



Jacobsen catalyst anchored onto modified carbon xerogel as enantioselective heterogeneous catalyst for alkene epoxidation

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ABSTRACT

Two types of carbon xerogels were prepared using two different methodologies where the pH of the solution during the sol–gel processing, formaldehyde/resorcinol ratio and the drying method, were varied (01CX and 02CX). The samples show distinct textural properties: 02CX material has higher mesopore area and micropore volume than 01CX, but the pore radius of the latter material is three times larger than the former. Activation of the materials under 5% O₂ (in N₂) at 440 °C introduces surface oxygen groups, mainly phenol and carbonyl/quinone groups with small quantities of carboxylic anhydrides. Treatment with sodium hydroxide solution converted the phenol groups into phenolates and promotes hydrolysis of carboxylic anhydrides into carboxylates.

A modified *Jacobsen* catalyst was directly immobilised via axial coordination of the Mn(III) metallic centre onto the phenolate/carboxylate groups of the sodium modified carbon xerogels. The catalysts were tested in the asymmetric epoxidation of styrene, α -methylstyrene and 6-cyano-2,2-dimethylchromene using *m*-CPBA/NMO, NaOCl or PhIO as oxygen sources. The catalysts show some activity and enantioselectivity, eventhough loss of Mn is evident. Blank runs involving the carbon xerogel and the oxidants suggest that the oxidants do not attack the surface hydroxyl groups responsible for the metal complex immobilisation.

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1. Introduction

Carbon materials are good catalyst supports especially for liquid phase reactions, since they present some advantages over conventional inorganic supports, such as higher stability in acid and basic media. Conventional inorganic supports such as alumina and silica are dissolved at high pHs and the former is also attacked even at very low pHs [1]. In addition to higher stability, both the porous texture and surface chemistry of carbon materials can be modified by appropriate methodologies [2].

Recently, there has been a growing interest for polymer based porous carbon because they can be easily produced in the form of monolith or membrane, useful in more advanced applications. Activated carbons obtained from natural precursors are not suitable in this regard. Also, the porous texture and surface chemical properties of polymer based carbon xerogels can be easily tailored to meet specific requirements. Pekala has described the synthe-

sis of carbon xerogels by sol–gel condensation of resorcinol and formaldehyde and subsequent carbonisation of the organic aerogel [3]. Reports are also available on the modification of porous texture and surface chemical properties of carbon xerogels [4–6]. Carbon xerogels possess all the qualities required of a good catalyst support. High surface area, high porosity, tunable pore size, open pore network, high density, stability in severe reaction media, etc., make them natural choice as catalyst support. Also they can be formed according to user's need like monolith, membrane, particulate or powder.

Manganese(III) *salen* complexes have been reported as highly active and enantioselective catalysts in the epoxidation of unfunctionalised alkenes in homogeneous phase, using a wide range of oxidants [7,8]. 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 [9,10]. Moreover, anchoring of the Mn(III) *salen* complexes onto supports has been found to increase the catalyst stability, since the main deactivation process observed in homogeneous phase, formation of inactive dimeric μ -oxo Mn(IV) species, is hindered by local site isolation of the complexes in a solid matrix [9,10].

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We have been using different strategies for the immobilisation of manganese(III) complexes with *salen* ligands onto activated carbons, and the resulting catalysts proved to be efficient and reusable in epoxidation reactions [11–16]. Now we intend to extend and improve the established methodologies to new carbon materials such as carbon xerogels. We already tested these materials as supports for a non-chiral manganese(III) *salen* complex which possessed an extended ligand π system and two reactive hydroxyl groups on the aldehyde fragment [17]. We found that complex immobilisation took place preferably by covalent bond between the surface oxygen functional groups and the ligand reactive OH groups rather than by π – π interactions and that the size and shape of the carbon xerogel pores played an important role in the final loading of the manganese(III) *salen* complex [17]. Therefore, herein we report the immobilisation of a chiral manganese(III) *salen* complex (a modified *Jacobsen* catalyst) onto two carbon xerogels with different pore size, after chemical treatment with O_2 and NaOH, using a methodology tested for activated carbons [14]: direct anchoring of the complex through axial coordination of the metal centre onto pre-formed phenolate and carboxylate carbon surface groups. The resulting anchored catalysts were tested in the asymmetric epoxidation of styrene, α -methylstyrene and 6-cyano-2,2-dimethylchromene using several oxygen sources.

2. Experimental

2.1. Materials and reagents

Formaldehyde, resorcinol, silver perchlorate, (*R,R*)-(–)-*N,N'*-bis(3,5-di-*tert*-butylsalicyldene)-1,2-cyclohexanediaminomanganese(III) chloride (*Jacobsen* catalyst), styrene, α -methylstyrene, 2,2-dimethyl-6-cyanochromene, 3-chloroperoxybenzoic acid (*m*-CPBA), 4-methylmorphine *N*-oxide (NMO), chlorobenzene and sodium hypochlorite solution were obtained from Aldrich. Sodium hydroxide and sodium carbonate were obtained from Merck (*p.a.*). All the solvents used were from Merck (*p.a.*), except dichloromethane and acetonitrile used in the catalytic experiments which were from Romil (HPLC grade).

