



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, even though 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

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