



## Recycled carbon (RC) materials made functional: An efficient heterogeneous Mn-RC catalyst



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### ABSTRACT

A Mn<sup>II</sup>-Schiff-base catalyst was synthesized and covalently immobilized onto Pyrolytic Carbon surface from waste tyres (**PC<sub>ox</sub>**), resulting in the heterogeneous catalyst **Mn<sup>II</sup>-L@PC<sub>ox</sub>** which was evaluated for degradation of methyl orange (MO) using NaIO<sub>4</sub> as oxidant. Importantly, no additive as co-catalyst was needed. For comparison, a reference heterogeneous catalyst **Mn<sup>II</sup>-L@AC<sub>ox</sub>** was also tested, using Activated Carbon (**AC<sub>ox</sub>**) as carbon matrix. The catalytic and recyclability data of **Mn<sup>II</sup>-L@PC<sub>ox</sub>** catalyst demonstrate that it is superior, in terms of TONs and TOFs vs. **Mn<sup>II</sup>-L@AC<sub>ox</sub>**. To study the reaction path, electron paramagnetic resonance spectroscopy was used to monitor the redox evolution of the Mn-centers. Furthermore, a full mapping of the catalytic degradation of MO and product formation was carried out using LC-MS and HPLC. Combining catalytic and spectroscopic data we discuss the protective effect of the **PC<sub>ox</sub>** matrix on Mn-centers; it allows their rapid redox evolution to higher oxidation states.

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### 1. Introduction

Annually, azo-dyes are produced and utilized in large quantities in diverse applications including textiles, paint pigments, printing inks and food coloring [1–4]. The presence of dyes in effluent and industrial wastewater entails considerable environmental/economic concern, including health risks [1–7]. Among various oxidative transition metal catalysts, manganese is advantageous, e.g., as it is economic, efficient and environmental friendly metal [8–10]. Non-heme manganese complexes are often easily prepared/handled as catalysts and this is a reason why they have received considerable attention [8–10]. In this context, new, efficient, selective, low-cost and easy to prepare Mn-catalysts remain at high demand in the field of oxidation catalysis [8]. So far, catalytic degradation of organic dyes by non-heme Mn<sup>II</sup>-HCO<sub>3</sub><sup>−</sup> catalysts has been reported under mild reaction conditions, e.g., using H<sub>2</sub>O<sub>2</sub> as oxidant [11–16]. Rothbart et al. investigated the oxidative degradation of Orange II by Mn<sup>II</sup>-HCO<sub>3</sub><sup>−</sup> and peracetic acid [13,14]. Ember et al. postulated that the formation of highly reactive manganese intermediates in the presence of carbonates in aqueous

solution, with no coordinative ligand, can lead to degradation of organic dyes [12]. H<sub>2</sub>O<sub>2</sub> as oxidant can be used in cases where dismutation of H<sub>2</sub>O<sub>2</sub> does not occur, and relatively mild redox potentials i.e., around 300 mV, are sufficient [8–14]. In the case where higher redox potentials have to be accessed and/or H<sub>2</sub>O<sub>2</sub> dismutation is a limiting factor, oxidants other than H<sub>2</sub>O<sub>2</sub> have to be used. Chellamani et al. reported the kinetics and mechanism of methyl-phenyl-sulfides oxidation catalyzed by Mn<sup>II</sup>(salen) complexes, with NaIO<sub>4</sub> as oxidant [17].

Catalytic efficiency is only one of the key-prerequisites for technologically exploitable Mn-catalysts. Stability/reusability of the catalyst is an equally important parameter for catalytic reactions. In this context, recovery and reuse of the used catalyst is a challenging task that has to be considered. This can be achieved by replacing a –successful– homogeneous catalyst by an active heterogeneous one. Heterogenization changes the synthetic process toward a more desirable and clean one, providing advantages e.g., such as easy handling, easy product separation, catalyst recovery and lower waste's production. To this front, the heterogenization of a metal-catalyst on a solid support has been proven fruitful in the recovery and reuse of catalysts [8–10,18–25]. Furthermore, the use of inorganic support materials with covalently-bound active centers as heterogenised catalysts endows the homogeneous systems with attractive features such as zero catalyst leaching, catalyst stability and recovery [8–10].