2.2. Synthesis of mesoporous carbon and activation

Two types of mesoporous carbon xerogels, denoted as 01CX and 02CX, were synthesised by the conventional sol–gel technique using formaldehyde and resorcinol following two different methodologies. Detailed procedures were described elsewhere [17]. In brief, sol–gel processing with a formaldehyde/resorcinol ratio of 1.85 at pH 6.1 (adjusted by dilute NaOH solution), followed by removal of water by direct drying in an air oven during a period of seven days and subsequent carbonisation led to sample 01CX. Whereas, sol–gel processing with a formaldehyde/resorcinol ratio of 2.0 at pH 6.85 (adjusted by dilute Na_2CO_3 solution), followed by removal of water by sequential exchange with acetone and cyclohexane and subsequent drying and carbonisation led to sample 02CX.

In order to generate surface oxygen groups, the carbon materials were subjected to activation by diluted oxygen flow (in nitrogen). A detailed procedure is described elsewhere [17]. In brief, the carbon materials were activated under 5% O_2 (in N_2) at 440 °C for 30 h and thus the surface activated samples 01CX-09 and 02CX-16 were obtained. The numbers 09 and 16 are the % burn-off (BO) values.

The activated samples 01CX-09 and 02CX-16 (1.10 g each) were then refluxed with an aqueous solution of sodium hydroxide (100 cm³, 13.3 mmol g^{–1}) for an hour; a decrease in the pH of the aqueous solution from 14 to 13 was observed [14,15]. These mate-

rials were washed with deionised water until constant pH (8) and then dried at 120 °C in an oven, under vacuum. These samples were designated as Na@01CX-09 and Na@02CX-16.

2.3. Anchoring of *Jacobsen* catalyst

The commercial *Jacobsen* catalyst was made to react with silver perchlorate in order to exchange the coordinated chloride anion to the non-coordinating perchlorate (CAT), in sequence to free the fifth coordinate position for direct anchoring of the complex onto the carbon xerogels. The effective substitution of the chloride by the perchlorate anion was checked by FTIR [18].

An ethanolic solution of the modified *Jacobsen* catalyst (290 μ mol) was refluxed with both modified carbon xerogels, Na@01CX-09 and Na@02CX-16 (0.70 g each). The anchoring process was monitored by UV–vis spectroscopy and a decrease in intensity of the electronic bands of the manganese(III) *salen* complex in the region 200–800 nm was observed. In order to remove physisorbed complex, the resulting materials were purified by Soxhlet extraction with ethanol for 8 h. Finally, the materials were vacuum dried in an oven overnight at 120 °C. The materials were designated as CAT@01CX-09 and CAT@02CX-16 and the amount of complex anchored in both materials was determined by ICP-AES.

2.4. Physico-chemical measurements

Textural characterisation of the samples was based on the analysis of nitrogen sorption isotherms measured at 77 K in a Coulter Omnisorp 100CX sorptometer. BET surface area (S_{BET}), mesopore surface area (S_{meso}) and micropore volume (V_{micro}) were calculated using the BET equation and the *t*-method, respectively, as described elsewhere [2]. Pore size distributions were obtained from the desorption branch of the isotherm using the Barrett, Joyner and Halenda (BJH) method [19].

Surface oxygen functional groups were characterised by temperature programmed desorption (TPD-MS). The analyses were performed in an apparatus described elsewhere [2]. The samples were subjected to a 5 °C min^{–1} linear temperature rise up to 1100 °C under helium flow of 25 cm³ min^{–1}. A SPECTRAMASS Dataquad quadrupole mass spectrometer was used to monitor the desorbed CO ($m/z=28$) and CO₂ ($m/z=44$) signals.

FTIR spectra of the commercial and modified *Jacobsen* complexes were obtained as KBr pellets in the range 400–4000 cm^{–1} using a Jasco FTIR-460 Plus spectrophotometer. Manganese ICP-AES analysis was carried out at “Laboratório de Análises”, IST, Lisbon (Portugal).

