Graphite and carbon black materials as catalysts for wet peroxide oxidation

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ABSTRACT

This study explores the application of non-porous carbon materials, two graphites (G-F, G-S) and two carbon blacks (CB-V and CB-C) as catalysts for wet peroxide oxidation (CWPO). The activity, efficiency and stability of these carbon materials have been evaluated using phenol as target compound. The catalyst screening experiments were carried out batch-wise at $C_{Phenol,0}$ = 1 g/L, $C_{H_2O_2,0}$ = 5 g/L, C_{cat} = 2.5 g/L, T = 80 °C and pH_0 = 3.5. The results allow concluding that CB-C was the most stable catalyst, although it showed a lower oxidation and mineralization activity than G-S and CB-V. Increasing the temperature up to 90 °C allowed complete phenol conversion and around 70% TOC reduction with 100% efficiency of hydrogen peroxide consumption upon 20 h reaction time at 5 g/L CB-C load. As a consequence of the initial oxidation of the carbon surface, the electrochemical properties of CB-C were favorably changed upon CWPO and its catalytic performance was improved from the first to the second use and then maintained upon successive applications in a five-cycle test.

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1. Introduction

Catalytic wet peroxide oxidation (CWPO) relies on the oxidation of organic water pollutants with hydroxyl and hydroperoxyl radicals produced upon decomposition of hydrogen peroxide in the presence of a catalyst, typically iron, under working temperatures of 50–130 °C and pressures of 1–5 atm. Homogeneous CWPO technology has been commercialized under different proprietary processes, US Peroxide, OXY-PURE®, OHP® and PROX T.E.C [1]. These commercial systems are attractive because of their simple design and cost-effective operation. The disadvantages of homogeneous CWPO are the sensibility to pH, which must be always within the 2.5–3.5 range and the continuous loss of the dissolved iron catalyst which moreover needs to be separated from the effluent to avoid additional pollution. These issues have driven the investigation of active and stable solid catalysts, which has resulted in a growing literature on heterogeneous CWPO. A comprehensive survey of recent research on solid catalysts for CWPO is provided in the reviews of Perathoner and Centi [2], Garrido-Ramírez et al. [3], Navalon et al. [4] and Dhaskshinamoorthy et al. [5]. According to them, most CWPO studies are devoted to the incorporation of Fe, Mn, Co or Cu, as oxide species, metal complexes or

in the form of nanoparticles on different supports, such as zeolites, mesostructured materials, silica, alumina, pillared clays and activated carbons. Some studies with supported noble metals such as Pt, Ru, Pd and Au, have been also recently published [1,6,7]. It must be highlighted the difficulty of comparing the results on the activity of the different catalysts since specific operating conditions, *i.e.* pH, pollutant/catalyst ratio, temperature, amount of hydrogen peroxide and the way of feeding it to the wastewater have been used.

The difficulty of developing suitable catalysts is noticed in the literature. Finding efficient and stable catalysts allowing detoxification of wastewater upon reasonable reaction times is an important challenge. Solid catalysts are usually unstable in the long term because of the leaching of the active phase as a consequence of the low pH caused by the presence of organic acids as by-products which also can give rise to the formation of metal complexes, particularly with oxalic acid [8,9].

The catalytic efficiency is associated to the selectivity for hydrogen peroxide decomposition into active hydroxyl and hydroperoxyl radicals, capable of breaking-down the organic pollutants instead of being consumed in un-productive (parasite) reactions. Efficient catalysts are desirable to provide the maximum TOC removal per unit of hydrogen peroxide, a crucial issue for the economy of the system. This concept is receiving increasing attention in the literature [10–13]. The interest for stable catalysts avoiding metal leaching has promoted the exploration of bare carbon materials, whose lower activity, compared to metal-bearing catalysts, can be

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compensated by working at higher loads, which does not represent a drawback if they can be purchased at a lower cost. Activated carbons have been the most commonly used carbon materials in CWPO [4,8,14–22]. They exhibit donor-acceptor surface properties. The electron-rich sites such as basic surface oxygen groups and basal planes allow hydrogen peroxide decomposition into radical species through an electron transfer reaction similar to the Fenton mechanism [23]. Their efficiency for the decomposition of hydrogen peroxide is highly dependent on the adsorption of the organic pollutants, as recently demonstrated by Dominguez et al. [22]. In that work, unprecedented hydrogen peroxide efficiencies of almost 100% were reported for the CWPO of phenol with activated carbons. Under the selected reaction conditions (high pollutant concentration, 5 g/L of phenol and pollutant/carbon mass ratio = 2), great part of the carbon surface was occupied by phenol and the amount of available active sites was reduced. As a consequence, better controlled hydrogen peroxide decomposition into hydroxyl and hydroperoxy radicals was achieved and these species efficiently reacted with phenol in the vicinity of the carbon surface, reducing parasitic recombination and allowing a more efficient consumption of hydrogen peroxide. Catalyst stability was an important issue analyzed in that work. The activated carbon showed a progressive deactivation upon successive uses as a consequence of condensation by-products formed on the carbon surface. The activity was easily recovered by oxidative thermal regeneration (350 °C, 24 h).

