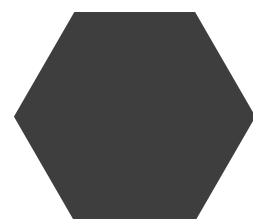


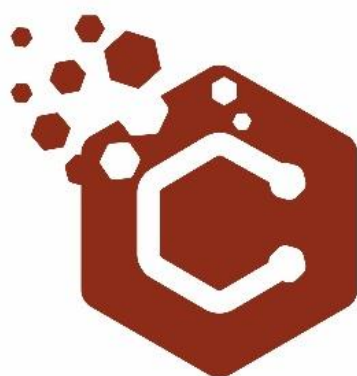
CARBOCATVIII

8TH INTERNATIONAL
SYMPOSIUM
ON CARBON
FOR CATALYSIS

PORTO, PORTUGAL
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Book of Abstracts



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26-29 JUNE 2018

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CATALYTIC WET PEROXIDE OXIDATION WITH MODIFIED CARBON NANOTUBES

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Catalytic wet peroxide oxidation (CWPO) uses H₂O₂ as a source of hydroxyl radicals (HO[•]) for the oxidation of organic species. This process is regarded as a potential solution for the treatment of aqueous effluents containing recalcitrant and toxic organic pollutants, difficult to remove by conventional biological processes, mainly if present at high concentrations (1–10 g L⁻¹) [1]. In a recent study, three magnetic carbon nanotube (CNT) samples, named A30 (N-doped), E30 (undoped) and E10A20 (partially N-doped), were synthesized by chemical vapor deposition and tested in the CWPO process [2]. It was revealed that N-doped hydrophilic surfaces promoted a fast decomposition of H₂O₂ into non-reactive species (H₂O and O₂), limiting the CWPO performance.

In the present study, the surface of the CNTs was modified by introducing oxygenated surface groups (oxidation with HNO₃, samples CNT-N), and by heat treatment at 800 °C for the removal of surface functionalities (samples CNT-HT). The effect of these modifications was analysed during 24-hours-CWPO-experiments of highly concentrated 4-nitrophenol solutions (4-NP, 5 g L⁻¹), at atmospheric pressure and 50 °C, adjusting the initial pH to 3, using a catalyst load of 2.5 g L⁻¹ and the stoichiometric amount of H₂O₂ needed for the complete mineralization of 4-NP. Given the magnetic properties of the Fe nanoparticles encapsulated inside the CNTs (formed during the CVD synthesis), catalyst separation after the catalytic reaction was easily achieved using a magnet.

The catalysts were characterized by elemental analysis, N₂ adsorption-desorption at –196 °C, transmission electron microscopy, X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), pH of the point of zero charge (pH_{PZC}) and water contact angle.

Both treatments led to higher apparent surface areas, which could be related to CNT endcaps opening during the treatments, and a thinning effect of the nanotube walls, especially visible in the CNT-N samples. The oxidation was more effective on the N-doped surfaces, finding double the amount of oxygen by XPS in A30N than in E30N. Increasing concentrations of released CO and CO₂ were detected during TPDs as well. Both, XPS and TPD results, showed that heat treatment leads to neutral or basic surfaces, with pH_{PZC} values around 8, while oxidation treatment results in materials with a more acidic surface (pH_{PZC} ≈ 2). The incorporation of O- and N-containing functionalities onto the CNTs after oxidation modified their hydrophilic properties, finding that the CNT-HT samples were less hydrophilic than the CNT-N ones (Figure 1).

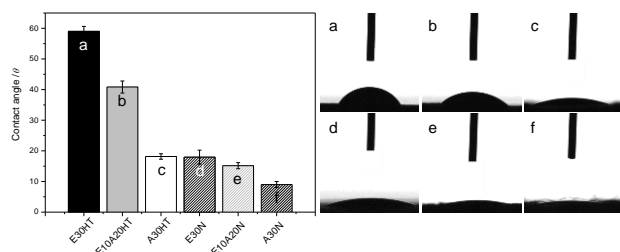


Figure 1. Contact angle measurements.

The high temperature treatment favoured the interaction between the 4-NP molecules and the CNT surface, enhancing significantly the activity of the CNTs towards CWPO, evaluated in terms of 4-NP and total organic carbon (TOC) conversion (Table 1). Among the CNT-HT samples, the more hydrophobic materials (E30HT and E10A20HT) promoted a controllable H₂O₂ decomposition into HO[•] radicals, being able to remove ca. 100% of 4-NP after 8 h of operation. On the contrary, the hydrophilic A30HT promoted the fast H₂O₂ decomposition into non-reactive species, resulting in a poor pollutant removal. On the other hand, the treatment of the CNTs with HNO₃ produced hydrophilic samples with opened ends, in which the decomposition of H₂O₂ was fast, hindering the CWPO due radical's recombination. Nevertheless, the reactivity generated inside the opened nanotubes favoured the reaction between the HO[•] radicals and the 4-NP molecules in the internal cylindrical tubes (confinement effect), allowing the reaction to occur before they disappear by scavenging effects. The highly efficient decomposition of H₂O₂ into HO[•] with E30HT results in a TOC conversion of ca. 60%, with ~3 mg C L⁻¹ of aromatic byproducts and 1 g C L⁻¹ of organic acids being detected after 24 h. The concentrations of the aromatic byproducts identified during the CWPO with E30HT follow the sequence: 4-nitrocatechol > hydroquinone > 1,4-benzoquinone > catechol. These intermediates almost disappear after 24 h, increasing the concentration of low-molecular-weight carboxylic acids (mainly malonic and malic acids).

Table 1. Removal of 4-NP by adsorption (Ads) and CWPO (X_{4-NP}); TOC removal, H₂O₂ decomposition and consumption efficiency (η).

	Ads. (%)	X _{4-NP} (%)	X _{H₂O₂} (%)	X _{TOC} (%)	η _{H₂O₂}
E30HT	8	100	59	59	100
E10A20HT	7	99	99	48	48
A30HT	4	35	99	22	22
E30N	14	99	90	54	60
E10A20N	7	60	42	43	31
A30N	8	48	100	2	2

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