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Activated *vs.* pyrolytic carbon as support matrix for chemical functionalization: Efficient heterogeneous non-heme Mn(II) catalysts for alkene oxidation with H_2O_2

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Dedicated to Professor Georgiy B. Shul'pin on the occasion of his 70th birthday.

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ABSTRACT

Two types of heterogeneous catalytic materials, **Mn^{II}-L$_3$imid@Cox** and **Mn^{II}-L$_3$imid@PCox**, have been synthesized and compared by covalent grafting of a catalytically active **[Mn^{II}-L$_3$imid]** complex on the surface of an oxidized activated carbon (**Cox**) and an oxidized pyrolytic carbon from recycled-tire char (**PCox**). Both hybrids are non-porous bearing graphitic layers intermixed with disordered sp^2/sp^3 carbon units. Raman spectra show that $(I_D/I_G)_{activatedcarbon} > (I_D/I_G)_{pyrolyticcarbon}$ revealing that oxidized activated carbon(**Cox**) is less graphitized than oxidized pyrolytic carbon (**PCox**). The **Mn^{II}-L$_3$imid@Cox** and **Mn^{II}-L$_3$imid@PCox** catalysts were evaluated for alkene oxidation with H_2O_2 in the presence of CH_3COONH_4. Both showed high selectivity towards epoxides and comparing the achieved yields and TONs, they appear equivalent. However, **Mn^{II}-L$_3$imid@PCox** catalyst is kinetically faster than the **Mn^{II}-L$_3$imid@Cox** (accomplishing the catalytic runs in 1.5 h *vs.* 5 h). Thus, despite the similarity in TONs **Mn^{II}-L$_3$imid@PCox** achieved extremely higher TOFs ***vs.*** Mn$^{\mathbf{II}}$-L$_3$imid@Cox. Intriguingly, in terms of recyclability, **Mn^{II}-L$_3$imid@Cox** could be reused for a 2th run showing a ~20% loss of its catalytic activity, while **Mn^{II}-L$_3$imid@PCox** practically no recyclable. This phenomenon is discussed in a mechanistic context; interlinking oxidative destruction of the Mn-complex with high TOFs for **Mn^{II}-L$_3$imid@PCox**, while the low-TOFs of **Mn^{II}-L$_3$imid@Cox** are preventive for the oxidative destruction of the Mn-complex.

1. Introduction

In nature, manganese can frequently be found in the catalytic redox center of several enzymes [1,2]. Mn-complexes bearing non-heme ligands i.e. such as salen-derived ligands have been promise as versatile catalysts in olefin epoxidation [3–5]. Manganese complexes of 1,4,7-triazacyclononane (tacn) or 1,4,7-trimethyl-1,4,7triazacyclononane (tmtacn) ligands, which were originally synthesized and studied as models for the oxygen evolving centre of photosystem II and for manganese catalase [6,7], were also employed as bleaching – [8] and epoxidation [9–12] – catalysts using H_2O_2 as oxidant. There is still great research interest for efficient non-heme Mn complexes in catalytic epoxidations of olefins [13–20].

Besides efficiency of Mn-catalysts, stability and reusability constitute equally important parameters for catalytic reactions. Thus, recovery and reuse of the used catalysts is a challenging task that has to be considered. In this context, catalyst heterogenization on a solid support provides advantages such as easy handling, easy product separation, catalyst recovery and reuse, and lower waste's production [21–23].

A variety of carbon materials have been used as catalyst-supports in heterogeneous catalysis such as graphite, carbon black, activated carbon (C) and pyrolytic carbon (PC) [24–26]. Carbons appear to be a very flexible support since they have high surface area and high porosity [27]. It has been shown that the surface area and porosity of carbons may be important factors for the preparation of the corresponding catalysts by influencing their features properties [24,28]. Within this context, the role of surface chemistry of carbons is also determinant [28]. When oxidation takes place, the surface of carbon becomes rich in a variety of oxygen-based functional groups i.e. carboxyl, carbonyl, lactonic and phenolic, at a broad range of concentrations which depend on the method of activation, the used reagents and the temperature of the process [29–33]. These functionalities can affect the synthesis of supported catalysts onto the carbons, by controlling the acid-base and hydrophilic character of the carbon surface [34–37]. So

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far, heterogenization of metal complexes has been realized *via* their adsorption or covalent grafting on carbon surfaces [38–47].

