2 films

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Carbon nanotubes (CNTs) are attracting great interest because of their unique properties and wide applicability [1]. Potential applications of CNTs include: fiber reinforcement for composites (high strength, high aspect

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