Carbon nanotubes as catalysts for catalytic wet peroxide oxidation of highly concentrated phenol solutions: towards process intensification

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ABSTRACT

Commercial multi-walled carbon nanotubes with different properties (two samples from Sigma-Aldrich, SA1 and SA2; one sample from Nanocyl, NC; and two samples from Shenzhen Nanotech, SZ and LSZ), and SA2 modified by hydrothermal treatment with concentrated sulfuric acid (SA2-H), were tested as catalysts in wet peroxide oxidation. Phenol was selected as model compound since it represents a class of noxious compounds for human health and for the environment and, due to this, phenol is typically considered in wastewater treatment studies. The experiments were carried out under the following intensified conditions: phenol concentration = 4.5 g L^{-1}, hydrogen peroxide concentration = 25 g L^{-1}, catalyst load = 2.5 g L^{-1}, pH 3.5, T = 353 K and 24 h.

The results demonstrated that phenol is poorly adsorbed in this type of carbon materials (11% as maximum when using the NC sample). However, in the catalytic experiments, complete removal of phenol is achieved when using some of the carbon nanotubes (SA1, NC and SA2), together with a remarkable total organic carbon removal (77, 69 and 67%, respectively). These materials have the less pronounced acidic character, which is often considered favorable for oxidation reactions in advanced oxidation processes and may explain the higher performance of SA1, NC and SA2 regarding the other materials. Leaching of Fe species into the solution was also observed in all cases (that can also have some influence on the degradation of phenol), SA1 leading to the highest concentration of Fe species leached (26 mg L^{-1}), followed by SA2 (2 mg L^{-1}) and NC (1 mg L^{-1}).

Considering the lower Fe leaching levels observed for SA2 and NC, these catalysts were then tested in consecutive reusability cycles. SA2 showed a superior performance than NC, but temperature-programmed desorption as well as thermogravimetric analysis suggested that the carbon material is oxidized by hydrogen peroxide at the employed conditions and/or that carboxylic acids are adsorbed on the catalyst surface after consecutive runs (mainly after the first use). However, only a slight decrease in the catalyst activity was observed.

1. Introduction

Organic pollutants such as phenol and its derivatives appear in wastewaters from pharmaceutical, paper, petrochemical and from many other industries. These compounds are very toxic and difficult to eliminate from wastewaters by conventional biological processes, in particular, when they are present in high concentrations (1–10 g L^{-1}) [1]. In the quest to solve this problem, different treatments have been studied based on physical and chemical processes (e.g., flocculation, precipitation, adsorption on activated carbon, ozonation, chlorination and coagulation) [2]. Advanced oxidation processes (AOPs) have been particularly investigated among the chemical treatments [3–5].

AOPs are conceptually characterized by the production of hydroxyl radicals (HO•), which are very reactive species capable to oxidize a wide range of organic compounds and to reduce the toxicity of many effluents. Most of these processes can be operated at (or close to) ambient temperature and atmospheric pressure

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[6]. Different oxidizing agents (typically hydrogen peroxide, ozone or/and oxygen) can be considered depending on the process [7]. Particularly, hydrogen peroxide (H_2O_2)—a colorless and non-toxic compound—is a powerful oxidizing agent that easily decomposes into environmental friendly products (i.e. water and oxygen), following Eq. (1).

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad (1)$$

If a suitable catalyst is used, the decomposition of H_2O_2 may proceed selectively through the formation of the highly reactive $HO^\bullet$ radicals. This process is known as catalytic wet peroxide oxidation (CWPO). The classical Fenton process is one of the most known homogeneous AOPs, where a mixture of H_2O_2 and Fe^{2+} ions are employed at low pH (2.5–3.0) to promote the decomposition of H_2O_2 into $HO^\bullet$ radicals, this process being considered one particular case of CWPO (i.e. a specific catalyst at specific operating conditions). Still, heterogeneous catalysts can be easier separated from the treated solution when compared to homogeneous catalysts, which is an important advantage relatively to the homogenous route [3]. Taking this into consideration, different supports, like activated carbons, pillared clays, zeolites, carbon xerogels and carbon nanotubes, have been employed in the last two decades to prepare transition-metal-supported catalysts for CWPO [4,8–14]. However, the loss of activity due to leaching of metal species when using heterogeneous catalysts, as well as further separation of these species from the treated water (when in quantities larger than those allowed by local directives), are some of the arising difficulties in the use of transition-metal-based catalysts. In order to overcome these drawbacks, metal-free carbon materials have also been tested as catalysts in CWPO, revealing promising activities [15–19].