2.5. Catalytic experiments

The catalysts, CAT@01CX-09 and CAT@02CX-16, were tested under constant stirring conditions in the asymmetric epoxidation of: (i) styrene in dichloromethane at –5 °C using *m*-CPBA/NMO as oxygen source, (ii) α -methylstyrene or 6-cyano-2,2-dimethylchromene in dichloromethane at 0 °C using NaOCl as oxidant and (iii) 6-cyano-2,2-dimethylchromene in acetonitrile at room temperature using PhIO as oxygen source. The oxidant used as well as the experimental conditions were different according to the substrate in study, because the asymmetric epoxidation of alkenes by Mn(III) *salen* complexes shows different reactivity depending on the substrate and oxidant in use [7,8]. Therefore the optimum homogeneous phase combinations of substrate/oxidant were adapted from the literature to the heterogeneous reactions. The composition of the reaction mixture was typically, 0.500 mmol of chlorobenzene (internal standard), 0.100 g of heterogeneous catalyst and: (i) 0.500 mmol of styrene, 1.00 mol

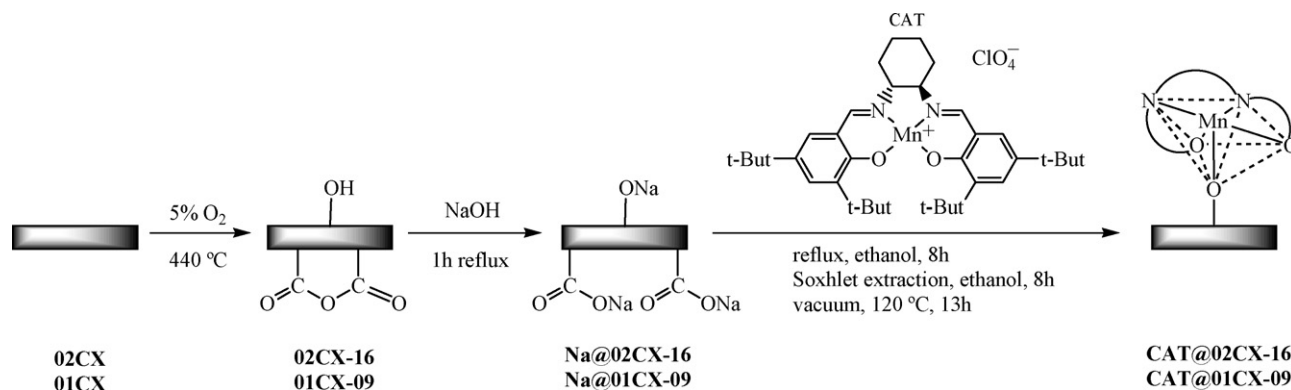


Fig. 1. Anchoring of the *Jacobsen* catalyst (CAT) onto carbon xerogels (CX) using a simple and straightforward method.

of *m*-CPBA and 2.50 mmol of NMO (co-oxidant), in 5.00 cm³ of dichloromethane at -5°C (sodium chloride in an ice bath); (ii) 0.500 mmol of 6-CN-2,2-diMeChromene or α -methylstyrene and 0.75 mmol of NaOCl, in 5.00 cm³ of dichloromethane at 0°C (ice bath); (iii) 0.250 mmol of 6-CN-2,2-diMeChromene and 0.12 mmol of PhIO, in 5.00 cm³ of acetonitrile at room temperature.

After the first run the catalysts were washed sequentially for 2 h by Soxhlet extraction with: (i) 100 cm³ of methanol and 100 cm³ of dichloromethane (system styrene/*m*-CPBA-NMO), or (ii) 100 cm³ of dichloromethane and 100 cm³ of acetonitrile (system 6-CN-2,2-diMeChromene or α -methylstyrene/NaOCl), or (iii) 100 cm³ of acetonitrile and 100 cm³ of methanol (system 6-CN-2,2-diMeChromene/PhIO). Finally, the materials were dried under vacuum at 120°C , overnight, and then reused using the same experimental conditions.

To provide a framework for the results obtained using the heterogeneous catalysts, all the three epoxidation systems were also carried out in homogeneous media under identical experimental conditions to those described above, using the same amount of the *Jacobsen* catalyst immobilised. The contribution of the supports to the epoxidation reactions was found to be insignificant: 2–5% substrate conversion after 48 h.

During the experiments 0.05 cm³ aliquots were withdrawn from solution, with a hypodermic syringe, filtered through 0.2 μm PTFE syringe filters, and analysed by non-chiral and chiral GC. Alkene conversion and epoxide selectivity were followed by analyzing the samples with a Varian CP-3380 gas chromatograph equipped with a fused silica Varian Chrompack capillary column CP-Sil 8 CB Low Bleed/MS (30 m \times 0.25 mm id; 0.25 μm film thickness) and flame ionization detector using helium as carrier gas. The enantiomeric excesses (%ee) of the epoxides were determined with the same chromatograph but using a fused silica Varian Chrompack capillary column CP-Chiralsil-Dex CB (25 m \times 0.25 mm id; 0.25 μm film thickness). Conditions used: 60°C (3 min), ramp $5^{\circ}\text{C min}^{-1}$, 170°C (2 min), ramp $20^{\circ}\text{C min}^{-1}$, 200°C (10 min); injector temperature, 200°C ; detector temperature, 300°C . Conversion (%) and enan-

tiomeric excess (%ee) were calculated using the following formula: $\%C = \{[A(\text{alkene})/A(\text{chlorobenzene})]_{t=0\text{h}} - [A(\text{alkene})/A(\text{chlorobenzene})]_{t=x\text{h}}\} \times 100/[A(\text{alkene})/A(\text{chlorobenzene})]_{t=0\text{h}}$; and $\%ee = [A(\text{major enantiomer}) - A(\text{minor enantiomer})] \times 100/[A(\text{major enantiomer}) + A(\text{minor enantiomer})]$, where *A* stands for area of the respective chromatographic peak.

