



# Green alcohol oxidation on palladium catalysts supported on amphiphilic hybrid carbon nanotubes



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## ABSTRACT

In this work, unique amphiphilic magnetic hybrid carbon nanotubes that contain on the same nanotube two different sections: a hydrophobic undoped part connected to a hydrophilic N-doped segment are synthesized and used as supports for palladium catalysts. These new Pd-supported catalysts have been used in the alcohol oxidation reaction using molecular oxygen in the liquid phase. The oxidation of 2-heptanol produces selectively the ketone, the oxidation of benzyl alcohol is very selective towards the aldehyde, and ethanol oxidation produces selectively acetic acid.

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## 1. Introduction

The oxidation of alcohols to aldehydes and ketones is one of the predominant reactions in organic chemistry, since aldehydes and ketones serve as starting material for a multitude of other reactions, but these compounds do not have the same broad commercial availability or stability than alcohols [1]. The synthesis of aldehydes may entail a selectivity problem – namely, their further oxidation to carboxylic acids – which can only be overcome through the selection of an appropriate oxidant and/or catalyst. The application of heterogeneous catalysis and molecular oxygen (or hydrogen peroxide) to oxidation reactions offers a green alternative to traditional, toxic chemical oxidants [2]. The advantage of using such oxidants lies in the formation of water as the sole co-product and the low cost of the oxygen/air. The use of water as a solvent and air as the oxidant makes the reaction interesting from both an economic and environmental point of view. Different catalysts, both homogeneous and heterogeneous, have been investigated in the alcohol oxidation reaction using molecular oxygen or hydrogen

peroxide in the liquid phase [3,4]. Many examples of homogeneous systems make use of palladium, copper, or ruthenium complexes, typically in toluene as solvent, and very few reports deal with water soluble homogeneous systems [5]. However, if these oxidations could be performed in water, they would be considerably safer, cheaper, and more environmentally friendly than many of the processes in use today [6]. Supported noble metals, such as palladium or platinum on carbon, are known to catalyze the aerobic oxidation of alcohols in an aqueous medium, but the method is generally limited to water-soluble substrates, such as carbohydrates [7]. Resasco et al. have recently shown that catalytic oxidation reactions can be performed at the water/oil interface provided amphiphilic nanohybrid catalysts are used [8,9]. Thus, composites based on hydrophobic carbon nanomaterials supported on hydrophilic oxide particles have been used to stabilize water-oil emulsions and catalyze reactions at the liquid–liquid interface. However, the mechanical fragility of the nanocomposite may lead to its collapse, *i.e.* separation of the carbon and oxide structures, during use. Catalytic oxidation of alcohol was also achieved in water under an atmospheric pressure of molecular oxygen by use of amphiphilic polymer-supported palladium nanoparticles [10], or by microgel-stabilized metal (Pd, Pt, Au) nanoclusters [11,12].

Herein, we describe the synthesis and characterization of magnetic amphiphilic N-doped CNTs, and their application as a support for palladium catalysts for oxidation of alcohols (heptanol-2,

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benzyl alcohol and ethanol). These unique hybrid amphiphilic CNTs contain, on the same nanotube, two different sections: a hydrophobic undoped part connected to a hydrophilic N-doped segment. They show a very interesting feature: due to the combination of hydrophobic/hydrophilic branches, they can interact with polar and apolar media and should behave like amphiphilic species. Additionally, due to the presence of remaining encapsulated Fe catalyst particles, these CNTs are magnetic, and thus could be easily recovered by the application of a magnetic field.

## 2. Material and methods

### 2.1. CNT synthesis

The hybrid carbon nanotubes were synthesized by a catalytic CVD process in a fluidized bed reactor using ethylene as carbon source and acetonitrile as carbon/nitrogen source. The FeMo catalyst supported on  $\text{Al}_2\text{O}_3$  was pre-reduced in hydrogen during 30 min at 650 °C. A typical experiment was carried out initially with ethylene ( $600 \text{ mL min}^{-1}$ ) to produce hydrophobic CNTs. After this first reaction stage the gas inlet was switched to acetonitrile/ $\text{N}_2$  in order to continue the nanotube growth doped with nitrogen. Four samples were produced: (i) ethylene alone for 30 min, (ii) acetonitrile/ $\text{N}_2$  for 30 min, (iii) ethylene for 10 min, followed by acetonitrile/ $\text{N}_2$  for 20 min, and (iv) acetonitrile/ $\text{N}_2$  for 20 min followed, by ethylene alone for 10 min. The CNTs were purified by aqueous solution of  $\text{H}_2\text{SO}_4$  (50 vol.%) under reflux for 3 h to facilitate the total dissolution of alumina and elimination of exposed iron particles contained in the nanotubes.

### 2.2. Pd/CNT catalyst preparation

In order to prepare the supported metal catalysts, the desired amounts of palladium(II) nitrate [ $\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2$ ] were added to an acetone solution (20 mL) containing 0.5 g of purified nanotubes, as to introduce 2 wt.% of metal phase. After stirring overnight at ambient temperature, the catalysts were filtered, washed with acetone and dried in an oven at 120 °C. The catalysts were then reduced at 300 °C for 2 hours in a horizontal oven under an argon and hydrogen flow (20 vol.%  $\text{H}_2$ ).