Carbon nanotubes (CNTs) have interesting properties when they are compared with other carbon materials, such as low mass-transfer limitations, high level of ordering and mechanical resistance, superior electronic properties and relatively high thermal stability in oxidizing conditions. CNTs are often produced by chemical vapor deposition (CVD) using metal nanoparticles as catalysts (such as Fe, Co, Ni, Cu, Au, Ag, Pt and Pd). In this catalytic method of synthesis, a hydrocarbon gas decomposes leading to the formation and growth of CNTs on the top surface of the catalytic nanoparticles [20]. It is thus natural to found metal nanoparticles in the composition of commercial CNTs. These metal species (especially Fe) are able to act as catalysts in the generation of $HO^\bullet$ radicals from H_2O_2 decomposition, as previously shown for commercial graphite [19]. Therefore, in addition to the recognized intrinsic catalytic activity of carbon materials, the effect of these metal nanoparticles on CWPO performance have to be considered when using CNTs as catalysts on their own for CWPO processes.

In the present work, six different commercial CNT samples were compared as catalysts for the CWPO process. A highly concentrated phenol ($4.5\,g\,L^{-1}$) solution was considered as model system, in order to simulate highly polluted wastewaters and to maximize the efficiency of H_2O_2 consumption, which is known to be favored by high phenol/carbon mass ratios [21]. Under these conditions, the carbon surface is expected to stay largely covered by the organic molecules, reducing the occurrence of parasitic scavenging reactions on the carbon surface and, consequently, increasing the degradation and mineralization of phenol. The stability of the catalysts that revealed better performances in screening experiments was further assessed in consecutive runs, an issue of relevance for actual applications of the CWPO process.

2. Experimental

2.1. Chemicals

Phenol was obtained from Sigma–Aldrich (99 wt%). Hydrogen peroxide solution (30%, w/w), *p*-benzoquinone (99.5 wt%) and catechol (98 wt%) were purchased from Fluka. Hydroquinone (99 wt%), resorcinol (99 wt%), titanium(IV) oxysulfate (~15 wt% in dilute sulfuric acid, 99.99% trace metals basis) and hydrochloric acid (37 wt%) were purchased from Sigma-Aldrich. Sulfuric acid (95 wt%) and methanol (99.9 wt%) were obtained from VWR PRO-LABO Chemicals. All the solutions were prepared with distilled water.

2.2. Carbon nanotubes (CNTs)

Six different samples of commercial multi-walled carbon nanotubes (MWCNTs) were considered in this work, namely: (i) SA1/Sigma-Aldrich, ref. 677248 (>90% carbon basis, O.D. × I.D. × L: 10–15 nm × 2–6 nm × 0.1–10 μm); (ii) SA2/Sigma-Aldrich, ref. 724769 (>95% carbon basis, O.D. × L: 6–9 nm × 5 μm); (iii) NC/NANOCYL^{TM}, ref. NC3100 (>95% carbon basis, average diameter of 9.5 nm and length of 1.5 μm); (iv) SZ/Shenzhen Nanotech, ref. MWCNT-10 (>97% carbon basis, O.D. × L: <10 nm × 5–15 μm); (v) LSZ/Shenzhen Nanotech, long CNTs with ref. L-MWCNT-60100 (>97% carbon basis, O.D. × L: 60–100 nm × 5–15 μm); (vi) SA2-H, resulting from the hydrothermal treatment of SA2 ($10\,g\,L^{-1}$) with concentrated sulfuric acid ($18\,mol\,L^{-1}$) during 3 h at 423 K. The recovered solids were further thoroughly washed with distilled water until the neutrality of the rinsing waters was reached and dried in an oven for 18 h at 383 K.

2.3. Characterization techniques

The catalysts were characterized by different techniques. The textural properties were determined from the N_2 adsorption–desorption isotherms at 77 K, obtained in a Quantachrome NOVA 4200e adsorption analyzer. The specific surface area (S_{BET}), pore volume (V_{total}) and micropore volume (V_{mic}) were determined using the *t*-method and the BJH pore distribution [22,23].

The pH of point of zero charge (pH_{PZC}) was determined by pH drift tests, following the procedure described elsewhere [24]. Namely, five solutions with varying initial pH were prepared using HCl and NaOH solutions (0.02 and $1.0\,mol\,L^{-1}$) and NaCl ($0.01\,mol\,L^{-1}$) as electrolyte. 50 mL of each solution was contacted with 0.15 g of carbon sample and the suspension stirred for 24 h before the equilibrium pH was measured. The pH_{PZC} value of each carbon sample was determined by intercepting the obtained final pH vs. initial pH curve with the straight line final pH = initial pH [25,26].

Temperature-programmed desorption (TPD) analysis was performed in a fully automated AMI-300 catalyst characterization instrument (Altamira Instruments), equipped with a quadrupole mass spectrometer (Dymaxion, Ametek). The carbon sample (0.10 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at $5\,K\,min^{-1}$ up to 1073 K using a constant flow rate of helium ($25\,cm^3\,min^{-1}$). The mass signals $m/z = 28$ and 44 were monitored during the thermal analysis, the corresponding TPD spectra being obtained. CO and CO_2 were calibrated at the end of each analysis with the respective gases [27].

Thermogravimetric analysis (TGA) was performed using a Netzsch STA 409 PC equipment. The sample powders were heated in air (flow = $50\,cm^3\,min^{-1}$) from 323 to 1273 K at $10\,K\,min^{-1}$.