In order to study the influence of the oxidants on the carbon xerogel surface, blank experiments involving one of the parent materials, 01CX-09, and the oxidants *m*-CPBA, and PhIO, were also performed following the same experimental conditions.

3. Results and discussion

The modified *Jacobsen* catalyst (CAT) was immobilised onto the carbon xerogels by direct anchoring of the complex onto the phenolate and carboxylate groups, created by the chemical treatment of the carbon xerogels (01CX and 02CX) which involved the O₂ activation (01CX-09 and 02CX-16), followed by refluxing the materials with a solution of NaOH (Na@01CX-09 and Na@02CX-16), Fig. 1. Characterization of the materials in the different steps was performed by TPD and N₂-sorption studies.

3.1. Textural and surface chemical characterisation

Two different methodologies were applied to prepare carbon xerogels and the resulting samples were activated with diluted O₂ in order to create oxygen surface groups.

The textural properties are summarised in Table 1 and the pore size distributions are depicted in Fig. 2. The N₂-sorption isotherms obtained for both materials (not shown) are of type IV, typical of materials with mesopores. Material 02CX-16 has considerably higher mesopore surface area and micropore volume than the sample 01CX-09, but the average pore radius of the latter sample (5.6 nm) is three times larger than the former (1.8 nm). The difference in pore radius between samples 01CX-09 and 02CX-16 was attributed to the preparation pH during sol–gel processing. According to published literature, pore radius of final carbon material

Table 1

Textural and chemical properties of the carbon xerogel based materials. RP is the average pore radius.

Sample	S_{BET} (m ² g ⁻¹)	S_{meso} (m ² g ⁻¹)	V_{micro} (cm ³ g ⁻¹)	RP (nm)	CO ($\mu\text{mol g}^{-1}$)	CO ₂ ($\mu\text{mol g}^{-1}$)	Mn ($\mu\text{mol g}^{-1}$)
01CX-09	717	311	0.124	5.6	1505	171	–
Na@01CX-09	718	334	0.124	5.6	966	346	–
CAT@01CX-09	637	302	0.090	5.4	–	–	113
02CX-16	792	462	0.157	1.8	3981	389	–
Na@02CX-16	690	381	0.114	1.8	3042	697	–
CAT@02CX-16	595	369	0.071	1.8	–	–	76

decreases with increase in the sol–gel processing pH of the parent gel [4,17,20].

Upon sodium hydroxide treatment different changes on the textural properties of the two materials were observed. Textural properties hardly changed in case of 01CX-09, probably because of its wider pores, but for 02CX-16 the BET area, mesopore area and micropore volume decreased considerably. However, there was no change in the average pore radius for both materials.

The surface oxygen groups present on the oxidised carbon xerogels before and after sodium modification were characterized by TPD-MS (Fig. 3). The surface oxygen groups decompose with the evolution of CO (anhydrides, phenols, carbonyls) or CO₂ (carboxylic acids, anhydrides, lactones) [2]. The total amounts of CO and CO₂ released were calculated from the corresponding TPD-MS spectra and are shown in Table 1.

The CO TPD-MS profiles of both oxidised carbon xerogels (Fig. 3) show the presence of a peak at 650 °C that includes the decomposition of carboxylic anhydrides and phenol groups present on the surface of the material, and a higher temperature peak due to the decomposition of carbonyl/quinone groups. The high temperature broad peak in the CO₂ TPD-MS profiles of both oxidised carbon xerogels (Fig. 3) corresponds to the decomposition of carboxylic anhydrides and lactone groups.