For efficient heterogeneous catalysts via grafting of metal complexes onto carbon, the choice of the appropriate *spacer* group consists of another key parameter. This spacer should be bifunctional i.e. to react with both the surface groups of the carbon and the metal complex, to bridge them. Moreover spacer length, flexibility and degree of surface coverage [22,48–50] will ultimately affect the catalytic performance.

In the literature, there are very few examples of Mn oxidation catalysts immobilized on carbon. More specifically, their anchoring has been achieved either *via* adsorption [45,46,51], axial coordination to support [44,52] or covalent attachment [44]. It is obvious that the covalent bond formation between the metal complex and the support ensures minimum catalyst leaching during catalytic process [53].

Recently [25] we have reported an efficient protocol to covalently immobilized metal complexes onto the carbon surface, by generating a [metal complex-silane] precursor which is attached to the surface OH groups of the carbon [25]. The so-obtained Mn(II) heterogeneous catalysts have been proven to be effective and selective towards epoxides with H_2O_2 in the presence of CH_3COONH_4 [25]. Moreover they presented very good reusability indicating that they are stable against oxidative destruction [25]. The same protocol has been applied very recently by our group [26] to graft Mn(II)-catalyst onto the surface of PC for oxidative degradation of methyl orange [26].

It is obvious that – due to the rapid development of automobile industry – the amount of used tires is growing continuously. Thus, to face economic, managerial, environmental issues of used tires pyrolysis is considered to be the most environmentally acceptable and promising treatment method with low pollution emission. Pyrolytic char is one of the main products obtained by the pyrolysis process and its' applications are still being sought [54–56]. Thus, a post-production use of carbons and chars from waste tire is an attractive technology [57–63]. These materials have physical and textural characteristics similar to those of certain commercial carbon blacks [52,64]. Hence pyrolytic carbon char (**PC**) has great potential applicability, however so far applications in catalysis are still being scarce [26,64–66].

Here, a non-heme Mn(II) complex was covalently immobilized onto commercial activated carbon (**C**) and pyrolytic carbon char (**PC**). The Mn-complex bears a bio-inspired ligand with three imidazole moieties (L_3imid). The so-derived **Mn^{II}-L$_3$imid@Cox** and **Mn^{II}-L$_3$imid@PCox**, hybrid materials have been evaluated for alkene epoxidation catalysis. The main findings of the present work are (i) the activated carbon bears more structural defects than the pyrolytic one which is smoother, (ii) both **Mn^{II}-L$_3$imid@Cox** and **Mn^{II}-L$_3$imid@PCox**, catalysts are selective towards epoxide formation and, based on the achieved yields and TONs, none shows a clear superiority, and (iii) **Mn^{II}-L$_3$imid@PCox**, is kinetically faster than **Mn^{II}-L$_3$imid@Cox**, (iv) higher TOFs achieved by **Mn^{II}-L$_3$imid@PCox** are correlated with faster oxidative deactivation of the material.

2. Experimental

Activated commercial carbon(**C**) was purchased from Fluka (05120). The char (pyrolytic carbon, **PC**) used in this work was obtained via pyrolysis of used rubber tires. All substrates were purchased from Aldrich, in their highest commercial purity, stored at 5 °C and purified by passage through a column of basic alumina with methanol as the eluting solvent prior to use. Analytical grade acetone, methanol and ammonium acetate were from Aldrich and Merck respectively. Hydrogen peroxide was 30% aqueous solution. (3-glycidyloxypropyl)-trimethoxysilane was purchased from Fluka.