In the current work, we explore the application of other carbon materials such as graphite and carbon black, of much lower surface area that can be available at reasonable low cost. The activity of these carbon materials for hydrogen peroxide decomposition was already demonstrated in a previous work [23]. The purpose of the present study is to evaluate their activity, efficiency and stability in CWPO using phenol as target compound. It is expected that with these materials of low adsorption capacity, deactivation by adsorbed condensation by-products can be avoided, or greatly reduced.

To the best of our knowledge, there are no previous studies on the application of carbon blacks for CWPO, whereas graphites have been scarcely studied in that process yielding in general fairly poor results [14,24].

2. Experimental

2.1. Reagents

Aqueous phenol solutions were prepared (1 g/L) (Sigma–Aldrich) at pH = 3.5 (HCl, Panreac). Hydrogen peroxide solution (30%, w/w) was purchased from Sigma–Aldrich. Working standard solutions of phenol, hydroquinone, resorcinol, catechol, *p*-benzoquinone, acetic acid, formic acid, malonic acid, maleic acid all from Sigma–Aldrich and oxalic acid (Panreac) were prepared and used for high performance liquid chromatography (HPLC) and ionic chromatography (IC) calibration. Other reagents used in the analyses were H_2SO_4 (Panreac), C_2H_3N (Riedel-deHaën), Na_2CO_3 (Panreac), $NaHCO_3$ (Merck), $Na_2S_2O_8$ (Panreac), HPO_4 (Fisher), $C_6H_4COOHCOOK$ (Aldrich), $TiOSO_4$ (Riedel-deHaën). All these reagents were of analytical grade and were used without further purification. All the solutions were prepared with milli-Q water.

2.2. Catalysts

Commercial graphites, supplied by Fluka (G-F, ref.: 1249167) and Sigma-Aldrich (G-S, ref.: 282863) and two carbon blacks, supplied by Chemviron (CB-C, ref.: 2156090) and Vulcan (CB-V, ref.: CC72R) were tested as catalysts for CWPO of phenol. All samples were provided in powder form.

2.3. Catalyst characterization

Structural characterization of the carbon materials by powder X-ray diffraction (XRD) was carried out in a Siemens Model D5000 X-ray diffractometer, using Cu Kα (8.04 keV) radiation and a step of 0.02°/s for $2\theta = 5-100°$ and analyzed with PDF 2000 (JCPDS-ICDD) software.

The specific surface area (S_{BET}) values were obtained from the N_2 adsorption/desorption isotherms at 77 K using a Micromeritics Tristar apparatus on samples previously outgassed overnight at 150 °C to a reduced pressure <10^{-3} Torr in order to ensure a dry clean surface. The external or non-microporous surface area (A_{ext}) was calculated by the *t*-method. Elemental analyses were performed in a LECO Model CHNS-932 analyzer. Element identification in the carbon ashes was carried out by TXRF (Extra-II Rich & Seifert spectrometer). The amount of surface oxygen groups (SOG) in the carbons was accomplished by Temperature-programmed desorption (TPD) under N_2 (1000 NmL/min) as carrier gas. A carbon sample of 100 mg was placed in a quartz tube and heated at 10 °C/min from room temperature up to 900 °C. The evolved CO_2 and CO were measured by a SIEMENS gas analyzer (mod. Ultramat 22). Peaks deconvolution of the TPD spectra were adjusted to multiple Gaussian function by Peakfit 4.12 software.

Thermal gravimetric analyses (TGA) were performed on a Mettler–Toledo TGA/SDTA 851^e thermobalance in air atmosphere from 50 to 900 °C (10 °C/min).

Cyclic voltammetry (CV) measurements were carried out in a conventional three-electrode electrochemical cell, using a computerized potentiostat (Autolab PGSTAT 302, Eco Chemie). A glassy carbon electrode was used as substrate for the carbon samples, a gold electrode as the counter, a saturated Ag/AgCl, KCl electrode as the reference and HCl solution (pH = 3.5) as electrolyte. 20 μL of the carbon suspension (6 mg of carbon in 730 μL Milli-Q water) was dropped on the glassy carbon electrode to obtain a uniform film and subjected to CV (10 mV/s) under nitrogen atmosphere in the absence and presence of hydrogen peroxide (25 g/L) in the potential range from −0.6 to 1 V. From these measurements, the coulombic charge (CC) and the exchange current (i_o) were calculated. More detailed description of these tests has been reported elsewhere [23].

2.4. CWPO experiments

The CWPO runs were carried out batch-wise in a magnetically stirred three-necked glass reactor equipped with a reflux condenser. In a typical experiment, 45 mL of phenol solution (1 g/L) at pH = 3.5 (HCl) were placed in the reactor, along with the selected mass of carbon (0–0.375 g) and heated up to the desired temperature (80–90 °C). After that, 5 mL of an adjusted concentration of hydrogen peroxide aqueous solution were added and the stirring at 1200 rpm started. Effluents at different reaction times were taken from the reactor and immediately analyzed. After 24 h of reaction, the heating was switched-off and the reactor cooled to room temperature in cold water. Then, the catalyst was separated by filtration (0.45 μm Nylon filter) and dried at 60 °C. A blank experiment was carried out to assess the homogenous contribution. Phenol adsorption runs were performed at the same operating conditions as the oxidation tests but without hydrogen peroxide addition. The initial pH was set at 3.5 which is within the range most commonly reported in the literature for CWPO with iron catalysts [2]. All the experiments were performed by triplicate being the standard deviation always less than 5%.