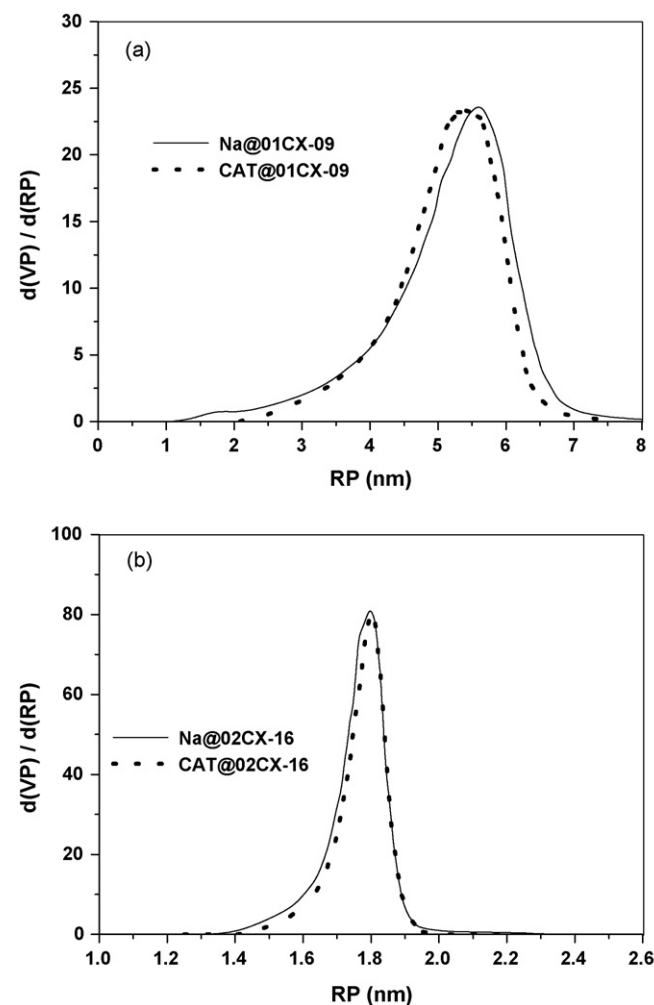


Fig. 2. Pore size distributions of the Na modified mesoporous carbon xerogels (a) Na@01CX-09 and (b) Na@02CX-16, before and after anchoring of *Jacobsen* catalyst. RP is the pore radius and VP is the pore volume.

After reflux of the samples with sodium hydroxide significant changes can be seen in the CO and CO₂ TPD-MS profiles: the peak at 650 °C in the CO TPD-MS profiles of both oxidised carbon xerogels (Fig. 3) almost disappears; instead, the peak intensity increases at around 775 °C. This clearly indicates the disappearance of the carboxylic anhydrides and phenol groups. Phenol groups are converted to Na-phenolates and probably they are comparatively more stable and hence decomposed at higher temperature. There is also an increase in oxygen groups that evolve as CO₂ at low temperatures (Fig. 3 and Table 1), which may be due to Na-carboxylate groups, formed from hydrolysis of carboxylic anhydrides promoted by the aqueous sodium hydroxide solution. These observations correlate well with previous TG-IR results reported by us for sodium hydroxide refluxed oxidised activated carbons [15]. Therefore, TPD-MS data indicate that reaction between sodium hydroxide and phenol groups took place giving rise to phenolate groups and also suggest that some hydrolysis of carboxylic anhydrides occurred giving rise to carboxylate groups, which can both act as coordinating sites for the penta-coordinate Mn(III) *salen* complex (CAT).

Immobilization of the Mn-complex onto Na@01CX-09 and Na@02CX-16 was confirmed by the ICP-AES manganese analysis. The extent of immobilization of Mn-complex is much higher onto the former material than the latter one (113 $\mu\text{mol g}^{-1}$ vs. 76 $\mu\text{mol g}^{-1}$). The higher immobilization efficiency obtained for Na@01CX-09 despite the lower amount of surface oxygen groups is a consequence of the higher pore radius that facilitates the diffusion of the Mn complex within the porous structure of the material towards the reactive carbon oxygen surface groups.

Complex immobilisation led to significant changes in the textural properties of the modified carbon xerogels, which are different for the two materials. Comparing with the parent materials (Na@01CX-09 and Na@02CX-16) the sample CAT@01CX-09 revealed a decrease of 12% for S_{BET} , whereas for CAT@02CX-16 the decrease was 14%; similarly, V_{micro} of CAT@01CX-09 showed a decrease of 27% which is less than that observed for CAT@02CX-16, which was as high as 37%. In terms of S_{meso} sample CAT@01CX-09 showed a higher decrease (9%) than CAT@02CX-16, which was only 3%. However, only for the former material there was a decrease in the average pore radius of approximately 3.5% (Fig. 2).

No direct evidence for the immobilization mechanism could be obtained from the characterization studies. Nevertheless, we propose that complex immobilization occurs by ionic exchange between the cationic Mn(III) *salen* complex and the sodium cations from as-created phenolate/carboxylate groups, which ultimately leads to the coordination of these surface groups to Mn(III) metallic center, Fig. 1; this immobilization mechanism was observed in the anchoring of the *Jacobsen* catalyst into an activated carbon treated with NaOH [14].

3.2. Catalytic experiments

The catalytic properties of the complex modified carbon xerogels are compiled in Table 2. These materials were active and enantioselective in the epoxidation of: (i) styrene, using *m*-CPBA as oxidant and NMO as co-oxidant; (ii) 6-CN-2,2-diMeChromene or α -methylstyrene, using NaOCl as oxidant; and (iii) 6-CN-2,2-diMeChromene using PhIO as oxidants.