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During last decade, our group [8,10] and others [18,21–23,25] have advanced the synthesis of successful Mn-based catalyst on SiO<sub>2</sub> supports, producing in this way heterogeneous Mn-based materials that are efficient for catalytic epoxidation and environmentally benign. Despite the legacy of SiO<sub>2</sub>, carbon materials constitute also an interesting family of supports for the preparation of heterogeneous catalysts, due to their physical and chemical surface properties [19,26,27]. Carbon materials display advantages over other widely used supports, e.g., SiO<sub>2</sub>, such as [i] resistance to both acidic and basic media, [ii] ability to modify their chemical properties to control polarity and hydrophobicity, [iii] stability at high temperatures and [vi] lower cost. Although carbon-supported catalysts are considered to be the best choice for many reactions, currently, few large-volume processes use these systems, and less than 1% of the activated carbon production worldwide is used as catalyst support [19,26,27]. The difficulty originates from the need to a better understanding of the various parameters interplaying, i.e., carbon surface groups, polarity/hydrophobicity and porosity, in conjunction with the redox evolution of the metal-catalyst. To address this task one has to combine analytical and in situ spectroscopic techniques as guidance for the mechanism and rate limiting steps. To this front, non-heme Mn catalysts have been extensively used, however a comprehensive detailed monitoring of catalytic cycle intermediates is difficult detectable, due to the transient character of reaction intermediates. They are very few examples i.e., in Mn-salen complexes, where the Mn(III) to Mn(V) transition has been detected by Electron Paramagnetic Resonance [28–30].

Using carbon from recycled tyres to catalytic technologies is a more demanding approach, as the evolution of automobile industry entails the disposal of a tremendous number of waste tyres which are responsible for a series of environmental problems. Among numerous technologies of disposing waste tyres, pyrolysis seems to be a promising, high-valued and environmental friendly technology. Pyrolytic char (PC) is one of the main products obtained after the pyrolysis process. PC has a contiguous structure with carbon black and this confers it with the general properties of carbonaceous materials, previously mentioned. PC bears abundant oxy functional groups inherently, without need for further oxidation process [31]. Several studies have reported the use of PC and Activated Carbon (AC) as adsorbents of several organic and inorganic compounds [31–33]. However, using carbon from recycled tyres as support for heterogeneous catalysts has not been –so far– reported in literature. Although, some reports refer immobilization of Mn catalytic complexes on the surface of activated carbons [34,35], however only Ji et al. [36] have reported immobilization of chiral Mn<sup>III</sup>-salen complexes on the surface of pyrolytic carbon for catalytic epoxidation of olefins. Very recently, a new synthetic methodology to covalently anchor Mn<sup>II</sup>-Shiff-base catalysts onto activated carbon (AC<sub>ox</sub>) has been reported by our group [34], resulting in heterogeneous Mn<sup>II</sup>-L@AC<sub>ox</sub> materials. These materials are effective and selective oxidation catalysts toward epoxides with H<sub>2</sub>O<sub>2</sub> [34].

Herein, we have used the synthetic protocol developed in [34] to prepare heterogeneous Mn<sup>II</sup>-Shiff-base catalysts onto pyrolytic carbon from recycled tyres (PC). The catalytic performance of the Mn-L@PC<sub>ox</sub> hybrid material was evaluated under strong oxidative conditions using NaIO<sub>4</sub> as oxidant. Degradation of methyl-orange in aqueous solution was studied as a model reaction. For the first time we exemplify that a highly recyclable Mn-L@PC<sub>ox</sub> heterogeneous catalyst, prepared using pyrolytic carbon from recycled tyres as support matrix, operates in aqueous solution. Importantly, no co-catalyst was needed. To further shed light on the underlying catalytic mechanism, we have combined catalytic and in situ Electron Paramagnetic Resonance (EPR) [28–30] spectroscopy. Based on detailed catalytic and EPR data a consistent catalytic mechanism is discussed.