Infrared spectra were recorded on GX Perkin-Elmer FT-IR System. Continuous-wave (c.w.) X-ray diffraction (XRD) patterns were performed with a D8 Advance Bruker X-ray diffractometer using Cu Ka radiation (k = 0.154 nm) as the X-ray source, scanning from 10° to 60° at a rate of 0.03°/2 s for the activated carbon and from 10° to 80° at a rate of 0.02°/2 s for the pyrolytic carbon. Thermogravimetric analysis were carried out with a Shimadzu, DTG-60 instrument, at a heating rate of 5 °C min^{-1} and a flow rate of synthetic air gas of 50 cm^3 min^{-1}. Raman spectra were recorded on a Renishaw 1000 micro-Raman spectrometer at 532 nm wavelength incident laser light. The N_2 adsorption-desorption isotherms were measured at 77 K on an Autosorb-1, Quantachrome porosimeter. Specific surfaces areas were determined with the Brunauer-Emmett-Teller (BET) method using adsorption data points. Scanning electron microscopy (SEM) was observed in a Jeol JSM 5600 system operating at 20 kV.

GC analysis was performed using a Shimadzu GC-17A gas chromatograph coupled with a GCMS-QP5000 mass spectrometer. Gas chromatography was performed using a SPB-5 column (30 m, 0.25 mm i.d, 0.25 μm). The temperature program for cyclohexene, cyclooctene, styrene, limonene ((4R)-1-methyl-4-prop-1-en-2-ylcyclohexene), cyclopentene, **1-methyl-1-cyclohexene** and alpha-pinene (4,6,6-trimethylbicyclo[3.1.1]hept-3-ene) was: 80 °C for the first 5 min, followed by a 10 °C min^{-1} temperature gradient to 150 °C for 5 min. The temperature program for trans-β-methylstyrene ((**1E)-1-propen-1-ylbenzene)** and *cis*-stilbene ((Z)-stilbene) was: 80 °C for the first 5 min, followed by a 10 °C min^{-1} temperature gradient to 220 °C for 1 min. For hex-1-ene: 50 °C for the first 5 min followed by a 10 °C min^{-1} temperature gradient to 150 °C for 5 min. Injector and interface temperatures were set at 230 °C and 290 °C, respectively. Chromatography grade helium was used as the carrier gas, linear velocity = 36.8 cm s^{-1} at column pressure 64.5 kPa.

2.1. Ligand synthesis

The synthesis and characterization of the L_3imid ligand has been described in full detail in our previous work [18].

2.2. Oxidation of activated carbon **C** and pyrolytic carbon

Activation of commercial activated carbon (**C**) and pyrolytic carbon (**PC**) has been achieved by oxidation with nitric acid (HNO_3) leading to the formation of surfacial carboxylic groups (—COOH) [25]. 5 g of **C** was refluxed with 90 ml 65% v/v HNO_3 for 6 h. The oxidized carbon (**Cox**) obtained was separated by filtration, washed exhaustively with distilled water until pH ~ 7 and dried under reduced pressure at 40 °C for 12 h. The same procedure was employed for the oxidation of **PC**. Here after the obtained oxidized carbons are abbreviated as **Cox** (oxidized commercial activated carbon) and **PCox** (oxidized pyrolytic carbon). *DRIFTS-IR:* (cm^{-1}, selected peaks): **C:** 3430: ν(O—H); 2922, 2853: ν(C—H); 1582, 1460 ν(C=C); 1167 ν(C—O). **Cox**: 3419: ν(O—H); 2959, 2919, 2850: ν(C—H); 1715: ν(C=O); 1580, 1472 ν(C=C); 1176 ν(C—O) (Fig. 1.A). **PC:** 3438: ν(C—OH); 2920, 2853: ν(C—H); 1632: ν(C=C); 1385: ν(C—OH); 1105: ν(C—C) (Fig. 1). **PCox**: 3438: v(O—H); 2917, 2848: v(C—H); 1704: ν(C=O); 1536, 1461 ν(C=C); 1382 ν(—CH_2—); 1106 ν(C—O) (Fig. 1B).

2.3. Synthesis of precursor silane-compounds and metalation of carbon materials

1.2 mmol of ***L*$_3$*imid*** and 1 mmol of (3-glycidyloxypropyl)-trimethoxysilane were stirred for 24 h in 40 ml of MeOH at 65 °C