The material CAT@01CX-09 is generally more active (higher substrate conversion and epoxide selectivity) than CAT@02CX-16 for all the alkenes tested, which may be due to the higher loading of the active complex. Larger pore radius of the support may also play a crucial role by decreasing diffusion limitations imposed by the porous structure of the material. In most cases, higher enantioselectivities were obtained with CAT@02CX-16 for the epoxides of α -methylstyrene and 6-cyano-2,2-dimethylchromene, which may

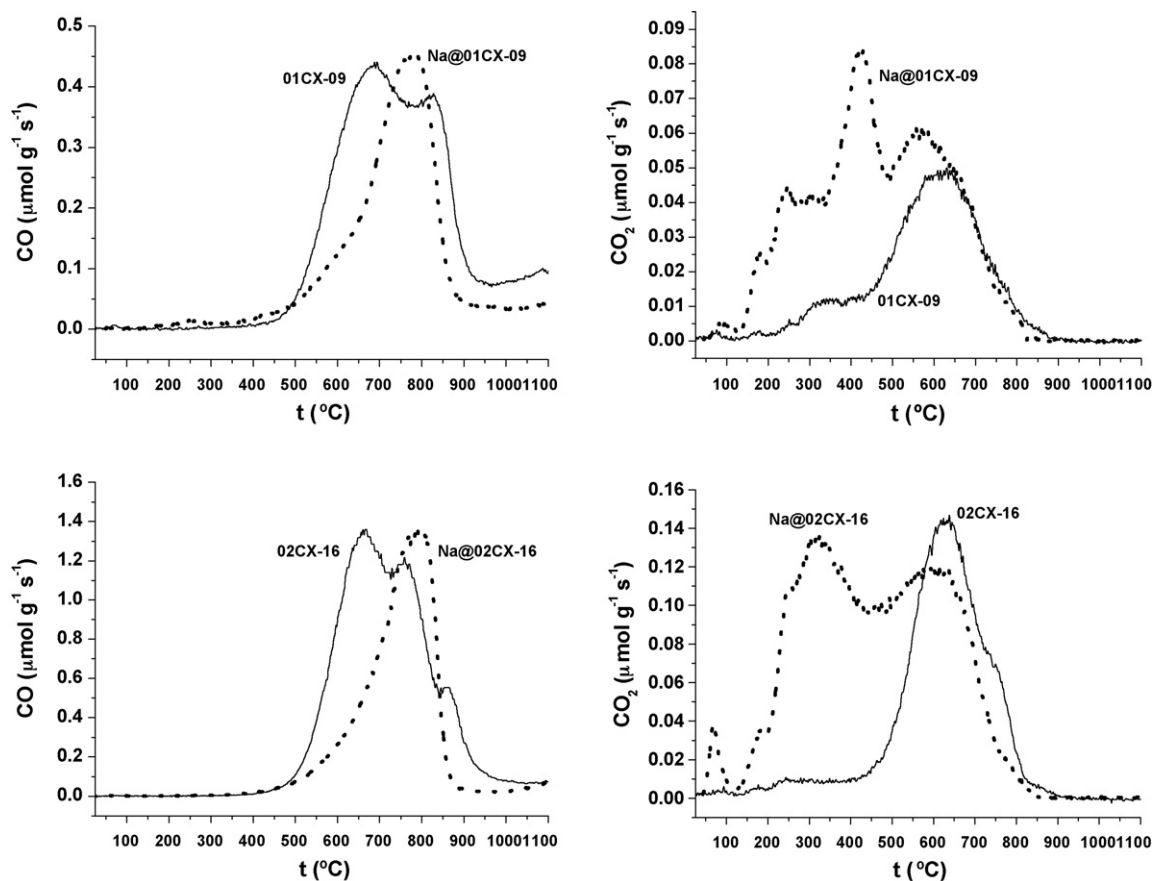


Fig. 3. CO and CO₂ TPD profiles of 01CX-09 and 02CX-16 before and after reflux with a NaOH solution.