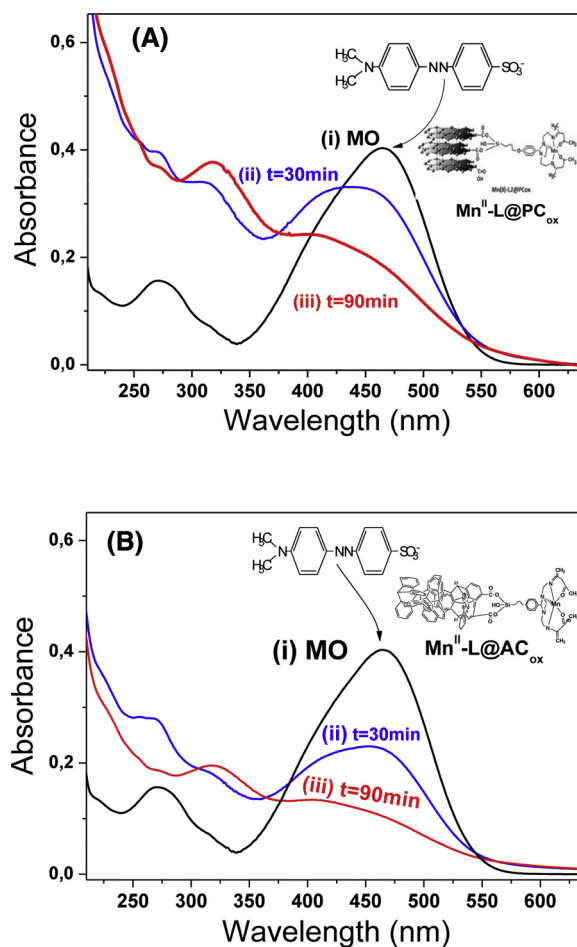
## 2. Experimental

### 2.1. Chemicals

Analytical grade acetonitrile (CH<sub>3</sub>CN) and ammonium acetate were purchased from Aldrich and Merck respectively. Methanol that used for the washes of the heterogeneous catalysts was purchased from Merck. Ultra-pure water was provided by a Milli-Q system (Millipore). Sodium periodate (NaIO<sub>4</sub>) and methyl orange (C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S, MO), that used for the catalytic procedure were purchased from Merck. Nitric acid 65% (HNO<sub>3</sub>) and ethanol both were purchased from Merck, (3-chloropropyl) trimethoxysilane from Fluka and manganese (II) chloride tetrahydrate was purchased from Sigma Aldrich.

### 2.2. Characterization methods

Isotherms of nitrogen (N<sub>2</sub>) adsorption–desorption were measured under liquid nitrogen temperature (77K) with a porosimeter Thermo Finnigan Sorptomatic 1990. The Specific Surface Areas of the samples were determined by the Brunauer–Emmett–Teller method (BET) using the adsorption points in relative pressures (*P/P*<sub>0</sub>) between the values 0,01 and 0,30. The points of isotherms' desorption show both the size and the distribution of pores' size using the Barret–Joyner–Halenda method (BJH). All samples were measured under high vacuum (10<sup>−4</sup> mbar) anaerobic conditions in



**Fig. 1.** Characteristic UV–vis spectra of (A) Methyl Orange degradation catalyzed by the heterogeneous catalyst Mn<sup>II</sup>-L@PC<sub>ox</sub> i) MO, ii) MO after *t* = 30 min of catalytic reaction, iii) after *t* = 90 min of catalytic reaction, (B) Methyl Orange degradation catalyzed by the heterogeneous catalyst Mn<sup>II</sup>-L@AC<sub>ox</sub>, i) MO, ii) MO after *t* = 30 min of catalytic reaction iii) after *t* = 90 min of catalytic reaction.

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