### 2.3. Characterization

The hybrid nanostructures were characterized using transmission electronic microscopy (TEM-FEI Tecnai-G2-20-FEI 2006, at 200 kV), CHN Perkin-Elmer elemental analyzer, Raman spectroscopy (SENTERRA at 633 nm), and TG/DTA Shimadzu, under air ( $10^\circ\text{C min}^{-1}$  to 900 °C). The textural characterization (BET surface areas,  $S_{\text{BET}}$ ) of the materials was based on the  $\text{N}_2$  adsorption isotherms determined at  $-196^\circ\text{C}$  with a Quantachrome Autosorb apparatus. EELS measurements for the K-edge absorption for C and N were used to estimate the stoichiometry of the nanotubes. EELS experiments have been performed with a Philips CM200 microscope. The samples were also analyzed by X-ray photoelectron spectroscopy (XPS) using a VG Escalab MKII spectrophotometer, which operated with a nonmonochromatized Mg K $\alpha$  source (1253.6 eV).

### 2.4. Catalytic test

The oxidation reaction of 2-heptanol was performed in a 30 mL stainless steel autoclave with magnetic stirring in a silicone oil bath. In a typical run, the reaction mixture contained 0.1 g of catalyst (1–2 mol%), 2 mmol of 2-heptanol, and a solution of 10 mL toluene and 5 mL water. The reactor was then pressurized with air (5 bar) before the temperature was increased to 80 °C and the reaction was

allowed to proceed for 3 hours. The analysis was performed in a Clarus 500 gas chromatograph, equipped with a split/splitless injector, a capillary column (Stabilwax®-DA Fused Silica 30 m, 0.25 mm i.d.) and a flame ionization detector (FID). After the reaction, the catalyst was separated from the reaction products by filtration.

## 3. Results and discussion

### 3.1. Magnetic amphiphilic hybrid carbon nanotube synthesis, functionalization and characterization

The CNTs were produced by catalytic-CVD using ethylene as carbon source and acetonitrile as C/N source. Four different materials were produced: (i) using  $\text{C}_2\text{H}_4$  only during 30 min (E30); (ii) using  $\text{CH}_3\text{CN}$  only during 30 min (A30); (iii) using  $\text{C}_2\text{H}_4$  for 10 min, followed by  $\text{CH}_3\text{CN}$  for 20 min (E10A20); and (iv)  $\text{CH}_3\text{CN}$  for 20 min, followed by  $\text{C}_2\text{H}_4$  for 10 min (A20E10). TEM images of the E30 sample showed the presence of very regular multi-walled CNTs with an average diameter of ca. 8 nm (Fig. 1a). Sample A30 presented the “bamboo-like” structure of N-doped CNTs, with larger diameters (ca. 14 nm, Fig. 1b). For E10A20 and A20E10, hybrid structures with two different sections in the same CNT were observed (Fig. 1e). It is also possible to observe in these heterostructures the presence of encapsulated metallic particles (Fig. 1f). As TEM is a very local probe technique, we may wonder if most CNTs are really a hybrid of hydrophobic/hydrophilic segments or if N-doped CNTs simply grow independently and separately from all C-CNTs. To verify this hypothesis we carefully check the outer diameter size distribution (Fig. 2). Indeed, if two populations of tubes were present (only carbon and only nitrogen-doped) we should observe a bimodal distribution (centred at 8 nm for only carbon, and at 14 nm for only nitrogen-doped) resulting from these two populations. The mean diameters of the hybrid structures were 9 and 11.5 nm, respectively, and it is obvious from Fig. 2 that the population corresponding to N-doped CNT between 13 and 22 nm is noticeably absent for samples E10A20 and A20E10. We have also independently checked that for a single carbon source (ethylene or acetonitrile) the mean outer diameter of the CNTs does not change with reaction time.

The introduction of nitrogen in the carbon structure induces a decrease of the yield of the reaction, an increase in tube diameter and in the  $d_{002}$  distance (Table 1).

Another noteworthy difference between these different types of nanotubes is related to the interstitial space between individual CNT (Por. diameter in Table 1). The quality and the dimension of interstitial space primarily rely on the relative position of individual CNTs, which is in turn determined by the synthetic conditions. The common purification process of CNTs normally involves the ultrasonic, stirring, filtration as well as other steps that may dramatically change the shape, quality and volume of the interstitial spaces. In our case, the presence of nitrogen in the samples induces a decrease of the interstitial space between individual CNT.

The N content was determined by elemental analysis and the results are shown in Table 1. The sample E30 showed 94.6% carbon with no nitrogen or hydrogen being detected. For E10A20, the N content increased slightly to 1.0%, which should correspond to ~18% of N-doped section in the sample. On the other hand, for the sample A20E10 the N content reached 2.8% (~52% of N-doped section in the sample), which further increased to 5.4% for A30. The C+N content ranged between 94.6% (E30) and 84% (A30), with intermediate values (90.2%) for E10A20 and A20E10. The remaining material should consist of oxygen and remaining catalyst particles encapsulated in the carbon structure. The presence of higher amount of remaining catalyst in nitrogen-doped CNT is explained by the lower yields obtained when acetonitrile is used during

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