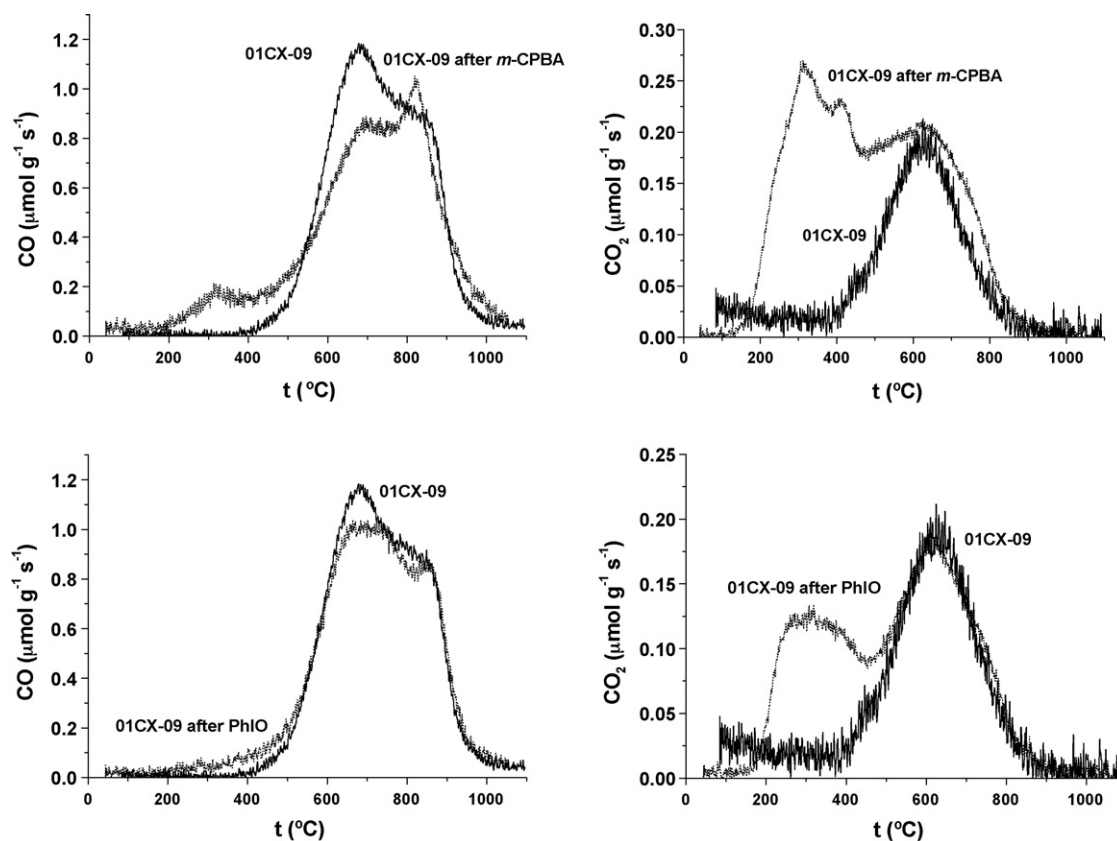


Fig. 4. CO and CO₂ TPD profiles of 01CX-09 before and after treatment with different oxidants.

Table 2
Catalytic properties of the carbon xerogel based materials.

Catalyst	Alkene/oxidant	Run	t (h)	%C ^a	%S ^a	%ee ^b
CAT	Styrene/ <i>m</i> -CPBA-NMO ^c	hom	1	99	91	47
CAT@01CX-09		1st	4	26	81	31
		2nd	4	15	66	3
CAT	α -Me-styrene/NaOCl ^d	hom	24	44	79	63
CAT@01CX-09		1st	24	24	3	41
		2nd	24	15	1	72
CAT	6-CNchromene/NaOCl ^d	hom	24	16	96	88
CAT@01CX-09		1st	48	5	79	82
		2nd	48	14	3	46
CAT	6-CNchromene/PhIO ^e	hom	24	38	79	76
CAT@01CX-09		1st	72	10	65	57
		2nd	72	13	34	33
CAT	Styrene/ <i>m</i> -CPBA-NMO ^c	hom	1	99	94	46
CAT@02CX-16		1st	4	16	69	32
		2nd	4	7	26	7
CAT	α -Me-styrene/NaOCl ^c	hom	24	30	74	73
CAT@02CX-16		1st	24	18	2	74
		2nd	24	18	1	85
CAT	6-CNchromene/NaOCl ^c	hom	24	2	97	88
CAT@02CX-16		1st	48	5	86	79
		2nd	48	8	6	42
CAT	6-CNchromene/PhIO ^d	hom	24	39	83	77
CAT@02CX-16		1st	72	5	17	73
		2nd	72	0	0	0

^a %C–alkene conversion, %S–epoxide selectivity: determined by non-chiral GC.

^b Enantiomeric excess: determined by chiral GC.

^c Experimental conditions: 0.500 mmol of styrene, 0.500 mmol of chlorobenzene (internal standard), 2.50 mmol of NMO (co-oxidant), 0.100 g of heterogeneous catalyst and 1.00 mol of *m*-CPBA, in 5.00 cm³ of dichloromethane, at –5 °C.

^d Experimental conditions: 0.500 mmol of 6-CN-2,2-diMeChromene or α -methylstyrene, 0.500 mmol of chlorobenzene (internal standard), 0.100 g of heterogeneous catalyst and 0.75 mmol of NaOCl, in 5.00 cm³ of dichloromethane, at 0 °C.

^e Experimental conditions: 0.250 mmol of 6-CN-2,2-diMeChromene, 0.500 mmol of chlorobenzene (internal standard), 0.100 g of heterogeneous catalyst and 0.12 mmol of PhIO, in 5.00 cm³ of acetonitrile, at room temperature.

be a consequence of the very low epoxide selectivity (former alkene) or very low substrate conversion (latter alkene).

Generally, heterogeneous asymmetric epoxidation reactions showed lower performance than the corresponding homogeneous phase reactions. Interestingly, catalyst CAT@02CX-16 showed higher enantiomeric excess than the homogeneous counterpart in the epoxidation of α -methylstyrene with NaOCl. However, the other epoxidation reactions showed lower enantioselectivities with the heterogeneous catalysts in comparison to their homogeneous counterparts.

The heterogeneous catalysts were reused in a second run. The Mn content after two catalytic cycles was determined by ICP-AES analysis. The results are compiled in Table 3, along with those obtained for the materials before the catalytic reactions.

With the exception of the epoxidation of α -methylstyrene with NaOCl where no changes were observed in the enantioselectivity, or catalytic activity, reuse of both heterogeneous catalysts in the different epoxidation conditions resulted in a loss of enan-

tiomeric excess and catalytic activity. Analysis of Mn content after catalyst reuse indicates that there is some loss of the Mn complex (Table 3), what can explain, to some extent, the observed catalytic results. Epoxidation using PhIO as oxidant for both CAT@01CX-09 and CAT@02CX-16 led to the lowest Mn leaching. In part this result may be a consequence of the higher resistance to decomposition of the manganese(III) *salen* catalysts under this epoxidation condition [11–14]. However, reuse of the latter catalyst did not result in any substrate conversion.

The epoxidation reactions with NaOCl as oxygen source led to extensive Mn leaching (as high as 60%), indicating that for this type of anchored complex, this oxidant has a pernicious effect. The epoxidation with *m*-CPBA as oxidant has different extents of Mn leaching for the two materials: the one with the smaller pores showed the lowest leaching, while the material with wider pore showed the highest leaching.

In terms of the materials, CAT@01CX-09 showed higher Mn leaching than CAT@02CX-16. The general lower leaching percentages exhibited by CAT@02CX-16, can be due to the confinement of the bulky complex within its pores, which are smaller than those of CAT@01CX-09, which can result in a strong interaction between the Mn complex and the reactive oxygen surface groups.

Moreover, data from the blank runs performed using the parent material 01CX-09 under the same experimental conditions are shown in Fig. 4 in order to study the effect of the oxidants used on the surface oxygen groups of the carbon xerogel. No significant changes in the CO TPD profiles is observed, suggesting that the surface hydroxyl groups responsible for the complex immobilization are not attacked by the different oxidants used in the catalytic experiments. The CO₂ TPD profiles show an increase in

Table 3
Mn ICP-AES analysis of the heterogeneous catalysts before reaction and after two consecutive cycles of catalysis.

Experimental conditions	Mn (μ mol/g)	
	CAT@02CX-16	CAT@01CX-09
Before catalysis	76	113
Styrene/ <i>m</i> -CPBA-NMO	53	35
α -Me-styrene/NaOCl	27	47
6-CNchromene/NaOCl	27	42
6-CNchromene/PhIO	53	62

the low temperature decomposition region, which is assigned to the formation of carboxylic acids upon reaction with the different oxidant species, as expected. From these data, we propose that the oxidizing conditions, to which the heterogeneous catalysts are exposed to, are not responsible for the observed complex leaching. In this context, we can assign the observed complex leaching to the complex degradation under the reaction conditions, and not to the destruction of the complex-support bond.

4. Conclusions

Two types of carbon xerogels were prepared using two different methodologies where the pH of the solution during the sol–gel processing, formaldehyde/resorcinol ratio, and the drying method were varied, which resulted in carbon xerogels with distinct textural properties: the O2CX material has higher mesopore area and micropore volume than the O1CX material, but the pore radius in the latter material is three times larger than the former. Activation of these materials introduces mainly phenol and carbonyl/quinone groups.

These materials were refluxed with a sodium hydroxide solution which converted the phenol groups into phenolates and induced some hydrolysis of carboxylic anhydrides giving rise to carboxylate groups; these groups were available to act as coordination sites for immobilization of the modified *Jacobsen* catalyst by axial coordination to the Mn(III) metallic centre. The material with higher pore radius anchored higher amount of the homogeneous catalyst.

These materials were tested as heterogeneous catalysts in the asymmetric epoxidation of styrene, α -methylstyrene and 6-cyano-2,2-dimethylchromene using *m*-CPBA/NMO, NaOCl or PhIO as oxygen sources. The heterogeneous catalyst CAT@O1CX-09 is generally more active for all the alkenes tested than CAT@O2CX-16, which may be due to the higher loading of active complex and larger pore radius of the material. However, higher enantioselectivities were obtained with CAT@O2CX-16 for the epoxides of α -methylstyrene and 6-cyano-2,2-dimethylchromene, probably due to confinement effects.

In the case of the asymmetric epoxidation of α -methylstyrene with NaOCl constancy of catalytic activity and enantioselectivity were observed upon reuse of both heterogeneous catalysts, whereas for the epoxidation of 6-cyano-2,2-dimethylchromene using NaOCl or PhIO as oxygen sources no general decrease in the catalytic activity is observed, but the enantioselectivity decreases.

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